The Vanderbilt **RUBBER (*) HANDBOOK**

Fourteenth Edition Edited by Martin F. Sheridan

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Offices and Laboratories

Corporate Headquarters and Laboratories

30 Winfield Street, Norwalk, CT 06855-5150 Phone: 203-853-1400 • FAX: 203-838-6368 Web site: www.rtvanderbilt.com

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> Wayne Vanderhoof Global Business Manager Rubber & Plastics

West Coast

6281 Beach Blvd., Suite 204 Buena Park, CA 90621 Phone: 714-670-8084 • FAX: 714-739-1488

> lan Begley Sales Manager – West Coast

Genève

Vanderbilt International Sàrl

World Trade Center II, 29, route de Pré-Bois CH-1215 Genève 15, Switzerland Phone: 011 41 (0) 22 929 5734 • FAX: 011 41 (0) 22 929 5752

> John Benton Managing Director

Beijing

Vanderbilt Trading Ltd.

8 Hnagfeg Road, Room 226 Science Town, Fengtai District Beijing 100070, China Phone: +8610 58051526 • FAX: +8610 58051525 Junbing Yao, PhD General Manager

Manufacturing Operations

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Contributors

Larry K. Adkins Aaron Ala William F. Barham Dave Bender Anke Blume, PhD Carrie Burr John T. Byers John J. Carr Peter A. Ciullo Joseph E. DeMello Judy Douglas, PhD Aik-Hwee Eng, PhD P. A. Ferrandez Jennifer Forque Mike Gozdiff Daniel L. Hertz. Jr. Tom Jablonowski Theodore D. Johnson Eric Jourdain Joshua R. Kelley Vipin M. Kothari Kent Little Gary Marchand Edward McBride Alan A. McNeish Ted Muzyczko Chris Nola Eng-Long Ong, PhD Charles P. Rader, PhD David Rosbottom Gordon Schorr Mark Shanbaum M.A. Stewart

Jim Ahnemiller Ralph A. Annicelli Don Beeman David Benko Frank Borenski George Burrowes Joseph C. Caprino Dwight Chasar, PhD Marty Cohen Michael DiPino llan Duvdevani Christopher D. Favreau David Flood James V. Fusco Samuel C. Harber Tom Hofer Sunny Jacob, PhD Mark S. Jones Jonathan Karas Srdjan Kisin Ron LaFlair. PhD John M. Long Eric P. Marsden, PhD Linda McGinley Michael A. Melotto Werner Niedermeier, PhD Geoff Normanton Hank Parker, PhD **Brendan Rodgers** Paul Sandstrom John A. Sezna Ron Stevens, PhD James F. Walder

Vanderbilt Associates

Vanderbilt people who have made significant contributions to the development of the information in this book are:

Dan Bowen Lea Ann Coreau Becky Decker Ken Kelly Karen Marie Smith Paul Vanderbilt Ann Vento

Foreword

R. T. Vanderbilt Company, Inc. is pleased to present the fourteenth edition of *The Vanderbilt Rubber Handbook*. As with our earlier editions, the purpose of this Handbook is essentially the same – to continue a long-standing tradition of technical service to the rubber industry.

We believe that individuals entering the field of specialized rubber applications will find this Handbook helpful for both general information and as a guide for rubber compounding and processing. This Handbook is also meant to serve as a reference source for the experienced compounder.

This edition is the first to use color, the primary intention being to assist the interpretation of data provided in charts and graphs. It contains a number of new chapters, along with timely updates of chapters in prior editions, written by individuals well-known and highly qualified in their respective areas of rubber technology. We extend our sincere appreciation to these authors and to their companies for their willingness to devote time and effort to this publication.

Although throughout this Handbook we have intentionally placed emphasis on the pertinent Vanderbilt manufactured, mined and distributed materials, we believe that the use of Vanderbilt trade names does not compromise good compounding principles. However, the familiar "blue section" toward the center of the Handbook, which listed Vanderbilt material's technical specifications, has been removed in the interest of reducing the total number of pages. This section has become obsolete since materials specs are covered in regularly updated detail on the Vanderbilt website (www.rtvanderbilt.com).

We have made every attempt to assure the accuracy of this publication. Nevertheless, we cannot be certain that all errors have been found and corrected. In addition, the rapid commercial changes in the rubber industry make complete accuracy impossible. Readers should therefore verify compounding and processing suggestions through work in their own factory situations.

R.T. Vanderbilt Company devotes significant resources to developing technical literature that illustrates the effective use of our products. This book is one example. Inquiries on specific topics are welcome.

Martin F. Sheridan Editor

April, 2010

Raw Material Substitution: Proceed with Caution

"One of the cardinal rules of formulation is never buy a raw material based solely on a salesperson's assertion that he or she has got the exact equivalent of what you're already buying, only cheaper.

Whether a lab person or an office employee, the people who violate this rule will not only cause untold grief for themselves and their companies but also create inventory hassles and transportation expenses for their companies and their distributors. And everyone tries to figure out what happened.

Two things usually suffice to keep a formulator out of trouble. The first is a thorough laboratory evaluation of potential raw materials, coupled with small-scale plant evaluation before going into full production. The second is an ongoing quality control (QC) program for incoming raw materials and in-process products, once specifications have been set."

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CHAPTER I Introduction

THE STRUCTURE AND PROPERTIES OF RUBBER

by Martin F. Sheridan

R. T. Vanderbilt Company, Inc.

Rubber is composed of very large molecules. Each molecule contains thousands of atoms arranged successively in a long chain or string-like manner. The arrangement of the atoms repeats in a regular cycle, so the structure can be written as a certain segment which is repeated "n" times. Rubber is one of a group of materials which are called polymers, from the Greek, meaning many units. Each polymer is commonly named after the raw material, or monomer, used to make it. Some typical monomers are:

H H H H	H H
C=C-C=C	C=C
H H	H H
butadiene	<i>ethylene</i>
H H H H C=C-C=C H H isoprene	$H C_{6}H_{5}$ $C = C$ $H H$ H $Styrene$
H CI H	H CN
C=C-C=C	C = C
H H H	H H
Chioroprene	acryioninne

Chapter 2 will describe in greater detail how rubbers are made from these basic "building blocks". This chapter will focus on the structural features which give rise to elasticity and other characteristics of rubber.

Molecular Weight

The hydrocarbon polymer with the least complicated repeating unit structure is a plastic which is made by polymerizing ethylene. The polymerization of monomers with one double bond proceeds by opening up the double bond to form links between the repeating segments:

 $\begin{array}{rcl} n & CH_2=CH_2 \rightarrow & \label{eq:charged} CH_2=CH_2 \rightarrow & \label{eq:charged} ethylene & polyethylene \end{array}$

Selected properties of hydrocarbons which are homologues of polyethylene are shown in Table 1. The compounds are arranged in order of increasing molecular weight (m.w.). As molecular weight increases, the density, melting point and boiling point also increase, the last property to the point where the material decomposes before it distills. The lowest m.w. linear hydrocarbons are gases at room temperature. With increasing m.w., the materials become liquid. With a further increase in m.w., the viscosity of the liquids increases, and eventually greases and soft, wax-like solids are formed. Tough, crystalline plastics are obtained at a sufficiently high m.w.

High molecular weight is necessary for strong, load bearing polymers, both in rubbers and in plastics. Higher m.w. rubbers are stronger and more capable of dilution with oils and extending fillers. However, viscosity is roughly proportional to m.w., and eventually the m.w. of a polymer can be too high to process.

n	M.W.	Common Name	Appearance	Density* Mg/m ³	M.P. °C	B.P. °C
1	30	ethane	gas	0.57	-183	-89
2	58	butane	gas	0.60	-138	0
3	86	hexane	colorless liquid	0.66	-95	68
4	114	octane	colorless liquid	0.70	-57	123
5	142	decane	colorless liquid	0.73	-30	174
10	282	eicosane	soft, white solid	0.79	38	343
25	700	low m.w. polyethylene	soft, white solid	0.88	92	d
75	2,100	low m.w. polyethylene	white solid	0.92	106	d
7,500	210,000	high den. polethylene	white solid	0.95	120	d

Table 1: Properties of Selected Hydrocarbons: +CH2-CH2+,

* density of ethane liquid at -108°C; butane at 0°C; all others at 23°C M.P. = melting point; B.P.= boiling point; d=decomposes

Molecular Structure

The regular, repeating structure of polyethylene allows neighboring segments to align in perfect order to form crystals. Polyethylene can be 65% to 95% crystalline, the crystals being the source of rigidity in this plastic. To make a rubbery polymer, it is necessary to minimize crystallization by breaking up the structural regularity of repeating $-CH_{2}$ - segments.

One way to prevent regular alignment is to add occasional side groups. By copolymerizing ethylene with 25 % to 50% propylene, ethylene-propylene rubber (EPM) is obtained:

n CH=CH₂ + n CH=CH₂
$$\rightarrow$$
 + CH₂-CH₂

The occasional methyl $(-CH_3)$ group sticking out from the polymer chain is believed to prevent neighboring chain segments from aligning perfectly enough to crystallize. A little crystallization can be used to provide cold green (uncured) strength. The high green strength EP Rubbers are therefore relatively high in ethylene content.

Side groups other than methyl can be used to interrupt crystallization; for example, chlorinated and chlorosulfonated polyethylene. These side groups are polar in nature, so they also provide resistance to swelling upon immersion in oil.

A second approach to obtaining elasticity by minimizing crystallization is to include unsaturation or double bonds in the polymer chain. Diene monomers have two double bonds and polymerize mainly by what is called 1,4 addition. That is, the repeat segments are joined at the first and fourth carbon atoms, with the remaining double bond shifted to join the second and third carbon atoms as shown for polybutadiene (BR):

The double bond in the polymer prevents rotation, which is possible with carbon-carbon single bonds. The inability to rotate freely is thought to hinder the alignment of molecular segments and thus inhibit crystallization. In addition, the rigid double bond gives rise to two possible forms. These are geometric isomers, called *cis* and *trans*, depending on whether the polymer continues on the same side (*cis*) of the double bond or on the opposite side (*trans*):



In making emulsion copolymers of butadiene with either styrene (SBR) or acrylonitrile (NBR), catalysts which generate free radicals are used. With these catalysts, the butadiene segments are obtained as a mixture of *cis* and *trans* structures. Both SBR and NBR are non-crystallizing and require reinforcing fillers to provide good strength properties.

When butadiene is polymerized in solution with stereospecific catalysts, the ratio of *cis* and *trans* can be varied as desired. These catalysts are used to make high *cis* BR and to control the structure of solution SBR.

Both side groups and double bonds can be incorporated into the polymer structure to produce highly resilient rubbers. Two examples are shown below:



The polymers are shown as they are normally manufactured. *Cis*-1,4-polyisoprene (IR) nearly duplicates the structure and properties of natural rubber (NR). Polychloroprene (CR) has predominantly *trans* structures. Like high *cis* BR, the structure is sufficiently regular so that IR, NR and CR crystallize on stretching. This characteristic provides high strength in unfilled or gum compounds.

Polarity

The incorporation of polar side groups into the polymer structure provides resistance to swelling when immersed in hydrocarbon oils. These "oil-resistant" rubbers commonly include electronegative atoms from Groups 5 to 7 of the periodic table. While these atoms form covalent bonds with carbon, the electron pair of the bond is slightly displaced toward the electronegative atom. This creates a slight negative charge on the electronegative atom and a slight positive charge on the carbon. The dipolar nature of these bonds provides oil resistance and other properties not found in rubbers containing only carbon and hydrogen atoms.

The effect of different polar groups is shown in Table 2A for one-carbon molecules. For long chain polymers, the oil resistance improves as the number of polar groups increases. However, this is not purely an additive effect. As shown in Table 2B for simple molecules, the presence of multiple polar bonds may partially or completely offset each other and reduce or eliminate the dipole moment.

A. Different Subst	ituents		B. Multiple Substitu	ients	
		Dipole			Dipole
	Molecular	Moment		Molecular	Moment
Common Name	Formula	Debyes	Common Name	Formula	Debyes
methane	CH ₃ -H	0	methane	CH₄	0
methyl chloride	CH ₃ -Cl	1.87	methyl chloride	CH ₃ CI	1.87
methyl fluoride	CH ₃ -F	1.85	methylene chloride	CH,CI,	1.60
methyl mercaptan	CH ₃ -SH	1.52	chloroform	CHCI	1.01
methyl alcohol	CH ₃ -OH	1.70	carbon tetrachloride	CCI	0
formaldehyde	CH ₂ =O	2.33		-	
hydrogen cyanide	CHĒN	2.98			

Table 2: Effect of Polar Substituents

Dipolar molecules orient in an electric field. When an alternating electric field is applied, the orientation of the dipoles switches back and forth to follow the changing electric field. This movement generates heat and a rise in temperature. Thus, polar rubbers are easily heated by microwave ovens.

Increasing the number of polar substituents in a polymer usually increases density, reduces gas permeability and gives inferior low temperature properties.

Glass Transition

When the temperature is lowered, rubbers become stiff and brittle. The rubbers which undergo strain-induced crystallization will also crystallize when stored at low temperature. However, all rubbers eventually stiffen to a rigid, amorphous glass at a temperature called the glass transition (T_g) . The temperature at which this happens is one of the indications of the low temperature service limit of the rubber.

The value of T_g obtained depends on the method of measurement, particularly the time scale of the test. Some low temperature tests do not measure an actual glass transition, but rather stiffness or brittleness. As shown in Table 3, T_g values are dependent on the structure or composition of the polymer. However, T_g is not only determined by the main basic structure, but also by the degree of crosslinking and any isomerization (*cis/trans* conversion) during vulcanization. Furthermore, compounding - especially the incorporation of some plasticizers - can affect the T_g values obtained. The determination of a realistic low temperature service limit should be measured in each specific formulation under actual or closely simulated conditions of service.

Block Copolymers

The copolymers of styrene and butadiene in Table 3 were prepared by emulsion polymerization. This method gives a random distribution of styrene and butadiene segments. For these copolymers, the glass transition temperature increases in proportion to the level of styrene.

						-
% styrene	0	23	36	53	75	100
% butadiene	100	77	64	47	25	0
Tg, ℃	-79	-52	-38	-14	+13	+100

Table 3: Glass Transition of Styrene-Butadiene Polymers

It is possible to obtain a block of hard, styrene segments at each end of a rubbery butadiene block by using special catalysts and polymerization conditions. This results in a thermoplastic rubber, abbreviated as SBS which stands for the specific styrene and butadiene monomers. Many other thermoplastic rubber compositions are possible, and are discussed in Chapter 2. All share a two-phase morphology: a soft, rubbery phase and a hard, plastic phase. The plastic phase provides crosslinks between polymer chains which prevent flow at room temperature. The block copolymers show two Tg's, one for each phase.

Other Features

The main features of polymers which determine physical properties are their molecular weight and the structure of the repeating segments. However, it is possible to trade off some strength properties to gain processing advantages for specific applications. By making branched chains rather than purely linear ones, low viscosity polymers for solution applications are obtained. By lightly crosslinking to form insoluble or gel polymer, better calendering and extruding polymers can be obtained. By broadening the distribution of molecular weights (MWD), polymers that mix more easily can be obtained. The compounder can also broaden MWD by blending different viscosity polymers or adding hydrocarbon process oils.

In some cases, diene polymers can add to the growing polymer chain by 1,2 addition (also called vinyl addition). This creates labile hydrogens or reactive halogens on tertiary carbon atoms. A small amount of this type of structure in the polymer can assist cross-linking reactions.



1,2-polybutadiene

1,2-polychloroprene

In 1,2 addition of a diene monomer, the remaining double bond is on a pendant side group rather than in the backbone of the polymer chain. Incorporating a small percentage of diene monomers by 1,2 addition into otherwise fully saturated polymers permits sulfur crosslinking, without detracting from the good thermal and oxidative stability of the saturated polymer.

Typical properties of selected rubbers are shown in Table 4, ranked by density. Only a sampling of available rubbers is shown. For those listed, a wide range of properties can be achieved by compounding, as discussed in the next chapter. Other types of polymers are available that further improve performance properties. Each specific type of rubber is discussed in greater detail in Chapter 2.

Table 4: Typical Properties of Rubber

Hydrocarbon Rubbers								
Common Name and ASTM Density Tg Service								
Approximate Formula Abbr. Mg/m ³ °C Temp. °C								
Ethylene-propylene	EPDM	0.87	-55	125				
CH ₃ (-CH ₂ -CH ₂ -) ₃ -(-CH-CH ₂ -)-(diene) _{0.2}								
Polybutadiene	BR	0.90	-85	70				
CH ₂ -CH=CH-CH ₂								
Natural, polyisoprene	NR, IR	0.91	-75	70				
CH ₃ CH ₂ -C=CH-CH ₂								

Butyl, polyisobutylene	I	IR	0.92	-65		100
	CH3	CH3				
~~~(-	 -CH₂–C–	) ₅₀ –(–CH ₂ –	-C=CH-(	CH ₂ –)		
	CH3					
Crosslinked polyethylene	XI	LPE	0.92	-110		125
	~	CH ₂ –CH	2~~~			
Styrene-butadiene	S	BR	0.93	-55		70
			C ₆ ⊦	5		
~~~ (-1	CH ₂ –CH=	=CH–CH ₂ –)	) ₅ –(–ĊH-	-CH ₂ )		
Block copolymer	S	BS	0.94	-70, +9	90	65
C ₆ H ₅				C ₆ H ₅		
(–ĊH–CH	₂ –) _X –(–Cł	H ₂ CH=CH-	-CH ₂) _Y -	-(–ĊH–CH ₂ –	·) _x	
	x = ca	a. 100, y =	ca. 100	C		
Specialty Rubbers						
Common Name and Approximate Formula	ASTM Abbr.	Density Mg/m³	Tg °C	Hetero- atom Percent	Service Temp. °C max	903 Oil Swell % max
Common Name and Approximate Formula Nitrile	ASTM Abbr. NBR	Density Mg/m ³ 0.98	T g ° C -40	Hetero- atom Percent 9% N	Service Temp. °C max 100	903 Oil Swell % max 40
Common Name and Approximate Formula Nitrile	ASTM Abbr. NBR	Density Mg/m ³ 0.98	T g ° C -40 ⊂N	Hetero- atom Percent 9% N	Service Temp. °C max 100	903 Oil Swell % max 40
Common Name and Approximate Formula Nitrile	ASTM Abbr. NBR	Density Mg/m ³ 0.98 =CH-CH ₂ -7	Tg °C -40 -40 	Hetero- atom Percent 9% N -CH ₂ -)	Service Temp. °C max 100	903 Oil Swell % max 40
Common Name and Approximate Formula Nitrile	ASTM Abbr. NBR CH ₂ -CH=	Density Mg/m ³ 0.98 =CH-CH ₂ -;	T g ° C -40 CN ↓ 0 ₂ -(-CH-	Hetero- atom Percent 9% N -CH ₂ -)	Service Temp. °C max 100	903 Oil Swell % max 40
Common Name and Approximate Formula Nitrile (ASTM Abbr. NBR CH ₂ -CH= MQ	Density Mg/m ³ 0.98 =CH–CH ₂ –7 0.98	T g °C -40 CN)₂-(-CH- -110	Hetero- atom Percent 9% N -CH ₂ -) 38% Si 22% O	Service Temp. °C max 100 225	903 Oil Swell % max 40 80
Common Name and Approximate Formula Nitrile (-4 Silicone	ASTM Abbr. NBR CH ₂ -CH= MQ	Density Mg/m³ 0.98 =CH−CH₂−; 0.98 CH₃	Tg °C -40 CN ₀₂-(-CH-	Hetero- atom Percent 9% N -CH2-) 38% Si 22% O	Service Temp. °C max 100 225	903 Oil Swell % max 40 80
Common Name and Approximate Formula Nitrile (ASTM Abbr. NBR CH ₂ CH=	Density Mg/m ³ 0.98 =CH-CH ₂ -7 0.98 CH ₃ SI-O-	T g °C -40 CN 02−(−CH- -110	Hetero- atom Percent 9% N -CH ₂ -) 38% Si 22% O	Service Temp. °C max 100 225	903 Oil Swell % max 40 80
Common Name and Approximate Formula Nitrile (-0 Silicone	ASTM Abbr. NBR CH ₂ -CH= MQ	Density Mg/m ³ 0.98 =CH-CH ₂ -7 0.98 0.98 CH ₃ SI-O- CH ₃	T g • C -40 D₂-(-CH- -110	Hetero- atom Percent 9% N -CH ₂ -) 38% Si 22% O	Service Temp. °C max 100 225	903 Oil Swell % max 40 80
Common Name and Approximate Formula Nitrile (-4 Silicone	ASTM Abbr. NBR CH ₂ -CH= MQ	Density Mg/m ³ 0.98 =CH-CH ₂ -; 0.98 CH ₃ SI-O- CH ₃	Tg °C -40 ○2-(-CH- -110	Hetero- atom Percent 9% N -CH2-) 38% Si 22% O	Service Temp. °C max 100 225	903 Oil Swell % max 40 80
Common Name and Approximate Formula Nitrile (ASTM Abbr. NBR CH ₂ -CH= MQ	Density Mg/m ³ 0.98 =CH-CH ₂ -7 0.98 CH ₃ SI-O - CH ₃ CH ₃ 1.13	Tg °C -40 CN ↓ 02-(-CH -110 -110	Hetero- atom Percent 9% N -CH2-) 38% Si 22% O 25% O 1% CI	Service Temp. °C max 100 225 225	903 Oil Swell % max 40 80 80
Common Name and Approximate Formula Nitrile ((Silicone Ethylene acrylate	ASTM Abbr. NBR CH ₂ CH= MQ AEM	Density Mg/m ³ 0.98 =CH-CH ₂ -, 0.98 CH ₃ SI-O- CH ₃ CH ₃ 1.13	Tg °C -40 CN ↓ −2-(-CH- -110 -30	Hetero- atom Percent 9% N -CH ₂ -) 38% Si 22% O 25% O 1% Cl ipolymer	Service Temp. °C max 100 225 225	903 Oil Swell % max 40 80 80
Common Name and Approximate Formula Nitrile (-4 Silicone Ethylene acrylate Te (CH2-CH2)_x	ASTM Abbr. NBR CH ₂ -CH= MQ AEM rpolymer (CH-CH ₂	Density Mg/m ³ 0.98 =CH-CH ₂ -7 0.98 CH ₃ SI-O- - CH ₃ 1.13	Tg °C -40 CN -40 -110 -110 -110 -30 (CH₂-CF	Hetero- atom Percent 9% N -CH2-) 38% Si 22% O 25% O 1% Cl ipolymer 42)x-(CH-CH	Service Temp. °C max 100 225 225 150	903 Oil Swell % max 40 80 80
Common Name and Approximate Formula Nitrile (-(Silicone Ethylene acrylate Te (CH ₂ -CH ₂),	ASTM Abbr. NBR CH ₂ -CH= MQ AEM rpolymer (CH-CH ₂ - O=C	Density Mg/m ³ 0.98 =CH-CH ₂ -7 0.98 CH ₃ SI-O- I CH ₃ 1.13 1.13	Tg °C -40 CN -40 -110 -110 -110 -30 □ (CH ₂ -CH	Hetero- atom Percent 9% N -CH ₂ -) 38% Si 22% O 25% O 1% Cl ipolymer 4 ₂) _x -(CH-CH C=O	Service Temp. °C max 100 225 225 150 22yy	903 Oil Swell % max 40 80 80

Polyacrylate	ACM	1.13	-30	25% O 1% Cl	150	60
	0=Ç-00	C_4H_5	O-C ₂ H	₄CI		
~	~~ (–CH–C	CH ₂ -) ₃₀ -(-	∣ -CH–C⊦	l₂−)x ~~~		
		2 00				
Chlorinated polyethylene	СМ	1.18	-40	36% CI	150	80
		CI				
	~~ CH0	 СН. – С.Н.–	-СН.–С	.H. ~~~		
	01.2		02			
Chlorosulfonated polyethylene	CSM	1.18	-50	35% Cl 1% S	125	80
	ĊI			SO ₂ CI		
~~ (–CH ₂ –CH ₂	–CH₂–CH	I–CH ₂ –CH	I_–CH ₂ –	-)₁₂–(–CH–CH	_ _)~~~	
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#### by Dwight W. Chasar* and Robert W. Layer*

Emerald Performance Additives, LLC Akron, OH *Retired

A rubber polymer by itself has such poor properties that is has limited commercial value; a variety of materials must be added to improve its properties and make it commercially useful. The science of adding these ingredients to rubber in order to produce the best possible product and ensure efficient, trouble-free manufacturing is known as compounding. In order to select the most suitable elastomer and additives from the multitude of available products, the rubber compounder needs to be thoroughly aware of the following areas of rubber chemistry and technology:

- 1. Properties of individual elastomers.
- 2. Modifying materials, which affect cost, processing and vulcanizate properties.
- 3. Vulcanizing or curing systems.
- 4. Antidegradants.
- 5. Mixing procedures.
- 6. Test methods for evaluating processing, curing and vulcanizate properties.

This section gives an overview of these important areas of rubber compounding. For reasons which follow, emphasis will be placed on curatives and antidegradants.

#### **Elastomers and Modifying Ingredients**

The first step in effective compounding is the selection of the proper elastomer. The inherent properties unique to each elastomer, such as the oil resistance of NBR, the ozone resistance of EPDM and the high resilience of NR, determine the suitability of an elastomer for any given application. The important characteristics of each rubber will be covered individually in Chapter 2. Of the materials added to the formulation, fillers play a dominant role in determining factory processing and vulcanizate properties. Fillers are used 1) to reinforce and increase strength properties, 2) to act as coloring agents, 3) to extend and dilute, 4) to lower costs, and 5) to alter processing characteristics.

The size and shape of a filler particle have the greatest effect on the above properties. In general, fillers with a particle size of greater than 10 microns can be harmful to physical properties, due to the localized areas of stress, which they create. Fillers with a particle size between 1 and 10 microns, such as ground limestone and clays, neither harm nor help vulcanizate properties. They are used primarily as diluents. Semi-reinforcing fillers, which improve strength and modulus properties, have particle sizes from 0.1 to 1 micron. Reinforcing fillers, which significantly improve vulcanizate properties, have particle sizes of 0.01 to 0.1 microns.

Various oils are added to the rubber compound to improve processing and to lower cost without affecting vulcanizate properties. Processing oils, such as castor oil and sulfonated petroleum oils, are added to soften the rubber and facilitate mixing, extruding, etc. These oils are used at loadings of up to 10 parts per hundred of rubber (phr). Paraffinic, naphthenic and aromatic oils are used at much higher loadings to extend the rubber and lower cost without sacrificing physical properties. At this high loading, good compatibility between the elastomer and the oil is essential. Paraffinic oils are more compatible with the more highly saturated rubbers - EPDM and IIR, while aromatic oils are the most compatible with SBR, NR and BR. Staining increases in the order: paraffinic < naphthenic < aromatic.

Many other compounding ingredients are added to the compound to meet specific requirements: tackifier resins, blowing agents, colorants, desiccants, etc. However, the selection of the proper cure system is vital to the development of the desired vulcanizate properties. The most widely used cure systems are based on sulfur and require an accelerator and activators such as zinc oxide and a fatty acid.

#### Sulfur Vulcanization

Raw rubber is an entanglement of high molecular weight hydrocarbon chains; it therefore flows on standing and does not retain its shape. Thus, for rubber to become useful, its chains must be permanently linked together to increase its strength. In 1839, Charles Goodyear discovered that rubber chains could be linked together, i.e. vulcanized, by heating them with sulfur and white lead. In this process, sulfur linkages of various lengths form bridges between the rubber chains.

From 1839 to about 1906, rubber was vulcanized by Goodyear's method. Amajor change was the substitution of zinc oxide for the white lead. Nevertheless, it took hours, or even days, to vulcanize products. Accelerators were first discovered in 1906, when it was found that aniline greatly shortened vulcanization times. More efficient accelerators such as the mercaptobenzothiazoles, guanidines, dithiocarbamates and thiurams were discovered around 1920. As shown in Figure 1, these accelerators are derived from aniline and other amines. The delayed action sulfenamides were introduced in the 1930's. Today, the sulfur crosslinking of any unsaturated rubber can be accomplished in a matter of minutes by heating rubber with sulfur, zinc oxide, a fatty acid and the appropriate accelerator.



Figure 1: Classes of Accelerators

The vulcanization of rubber changes its physical properties. It increases viscosity, hardness, modulus, tensile strength, abrasion resistance and rebound, and decreases elongation at break, compression set, hysteresis and solubility in solvents. All these changes are proportional to the degree of crosslinking (number of crosslinks), except tensile strength which reaches a maximum at about one crosslink per every 150 monomer units.

The length of the sulfur crosslinks also affects the physical properties. Longer crosslinks (polysulfide crosslinks) improve tensile strength, tear strength and fatigue properties. On the other hand, shorter crosslinks (mono- and di-sulfide) improve thermal and oxidative stability and lower compression set.

Although the vulcanization of rubber mainly produces the desired sulfur type

crosslinks, unwanted products such as cyclic sulfides also form. From a practical point of view, these side reactions are ignored.

One of the very fortunate things about sulfur vulcanization is that it takes place in stages (see Figure 2):

- Stage one is the induction period when the curatives react with themselves in preparation for the crosslinking reaction. The induction period is very useful since it allows the compound to be safely mixed and formed without prematurely curing (scorching).
- 2. The second stage is the actual formation of crosslinks, i.e. the vulcanization of the rubber.
- 3. The third stage is the undesirable loss of crosslinks, called reversion, that occurs when heating is continued beyond the time needed to achieve an optimum cure.



Figure 2: Cure Characteristics of Various Accelerators

The chemistry of vulcanization can be viewed as a cyclical process during which the zinc-sulfur-accelerator active complex is continuously regenerated after sulfur crosslinks are formed (see Scheme 1). Step 1 corresponds to the induction period. Step 2 generates pendant accelerator linkages, the predecessor to crosslinks, while Step 3 corresponds to vulcanization in Figure 2. The hypothesis that the active complex is continuously regenerated implies that vulcanization will only stop when all the free sulfur is consumed.



Scheme 1

#### **Accelerated Sulfur Vulcanization**

Accelerators play an important role in the vulcanization of rubber and they affect the scorch safety, the rate of cure and the length and number of crosslinks. Accelerators are therefore frequently classified based on these characteristics, as follows:

Accelerator Type	Scorch Safety	Cure Rate	Crosslink Length
None		Very Slow	Very Long
Guanidines	Moderate	Moderate	Medium - Long
Mercaptobenzothiazoles	Moderate	Moderate	Medium
Sulfenamides	Long	Fast	Short - Medium
Thiurams	Short	Very Fast	Short
Dithiocarbamates	Least	Very Fast	Short

Scorch safety is related to the speed with which the accelerator is converted to its salt. Consequently, an accelerator's salt is very scorchy, its disulfide is somewhat less scorchy, while the more stable sulfenamides have the longest scorch safety of all. The addition of bases reduces scorch safety, since they catalyze salt formation. Retarders such as VANTARD® PVI increase scorch safety by trapping the accelerator anion, and thus interfere with salt formation.

The cure rate, efficiency and the length of the crosslinks formed by an accelerator are generally related. Accelerators based on the dithiocarbamyl group are faster curing and produce more and shorter crosslinks per mole than

do accelerators based on mercaptobenzothiazole. Figure 2 illustrates these characteristics for the various accelerator types.

While not shown in Figure 2, the simultaneous use of two different types of accelerators often results in enhanced activity due to synergism. The most notable example of this is the increased efficiency gained from the combination of the thiocarbamyl sulfenamide, CURE-RITE[®] 18, with a benzothiazole sulfenamide such as AMAX[®], in a ratio of two to one. This system produces a 33% higher modulus than AMAX alone at the same loading. At the same time, somewhat shorter crosslinks are formed.

Rubbers differ in their ease of vulcanization. Since crosslinks form next to double bonds, rubbers which are highly unsaturated are the most easily cured, for example NR > SBR > EPDM. Because of this, the amounts of sulfur and accelerator required to cure different rubbers vary. Conventionally, natural rubber is cured using about 2.5 phr of sulfur and 0.7 phr of sulfenamide accelerator. By comparison, SBR is cured with less sulfur (1.8 phr) and more accelerator (1.5 phr).

Although accelerators have an effect on the length of crosslinks, the latter can be altered more significantly by changing the sulfur to accelerator ratio. Progressively increasing the accelerator to sulfur ratio is described as going from a conventional to a semi-EV to an EV cure system, and produces progressively shorter crosslinks. These systems are primarily used where reversion resistance is required. Another way to produce shorter crosslinks is to replace some or all of the sulfur with a sulfur donor, such as VANAX[®] A or MORFAX[®].

Vulcanization temperature is also important. Optimum properties are obtained when curing is done at the lowest possible temperatures. However, higher temperatures are frequently used to increase productivity. Unfortunately, the modulus decreases as cure temperature is raised, no matter which accelerator is used (See Figure 3). Thus, to recover the modulus lost by raising the curing temperature, more curative must be added. More accelerator can also be added to minimize reversion.

Accelerators or other compounding ingredients can migrate to the surface (bloom) if used above their solubility limit. This becomes more of a problem for rubbers which require high accelerator loadings, such as EPDM. A mixture of accelerators is often used to prevent this problem. The sulfenamides and the higher molecular weight thiurams, such as BUTYL TUADS[®], have the best solubilities in most rubbers. The room temperature solubility of sulfur in rubber is about 2.5 phr. Where sulfur bloom is a problem, polymeric or "insoluble sulfur" can be used.



Figure 3: Effect of Cure Temperature on Torque and Reversion

#### **Other Cure Systems**

Peroxide curing is the next commonly used system. Compared to sulfur curing, peroxides offer the advantages of curing both saturated and unsaturated rubber and of producing quite thermally stable carbon to carbon crosslinks. The disadvantages of peroxide curing are poor tensile and tear strengths, incompatibility with many antioxidants, and higher cost.

Peroxides cure by decomposing on heating into peroxy radicals which abstract a hydrogen atom from the elastomer and generate a polymer radical. Most of these radicals immediately combine to form a crosslink. The rate of crosslinking is therefore directly proportional to the rate of decomposition of the peroxide. Consequently, cure rates and curing temperatures depend on the stability of the peroxide, which decreases in the following order: dialkyl > perketal > perester and diaryl peroxides.

A number of non-sulfur vulcanizing systems are used in specific applications. For example, metal oxides are used to cure NEOPRENE by converting its few active allylic chlorines from 1,2 addition into ether crosslinks, phenol-formaldehyde resole resins cure butyl rubber via an "ene" reaction to form thermally stable chroman crosslinks, and by a similar mechanism, p-benzoquinone dioxime cures butyl and other unsaturated rubbers.

#### Antioxidants

Once the desired properties are attained by properly compounding and curing a rubber product, it becomes necessary to prevent these properties from changing during service. Oxidative changes in particular can dramatically affect service life. Consequently, all products must contain an appropriate antioxidant to prevent degradation. Oxidation is a cyclical free radical chain process, as shown in Scheme 2.



Scheme 2

Oxidation is initiated whenever rubber chains are broken and carbon radicals are formed. This occurs during manufacture and in service whenever the rubber is mixed, flexed, stretched or heated. Once formed, these radicals set in motion a chain reaction by rapidly adding oxygen to become peroxy radicals (Step 1). These in turn abstract a hydrogen atom from the rubber (Step 2), regenerating carbon radicals (R•) to continue the cycle. Furthermore, the hydroperoxide formed in Step 2 decomposes into two more oxy radicals (HO• and RO•) in Step 3. These also react with the rubber in the final steps of additional cycles, and increase the rate of oxidation. It should be noted that unsaturated polymers oxidize more readily than saturated polymers.

Oxidation causes rubbers to either harden or soften. The reason is that the radicals formed in the above chain reaction, being highly reactive and very unstable, will be rapidly converted to more stable products. In most rubbers, these radicals combine and in the process form crosslinks, causing the rubber to harden (Figure 4). In natural rubber, the crosslinking of these radicals is hindered because of the bulkiness of the methyl side group. Consequently, these radicals prefer to disproportionate and cleave. This reduces the molecular weight and natural rubber softens on aging.



Figure 4: Aging of Elastomers

The oxidation of rubber can be slowed considerably and the service lifetime extended by adding antioxidants. Antioxidants are compounds which scavenge and destroy peroxy (ROO•) and alkoxy (RO•) radicals before they have a chance to react with the rubber in Step 2 (Scheme 2). They are therefore referred to as primary antioxidants. They are typically secondary aromatic amines and substituted phenols which have very reactive hydrogen atoms.

One class of primary antioxidant is the phenols (Figure 5). Phenolic antioxidants are generally used in non-black-loaded products for least discoloration. In protecting the vulcanizate, phenols produce colored reaction products (yellow, tan or pink), but the discoloration is significantly less than that produced with amines, the other main class of primary antioxidant. Consequently, phenols are generally called "nondiscoloring". Phenols may provide good resistance to aging until the antioxidant is consumed by the process of scavenging oxy radicals (ROO• and RO•; the former is shown in Steps 1 and 2 of Figure 5).



Figure 5: How Phenol Antioxidants Retard Oxidation

Aromatic amines (Figure 6) are the most effective primary antioxidants, but they are discoloring and can only be used where tan or darker colors are acceptable. Of the amine antioxidants, the diphenylamines, such as AGERITE® STALITE® S, and the polymeric dihydroquinolines, such as AGERITE RESIN D®, are the least discoloring. While all the p-phenylenediamines are highly discoloring, they possess the advantages of being metal ion deactivators, antiflex agents

and antiozonants. The effectiveness of amine antioxidants in vulcanizates is frequently improved by adding a mercaptobenzimidazole derivative such as VANOX[®] ZMTI. In addition to scavenging two oxy radicals like the phenols (Steps 1 and 2 of Figure 6), amines are also believed to enter into a cyclic process in which the nitroxyl radical is continuously regenerated while consuming oxy radicals (Steps 3 and 4 of Figure 6).



Figure 6: How Amine Antioxidants Retard Oxidation

Another method of slowing oxidation is to add a compound which destroys the hydroperoxides formed in Step 2 of Scheme 2 before they can decompose into radicals (Step 3) and start new chains. These materials, for example phosphites and sulfides, are called hydroperoxide decomposers or secondary antioxidants. When a primary and a secondary antioxidant are used together, a synergistic improvement in activity usually results. Thus, combinations of phenols and phosphites such as AGERITE GELTROL® are widely used to stabilize synthetic rubbers. Unfortunately, phosphites are destroyed during vulcanization and are not effective in vulcanizates.

For products to have maximum lifetimes, the antioxidants must not be lost during service. A major source of loss is the evaporation of the antioxidant, which often occurs with BHT, a monomeric phenol. To avoid this, the less volatile, higher molecular weight antioxidants are used. Bis-phenols such as AGERITE SUPERLITE[®] or VANOX GT are widely used as nonstaining antioxidants in rubber. For black compounds, AGERITE RESIN D is frequently favored since it is the least volatile, staining amine antioxidant.

Antioxidant activity is not a linear function of concentration. As the amount of antioxidant increases, less and less improvement in oxidative stability occurs (Figure 7). From the standpoint of cost, only enough antioxidant should be used to give the desired protection. For most antioxidants, this is about 1 phr.

The oxidative stability of vulcanizates can also be improved by shortening the length of the sulfur crosslink. The most effective way to do this is to decrease the amount of sulfur and increase the amount of accelerator used in the cure systems.



Figure 7: The Effect of Antioxidant Dose on Activity

Aging tests on rubber are carried out at 70 to 120 °C to enable results to be obtained in a matter of days. For natural rubber vulcanizates, loss of tensile strength is a measure of oxidative stability, while modulus increase (hardening) is used for SBR.

#### Antiozonants

The minute amounts of ozone present in the atmosphere (~5 pphm) will crack most rubbers if they are stretched. In many cases, the cracks are so large as to destroy the usefulness of the product. Ozone is generated in the atmosphere by the photolysis of oxygen, and its concentration therefore depends primarily on the amount of sunlight available. Unlike oxidation, ozone attack is not accelerated by increasing the temperature. Ozone directly reacts with, and cleaves, the double bonds of rubber. Thus, only rubbers with backbone unsaturation will be cracked by ozone. EPDMs which contain only pendant unsaturation will not crack. Furthermore, cracks will only develop if the rubber is stretched, since, without stretching, the underlying double bonds are not exposed to ozone.

Rubbers differ in their resistance to ozone. All of the highly unsaturated rubbers, such as NR, SBR, BR and NBR, are readily cracked. IIR and CR

are moderately ozone-resistant because of their low level of unsaturation and deactivated double bond, respectively. EPDMs are totally resistant.

Ozone cracking can be prevented in three ways: 1) coating the surface, 2) adding a chemical antiozonant, or 3) relieving internal stresses by adding ozone-resistant polymers. Ozone cracking can be prevented by adding waxes which bloom to the surface and form a protective barrier (VANWAX[®] H). Since this bloom is brittle, it is broken by flexing, so that waxes only protect rubber under static conditions. For service conditions which involve continuous flexing, p-phenylenediamine chemical antiozonants are used. These materials, for example 6PPD, scavenge the ozone before it reacts with the rubber. In this process, a barrier of ozonized product forms, which protects both the rubber and antiozonant from further attack. Both the N,N'-dialkyl and the N,N'-alkyl-aryl derivatives of p-phenylenediamine are excellent antiozonants, but the latter are more widely used since they are less scorchy and more resistant to oxidation. The diaryl derivatives, e.g. DPPD, are considerably less active and find use in the less reactive chloroprenes.

A common loading for antiozonants is 1.5 to 3 phr. Combinations of waxes and antiozonants are used where the conditions of service involve long periods of both static and dynamic stresses, as in tires.

There are no commercially available nonstaining antiozonants for NR or SBR. But the more ozone-resistant CR can be protected by materials which are nonstaining. Where the staining p-phenylenediamine antiozonants cannot be used, as in white sidewalls, blends of elastomers are used. Ozone protection is attained only when 30 phr or more of an ozone-resistant polymer are added to the ozone-susceptible rubber. Such blends work by relieving stresses at the tip of the growing crack when it encounters the dispersed ozone-resistant polymer phase.

There are a variety of ozone test methods. The rubber must be stressed in all cases. This can be done by bending or elongating the sample by about 20%. The stress can be applied to the sample statically, dynamically or intermittently, to simulate actual conditions of service. The sample can be aged outdoors, where the ozone concentration varies, or in an ozone chamber at a fixed ozone concentration, usually 50 pphm. Although one can measure the size and number of cracks formed, test results are often based on a somewhat subjective rating scale of 1 to 10.

#### Conclusion

Compounding high quality rubber products requires the use of a variety of ingredients. One of the purposes of this book is to help in the selection and use of these ingredients. Consequently, some of the most important ingredients, such as the elastomer and fillers, as well as mixing and testing procedures, are covered in detail in subsequent chapters.



## CHAPTER 2 Commercial Elastomers

#### NATURAL RUBBER

#### by Dr. Eng-Long Ong* and Dr. Aik-Hwee Eng**

*Kossan Rubber Industries Berhad (Formerly Malaysian Rubber Board) **Ansell (Shah Alam) Sdn.Bhd. Malaysia

Natural rubber is obtained from the *Hevea brasiliensis* tree, which originates in the Amazon jungle. The attempt to grow the rubber tree started in 1876 when 70,000 rubber seeds were collected from the Amazon jungle and planted in London's Kew Gardens. Of these, 2,800 seeds germinated. Subsequently, some of the young seedlings were brought to the botanical gardens at Heneratgoda, Ceylon (now Sri Lanka). In 1877 twenty two of the young rubber trees were then brought to Singapore, with half of the seedlings being planted there, and nine in Kuala Kangsar, Malaya (now Malaysia). These trees were commercially propagated into billions of trees throughout South East Asia. Today, Thailand, Indonesia and Malaysia are the major rubber producing countries, accounting for about 70% of the world's total natural rubber production.



### Figure 1: Surviving Rubber Tree from the Initial Seedlings Brought From the Amazon and Planted in Kuala Kangsar, Malaysia in 1877

#### Rubber Tree

The natural rubber tree is normally grown in a climate with a temperature range of 25° to 35°C and a minimum yearly rainfall of 2000 mm. It is a unique crop, being neither reproductive nor vegetative in origin, in comparison to other major crops.¹ The propagation of the *Hevea* tree is carried out by green-budding technique, whereby a bud from a selected tree is removed and inserted under the bark of the lower stem of a young seedling, which is called the rootstock, which subsequently becomes the trunk of the mature tree. All the offspring from the parent are known as clones. The young plants are usually grown in polyethylene bags and transplanted to the field when they have two or three whorls of leaves,

which normally takes two to three months. With the improvements in budding techniques and better agronomic and horticultural practices, the immaturity period has been reduced from 6 to 7 years to 4 to 5 years before they can be tapped for their latex. During the hot "wintering" period when the trees shed their leaves, which normally occurs over a period of several weeks in February through March, there is a drastic decrease in latex yield, as well as a decrease in the colloidal stability of the latex. The tree does not reach peak production until it is 12 to 15 years old. The economic life span of the tree is about 25 years, after which it is ready for replanting.

#### Clones

Initially, the trees from the Amazon and planted in South East Asia had a rubber yield of less than 500 kg per hectare per year. Over the years, many new clones have been bred by bud grafting, primarily to improve the latex yield. Other important features include resistance to wind damage, major leaf diseases, and tree dryness or brown bast, as well as improvements to good girth increment on tapping, good bark thickness, response to low-frequency tapping, response to chemical stimulation, and robust growth. Many clones with improved yield have been produced from the breeding programs carried out in the past (Table 1). Some modern clones, as demonstrated in large scale trials, are capable of yielding more than 3000 kg/ha/yr under optimum conditions. However, this is still well below the theoretical yielding potential of rubber tree of 10,000 kg per ha per year.² Today, the yield of rubber can be as high as about 2,600 kg/ha/year from a productive estate.³

Decade	Clone	Average Yield Over Several Years (kg/hectare/year)
1920	Unselected	600
1930	Pil B 84	1000
1950	<b>RRIM 501</b>	1400
1960	<b>RRIM 600</b>	2200
1970	PB 235	2500
1980	RRIM 901	2300
1990	RRIM 937	2500
2000	RRIM 2001	2950

Table 1: Improvements in Yield of Hevea Through Plant Breeding

Table 1 also shows that the yield from the various improved clones has reached a plateau value of 2500-3000 kg/ha/yr. The present clones are based on the original seedlings from Brazil and therefore have a very narrow genetic base. In 1981 the International Rubber Research and Development Board (IRRDB) organized an expedition to collect more wild *Hevea* materials from Brazil. The seedlings collected during this expedition are now being cross-fertilized and are expected to further improve the yield of latex.

In addition to the traditional objective of achieving a high rubber yield in the breeding program, attention is now also being given to the breeding of fastgrowing clones for timber production due to the increased demand for rubber wood based furniture in recent years.^{4,5} Currently, the rubber wood only accounts for about 2% of global wooden furniture market share, indicating that there is a vast untapped market potential in the rubber wood industries. This has led to the establishment of rubber forest plantation system in Malaysia where the rubber trees are grown with minimum maintenance such as weeding and manuring plus pest and disease rounds.⁶ This systems seems to be rather competitive as reflected by the high growth of height and diameter of trees, which allow them to dominate over surrounding vegetations. These fast-growing clones are known as latex timber clones (Figure 2). The dry rubber content of the latices from these clones is normally high, i.e., above 40%. Other properties of the latex are very similar to those of normal latex.^{7.8}



Figure 2: Rubber Trees Cloned from the RRIM 2000 Series Latex Timber

#### **Tapping and Stimulation**

In rubber plantations the rubber trees are planted in rows ranging from 250 to 400 trees per hectare. Rubber is found in the form of latex contained in latex vessels in the bark of the tree (Figure 3). Traditionally, natural rubber latex is obtained from the trees by making an incision in the bark with a special knife

in a process called tapping. The most common practice is to tap each tree half way round its circumference on alternate days (denoted as ½ S d/2). Latex flows rapidly immediately after tapping, but the flow will gradually stop after about four hours. The latex is allowed to flow into a cup and is collected 3 to 4 hours after tapping. The tapping is carried out in the morning before sun rises. A skilled rubber tapper can tap about 450 to 500 trees per workday. In areas where there is a shortage of tappers, a less intensive tapping system that involves tapping once every third, fourth or sixth day is practiced. In this case yield stimulation is usually employed. Recently, rain gutters have been incorporated to minimize the loss of tapping days, and to wash out late latex drips that occur after the tapper's collection. This can improve the yield by 400 to 700 kg/ha/year.⁹



Figure 3: The *Hevea* Tree Schematic (Inset: section of bark showing latex vessels)

Latex yield can be increased by applying ethephon (2-chloroethylphosphonic acid) to the scraped bark of the trees, thereby reducing the frequency of tapping the trees.^{10,11} When ethephon penetrates the trees it disintegrates and releases ethylene gas, which stimulates the tree's latex production. A yield increase per tree of just below 50% can be achieved with ethephon.
More productive methods of stimulating the trees, collectively known as Low Intensity Tapping Systems (LITS), have been developed recently. A technique known as RRIMFLOW, as shown in Figure 4, is a method of stimulating trees through the intermittent flow of ethylene gas.^{12,13} It uses a four inch short-cut system with a PVC applicator being fixed over lightly scraped bark, adjacent to the tapping panel. Ethylene gas is applied directly to the tree through the applicator after every second tapping. On certain tree clones, this method of stimulation can more than double the amount obtained using the conventional tapping system. Other similar techniques include the 'AAR Jacket System'¹⁴ and 'Hypodermic Latex Extraction'.¹⁵ REACTORRIM is a method of stimulating trees by slow release of ethylene gas that continuously diffuses into the latex vessel system through a button diffuser fixed to the bark.^{16,17} This tapping system yields 200 to 250% more latex than the conventional tapping system, and is suitable for trees more than fifteen years old.



Figure 4: RRIMFLOW Short-cut System (I/8S↑ d/4) Gas Stimulation of Rubber Tree Tapping

### **Natural Rubber Latex**

In the tree, natural rubber hydrocarbon (*cis*-polyisoprene) exists as minute particles, from which a dispersion of milky fluid is formed. This milky fluid is known as latex. The latex vessels, or laticifers, that contain latex can be found in

every part of the tree. Even embryos develop latex vessels in the early stage of their development. The density of the latex vessels is highest in the secondary phloem, and lowest in the wood.¹⁸ However, for practical reasons, latex is normally harvested by incising the latex vessels in the trunk at about 40 to 60 cm girth after at least four years of growth for sufficient girth.

Rubber particles in fresh latex of Hevea brasiliensis have been shown to have a bimodal distribution with a mean diameter of 1.07 micrometers.¹⁹ When natural rubber latex is centrifuged at a high speed, e.g., 15,000 g, it is separated into several fractions as shown in Figure 5.



Figure 5: Different Fractions of Centrifuged Natural Rubber Latex

The Frey-Wyssling complexes contain carotinoid compounds, which are normally orange or yellow in colour. The serum (C-serum) is colorless, containing water soluble materials such as minerals, water soluble proteins while the bottom fraction contains organelles originated from the lutoid particles. When field natural rubber latex of 30 to 40% dry rubber content is centrifuged at a lower speed, e.g., 7000 rpm or 6000 *g*, such as those used in the commercial latex concentrate production, the latex is separated into concentrated latex (cream) of 60% dry rubber content and skim latex of 5% dry rubber content. The rubber particles from the rubber cream fraction have been found to contain a much higher amount of adsorbed materials, such as lipids and proteins, than those from the skim fraction. The adsorption of these materials hinder the inter particle diffusion of the rubber molecules, forming a rough film that retains the topology of individual particles. In the case of skim particles, they coalesce more readily, forming a relatively uniform film.²⁰

Further investigation has shown that the lipid materials remained attached to the rubber molecule even after purification by centrifugation in the presence of surfactant, enzymatic deproteinization, and acetone extraction, indicating the lipids are part of the rubber molecules, The rubber cream fraction has been found to contain higher lipids than the skim rubber.²¹ Table 2 shows the difference in lipid content of different fractions of rubber, expressed in ester functional group.

Sample Ester group / mmol per kg (N					
Cream fraction	7.8				
Serum fraction	0.9				
Bottom fraction	8.6				

Table 2: Lipid Content of Rubbers from Centrifuged Latex by Ester Group

Since the average size of rubber particles in the cream fraction has been shown to be ten times larger than that in the skim rubber,²² it is reasonable to assume that small rubber particles represent a newer formed entity from which larger rubber particles are formed. This is supported by the observation that the molecular weight of the large rubber particles increased with increasing the particle size.²³ This is further enhanced by the observation that the small rubber particles have been found to have much higher rubber transferase activity than bigger rubber particles.¹⁹

# **Rubber Tree's Utilization of Latex**

As discussed earlier, plant such as *Hevea brasiliensis*, produces enormous quantities of latex, which utilizes much of its resources, in the rubber biosynthesis process. However, the utility of latex to the rubber tree is not clear.²⁴ Natural rubber is not known to be metabolized in the tree because the tree lacks enzymes that are capable of breaking it down.²⁵ It has been suggested that natural rubber protects the tree against injury or play a role in its defense system.^{26, 27} However, this does not seem to be true, because the presence of rubber does not deter herbivore feeding, insect attack or disease incidences.²⁸ Other possible functions such as a carbon sink, antioxidant, radical scavenger, or antidote to ozone toxicity have also been reported.^{24, 28-30} The possible utility of latex has also been investigated using the cDNA libraries from the latex of *Hevea brasiliensis* to analyze the genes expressed in the latex by single-run partial sequencing of the cDNA clones. Although defense gene was identified, there was insufficient evidence to prove that latex serves as defense mechanisms in the plant.³¹

# Natural Rubber Hydrocarbon

# Chemical Structure

Based on the ¹³C-NMR studies on the naturally occurring polyprenols and polyisoprene in latex obtained from Goldenrod and Sunflower, the  $\omega$ -terminal group, or the initiating end, has been found to contain two types of molecular groups, i.e., (1) a dimethylallyl group followed by two *trans* isoprene units, and (2) a dimethylallyl group followed by three *trans* isoprene units.^{32,33} In the case of the low molecular weight fraction of natural rubber, the expected dimethylallyl group

has not been identified. However, the NMR signals of the two *trans* isoprene units linked to the  $\omega$ -terminal have been observed. The signals indicated the presence of  $\omega$ -terminal in the form modified dimethylallyl group. This was further confirmed by ¹H-NMR studies using polyprenols as the model compounds.³⁴ The terminating end, i.e. the  $\alpha$ -terminal group, is expected to be a diphosphate, or its derivative, such as fatty acid or hydroxyl groups, based on the studies on rubbers from Goldenrod, Sunflower,^{32,33} and *Lactarius* mushrooms.^{35,36} Selective enzymatic decomposition and NMR studies indicated that the  $\alpha$ -terminal group is a phosphate and diphosphate linked to phospholipids.³⁷⁻³⁹ The fundamental structure of natural rubber is postulated to be as follows:

R is an unidentified group and  $\alpha$  is a phosphate or diphosphate linked to phospholipids. The n-value is in the range of 600-3000. ⁴⁰

## Figure 6: The Chemical Structure of Natural Rubber

### Abnormal Groups

Besides the isoprene units, the natural rubber molecule has also been reported to contain abnormal groups such as epoxide,⁴¹ ester,³² aldehyde,^{42,43} and lactone.⁴⁴ Further research has shown that the presence of trace amounts of *cis*-epoxide in production samples is likely to be the by-product of oxidative degradation of the isoprene unit that occurs during processing of the rubber.^{45,46} The presence of ester groups in commercial natural rubber is not due to lactone groups, but fatty acids which can be removed by transesterification with sodium methoxide.⁴⁷ Analysis of the methyl ester by ¹H-NMR revealed that it contains 20% unsaturated and 80% saturated fatty acids.⁴⁷ Recent studies indicated that the fatty acid groups are linked to the phospholipids at the  $\alpha$ -terminal as shown in Figure 6.³⁷⁻³⁹ The existence of aldehyde groups has been shown to be derived from the oxidation of olefinic groups of unsaturated fatty acids bonded to the natural rubber molecule.²¹

### Gel and Branching

There are two types of gel in natural rubber: macrogel or tight gel, and microgel or loose gel. Macrogel occurs as swollen rubber when dry rubber is allowed to dissolve in a rubber solvent.^{48,49} Microgel, on the other hand, is normally found to evenly disperse in the solvent. However, it can scatter light and therefore gives an opaque look to the rubber solution. Based on the swelling ratio of the gel in toluene, the average molecular weight between crosslink points in microgel was estimated to be  $2x10^5$  to  $5x10^5$  g/mol, indicating that it contains a loosely bound network, possibly tri- or tetra functional branch-points.⁵⁰⁻⁵³ Analysis of the gel shows it to contain a high level of proteins and minerals.^{51,54,55} Osmometry and NMR studies on fractionated natural rubber indicated that branching occurs in both low and high molecular weight molecules.⁵⁶ In addition, a significant reduction in

molecular weight of natural rubber has been observed after deproteinization and transesterification, indicating that the branch-points are associated with proteins and phospholipids, most probably located at the  $\alpha$ -terminal.^{40,57-59} The gel content of natural rubber depends on the polarity of solvent used, implying that it involves hydrogen bonding or/and ionic crosslinking.^{49,60,61} Natural rubber from the young seedlings has been found to contain similar level of gel as those from mature trees. However, it was observed that gelation occurred very easily in the case of seedling rubbers after purification and the gel fraction was solubilized by transesterification, indicating that the former has reactive functional groups which can form gel, similar to that in rubber from mature trees. ⁶²

Gel has a prominent stiffening effect on natural rubber and decreases the stress relaxation time.⁵² High gel content rubber showed higher green strength than low gel content rubber because the gel phase forms a network that permits orientation of the rubber segments on stretching, i.e., stretch-induced crystallization.⁵⁴ Natural rubber gels have been found to reduce the overall crystallinity of the polymer.⁶³⁻⁶⁵

## Storage Hardening

The progressive increase in Mooney viscosity of natural rubber on prolonged storage under ambient conditions has long been recognized.⁶⁶ This phenomenon is known as "storage hardening", and is not a desirable property of natural rubber as a raw material because it results in changes to its processing behavior. However, the technological aspect has been resolved,⁶⁷ and constant viscosity grade rubbers (CV grade) are now available, although the mechanism of storage hardening has yet to be conclusively explained.^{50,68,69}

The characteristics of the storage hardening process are: hardening is accelerated under low humidity conditions,⁷⁰ the process requires amino acids or proteins,⁷¹ and it can be inhibited by the addition of monocarbonyl reagent such as hydroxylamine, dimedone, or semicarbazide.⁷² Recent studies indicated that bonded fatty acids or their derivatives are responsible for the storage hardening. ^{55,73} Studies of natural rubber under accelerated storage hardening conditions revealed that the bimodal molecular weight distribution rubber gradually changed to unimodal, with the peak in the low molecular weight region slowly shifting to the high molecular weight region.⁷⁴ The Mw/Mn value was found to change from 14 to 3 after subjecting it to accelerated storage hardening conditions at 70°C in the presence of  $P_2O_5$ , due to the decrease in the low molecular weight fraction. Storage hardening was found to increase the plasticity retention index of natural rubber,⁷⁵ a measurement of ageing resistance, and contributes to the high green strength of natural rubber.⁷⁶ The rate of cold crystallization of natural rubber, however, has been found to be slower after storage hardening.⁷³

#### Molecular Weight (MW) and Molecular Weight Distribution (MWD)

Many factors, such as the rubber tree's age and clonal origin, the weather, frequency of tapping, method of rubber isolation, and treatment of the rubber sample before analysis (e.g., mastication or heating), have been known to affect the MW and MWD of natural rubber.

The effects of clonal variation on the MW & MWD of natural rubber derived from fresh latex have been investigated by Gel Permeation Chromatography (GPC).⁷⁷ The MW of natural rubber has been found to be either a distinctly bimodal distribution, where the peak height in the low molecular weight region is nearly equal (Type 1) or half that in the high molecular weight region (Type 2), or a unimodal distribution with a shoulder in the low MW region (Type 3) as shown in Figure 7. The MW is normally in the range of 10⁴ to 10⁷, with high MW and low MW peaks centered at 10⁶ and 10⁵, respectively. The polydispersity of MW, Mw/Mn, is usually wide, in the region of 2.5 to 10. The bimodal distribution has been found to be unchanged after decomposing the branch-points by deproteinization and transesterification, 40,62,78 indicating that it is a unique property of Hevea brasiliensis biosynthesis process. It could be a result from the action of two different enzyme systems in the biosynthesis of natural rubber. The natural rubber from the latex timber clones, i.e. fast growing and high latex yield, has been found to have Types 2 and 3 MWD as shown in Table 3. The MWD of rubbers from one month to three year old Hevea brasiliensis seedlings has also been investigated by gel-permeation chromatography and osmometry. A bimodal distribution was found with MW peaks at 2.0 X 106 and 1.2 X 10⁵. Unlike those from the mature tress, in this case, the high MW peak was smaller than the low MW peak. As the tree matures, the MW peak also increases accordingly shown in Figure 8.62

	Table 3:	Natural	Rubber	Molecular	Weight	Distribution	Types	from I	LTC
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Type 2 MWD	Type 3 MWD
PB260, PB350, PB355, PB359	RRIM908, RRIM921, RRIM2002
RRIM901, RRIM928, RRIM929	RRIM2008, RRIM2015, RRIM2016
RRIM936, RRIM937, RRIM938	RRIM2020, RRIM20025, RRIM2026
RRIM940, RRIM2001, RRIM2009	
RRIM2014, RRIM2023, RRIM2024	



Figure 7: Different Types of Molecular Weight Distribution





## **Non-rubbers**

*Hevea* latex as obtained from the tree consists not only of rubber hydrocarbon particles, but also of non-rubber substances, which include lipids, proteins, carbohydrates, acids, amines and some inorganic constituents. The non-rubber content can be affected by many factors such as climatic variations and clonal origin. It is generally known that some of these non-rubbers can affect the properties of latex concentrates and bulk rubber derived from the field latex.^{8,80,81}

Most of the non-rubber compounds in natural rubber are trapped, tenaciously held, or co-precipitated with the rubber during coagulation, due to their poor solubility in the aqueous medium or strong entanglement with the rubber molecule. A typical composition of field natural rubber latex is given in Table 4.

Component	Percentage by weight
Dry rubber content	36.0
Nitrogenous substances	1.7
Neutral lipids	1.0
Phospholipids	0.6
Ash	0.5
Inisitols and carbohydrates	1.6

<b>Fable 4: Typical Composition</b>	of Natural	Rubber	Latex
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## **Commercial Latices and Dry Rubbers**

The latex exuded by the tree upon tapping is called field latex. Latex is

collected as a premium product from the tapping cups, within 3 to 4 hours after tapping. This latex is normally processed into latex concentrate, or is coagulated with formic acid to form dry rubber. If the latex is left in the cup overnight, auto-coagulation of the latex will occur due to bacterial attack on the rubber proteins, which are a stabilizer for the latex. The auto-coagulated rubber is known as cuplump. A small amount of the latex coagulates as a thin film on the tapping cut to form tree lace. Along with the cuplump, a small proportion of tree lace is collected for later processing into dry rubber. Under normal conditions, latex contributes about 80% of the rubber output, while the cuplump and tree lace amount to about 20%.

## **Production of Natural Rubber Latices**

## Latex Concentrate

The dry rubber content (DRC) of field latex is in the range of 25 to 40%. The stability of this latex is low because it is very susceptible to bacterial attack. It is normally preserved by the addition of ammonia and centrifuged to produce latex concentrate. Other methods of concentration are evaporation and creaming. The centrifugation of natural rubber latex is the usual commercial method of concentration. This process essentially involves the passing of field latex through a centrifuge bowl rotating at a speed of 7,000 rpm, which separates the latex into a concentrated fraction of 60% DRC and a low skim fraction of about 5% DRC. About 70% of the commercial latex concentrate is high ammonia grade, containing 0.7% ammonia and 0.01% lauric acid, while the others are low ammonia grade, using a combination of 0.2% ammonia and other chemicals.82 as indicated in Table 5. More recently, several new and environmental-friendly preservative systems based on benzotriazole/triazine derivative or disodium octaborate tetrahydrate, have been found to be promising for natural rubber application.83 The major application of the latex concentrate is in the area of dipped goods, of which medical and household gloves account for more than half of the latex consumed.

Latex type	Preservation system (w/w)
High ammonia (HA)	0.7% ammonia + 0.01% lauric acid
Low ammonia METHYL TUADS [®] (TMTD) accelerator / ZnO (LA-TZ)	0.2% ammonia + 0.013% TMTD + 0.013% ZnO + 0.05% lauric acid
Low ammonia sodium pentachlorophenate (LA-SPP)	0.2% ammonia + 0.2% sodium pentachlorophenate
Low ammonia boric acid (LA-BA)	0.2% ammonia + 0.24% boric acid + 0.05% lauric acid
Low ammonia ETHYL ZIMATE [®] (diethyldithiocarbamate) accelerator (LA-ZnDEC)	0.2% ammonia + 0.1% ZnDEC + 0.05% lauric acid

Table 5:	Different	Types of	Commercial	Latex	Concentrates
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### Prevulcanized Latex

Like dry rubber products, the latex used to produce latex goods normally needs to be vulcanized to enhance the physical properties such as tensile strength, modulus, and tear strength. There are many ways of vulcanizing the latex, of which sulfur vulcanization is the most commonly used method.

Two types of latex vulcanization using sulfur systems are normally used: prevulcanization and post-vulcanization. Prevulcanized latex is produced by vulcanizing the rubber molecule in the liquid state so it can form a deposit of vulcanized rubber for making latex products without any further heating required to cure the products.⁸² Only drying is necessary to complete the process. To vulcanize the latex, crosslinking agents such as sulfur, ultra fast accelerators such as BUTYL ZIMATE (zinc dibutyldithiocarbamate), plus zinc oxide, a surfactant, and an antioxidant are added in dispersion form to NR latex concentrate and allowed to react at 20 to 70°C. Upon completion the prevulcanized latex is usually centrifuged to remove the excess sulfur, zinc oxide and proteins. Prevulcanized latex film must be leached in water to remove hydrophilic materials that hinder inter particle diffusion among the rubber molecules, and also to remove proteins and unused compounding ingredients and zinc oxide. The process can increase both the tensile strength and modulus of the latex film.

Post-vulcanization involves maturation of latex with the compounding ingredients in the latex state to achieve homogeneity and partial curing. The curing process is completed during drying to form dry rubber.

There are three major types of commercial prevulcanized latex, i.e., low, medium and high modulus dry film, as indicated in Table 6. The DRC of the latices is normally slightly above 60%. Medium modulus latex is used to make dipped goods such as gloves, catheters and baby bottles and pacifiers.⁸²

Туре	700% Modulus, MPa	Tensile, MPa	Elongation, %
Low modulus	8.5	30.0	1000
Medium modulus	11.0	30.0	900
High modulus	16.0	26.0	800

Table 6: Typical Properties of Commercial Prevulcanized Latices

## Double-centrifuged Latex

Double-centrifuged latex is prepared by centrifuging the latex concentrate a second time after diluting it to 30%. The re-centrifugation process further removes the non-rubber materials from the latex, resulting in lower protein and mineral content. The resulting rubber film has a light color and better electrical insulation properties.

## High DRC Latex Concentrate

This type of latex concentrate, made by either single-or double-centrifugation, has a DRC of 65-67%, which is as high as the creamed or evaporated latices. Because of its low water content, it dries faster than the 60% concentrate and is used in water-based adhesive manufacturing.

## Hydroxylamine-treated Latex

As previously indicated, the viscosity of natural rubber in latex, adjusted to

alkaline conditions, increases on storage over a period of several weeks, due to a crosslinking reaction. The process is thought to be similar to that of storage hardening of dry rubber because it can be minimized by the addition of 0.15% hydroxylamine to the latex immediately after concentration. The rubber from the hydroxylamine-treated latex has lower modulus and Mooney viscosity, and is particularly suitable for adhesive and shoe applications.

## Heveaplus MG® Latex

This latex is prepared by grafting methyl methacrylate onto the rubber molecule as a side chain. There are two grades currently in the market, Heveaplus MG 30 and Heveaplus MG 49, containing 30% and 49% polymethylmethacrylate, respectively. They are mainly used in adhesives and as reinforcing agents.

## Freeze-Thaw Stable (FTS) Latex

Natural rubber latex concentrate tends to destabilize when subjected to freezing and thawing. The addition of 0.2% sodium salicylate and 0.02 to 0.08% lauric acid to the latex increases its resistance to freeze destabilization.

#### Epoxidized Latex

This latex is prepared by allowing the non-ionic surfactant stabilized latex to react with peracetic acid or a mixture of hydrogen peroxide and formic acid at room temperature or lower. The reaction is essentially quantitative, with little side reactions. The latex normally contains 25% or 50% epoxide. The rubber has a higher glass transition temperature, improved impermeability to gases, and solvent resistance similar to that of NBR.

### Positized Latex

The surface of latex particles is normally negatively charged. By adding a cationic surfactant to the latex, it is possible to change the surface to a positive charge. This latex is used to treat textile fibers that possess a negative charge.

# Deproteinized Natural Rubber (DPNR) Latex

Natural rubber latex contains about 2% of naturally occurring proteins, and some of these proteins are still present in the latex after concentration. These proteins could increase water absorption, or the retention of water, in the rubber. More importantly, some of these proteins, mainly water-soluble ones in latex dipped goods such as gloves, can cause allergic reactions in a small number of susceptible individuals. Therefore, deproteinized latex has become desirable because of its low water-soluble protein content. DPNR latex is normally prepared by treating the latex with protease enzyme followed by centrifugation to remove the degraded proteins. Surfactants are normally added to the latex to displace the proteins and to stabilize the latex.

### Other Latices

Other special grade latices include low nitrosamine prevulcanized latex for baby pacifiers & teats, depolymerized latex concentrate for adhesive application and as Mooney modifier for CV rubber production, ammonia free latex for interior cleaning of buildings, medium ammonia preserved concentrate normally used for rubber thread and foam mattresses.

#### Storage and Handling of Latex

Since commercial latex contains ammonia, storage tanks should be made of stainless steel, mild-steel with a phenolic or epoxy resin coating or fiberglass reinforced polyester epoxy resin. Uncoated mild-steel is not suitable because of rusting. Copper and aluminum are attacked by ammonia and therefore should not be used. Iron and copper are pro-oxidant to the natural rubber molecule. Latex should also be stored in an enclosed container to reduce the evaporation of ammonia. A fall in the ammonia level may cause the volatile fatty acid content to increase rapidly. Exposure to contaminants such as inorganic salts, acids, organic solvents, should be avoided as they can destabilize the latex.⁸²

Latex will destabilize when it is subjected to high shear conditions, particularly during transfer from one container to another. Positive displacement gear, piston and closed-impeller centrifugal pumps are therefore not suitable for transferring latex. Only diaphragm pumps and single-screw pumps are recommended.

To avoid degradation of the rubber, latex should not be exposed to direct sunlight. The suitable storage temperature is 5 to 40°C. Due to its lower density, latex tends to form a cream on the surface of water when it is not agitated. Therefore, a low speed and periodical stirring are recommended.

## PRODUCTION OF DRY RUBBER FROM LATEX

Dry rubber may be classified into three categories: conventional, technically specified, and specialty rubbers.

#### **Conventional Rubbers**

The conventional types of NR include ribbed smoked sheet (RSS), air-dried sheet (ADS) and pale crepe rubbers.

### Rubber Smoked Sheet and Air Dried Sheet

This processing method has been used for a long time and is still practiced in small and medium rubber estates where transportation of the latex is a problem. The processing of RSS involves the following stages: latex collection, bulking, dilution of field latex DRC to about 12.5%, coagulation with formic acid, maturation for 2 to 18 hours, milling of the coagulum, and smoke-drying.

The milling operation allows the latex coagulum to be sheeted after maturation. The sheeting process actually squeezes out serum present in the coagulum and reduces its thickness to about 3.0 mm. Squeezing is accomplished by passing the coagulum through a set of 4 smooth rollers, and finally grooved rolls. The grooved rolls provide the ribbed design to the final sheet. The ribbed pattern increases the surface area and therefore accelerates the drying process. RSS is dried in a smokehouse, whereas ADS is dried in hot air chambers without smoke and therefore has a lighter color than RSS. A tunnel smokehouse is operated at temperatures of 45°C and 63°C, at the wet and dry ends, respectively. The dried sheets are visually graded. Visual grading is based on the recommendations provided by the International Rubber Quality and Packing Committee.

### Pale Crepe

In the production of pale crepe rubber, fresh latices with low yellow pigment are selected. The yellow pigment is normally removed by adding bleaching agent and fractional coagulation. After acid coagulation, it is rolled into thin sheets with rollers and dried by warm air.

### Brown and Blanket Crepes

These lower quality grades include Estate Brown Crepes, Thin Brown Crepes, Thick Blanket Crepes, Flat Bark Crepes and Pure Smoked Blanket Crepes. They are prepared from field coagulum, wet slabs of coagulum formed during the handling of latex, unsmoked sheets (partially dried, but unsmoked sheet rubber), and smoked sheet cuttings. The raw materials are subjected to intensive cleaning and blending while being milled through a battery of crepers driven at frictional speed. The resultant crepes are dried in long strips by natural ventilation in airy buildings for about two weeks, or occasionally by heat from hot water pipes. They are packed in 102 kg talc-coated bales. These lower quality international grades are now very rare because the same raw materials are used to make the lower grades of Technically Specified Rubbers.

## Classification of International Grades

Classification of the conventional grades of rubber into 8 different types is based on the source of raw materials and the method of processing (Table 7). These types are further subdivided into 35 international grades conforming to the grading system of the International Standards of Quality and Packing for Natural Rubber Grades (The Green Book). The Green Book grading is based on factors such as color, cleanliness, presence of bubbles and uniformity of appearance. Grading is determined by visual inspection and comparison with international samples.

Туре	Source	Grades	Total
Ribbed Smoked Sheet	Coagulated field latex	1X, 1, 2, 3, 4, 5	6
Pale Crepe	Coagulated field latex	1X, 1 (white) 1X, 1, 2, 3 (thick & thin)	2 8
<ul> <li>Estate Brown Crepe</li> </ul>	Estate cuplump, tree lace	1X, 2X, 3X (thick & thin)	6
Compo Crepe	Cuplump, tree lace, wet slab, RSS cuttings	1, 2, 3	3
Thin Brow Crepe	Cuplump, tree lace, wet slab, unsmoked sheet	1, 2, 3, 4	4
Thick Blanket Crepe	Cuplump, tree lace, wet slab, unsmoked sheet	2, 3, 4	3
Flat Bark Crepe	Cuplump, tree lace, earth scrap	Standard & Hard	2
Pure Smoked Blanket Crepe	Remilled RSS and RSS cuttings		1

Since there are no technical specifications, the rubber is graded visually based on the degree of dryness, contamination, virgin rubber, blisters, bubbles, level of oxidation, transparency, color, tackiness, and mold growth. In sheets, the dirt contamination can be sand, bark and burnt wood particles picked up during processing. Bubbles are caused by inadequate preservation of latex; and blisters by overheating during drying. Non-uniformity in color may be caused by enzymic darkening or by warm and moist conditions during storage and processing. In Brown Crepes, the common contaminants are sand and bark particles.

### **Technically Specified Rubber**

In 1965, Malaysia was the first country to introduce the Technically Specified Rubbers (TSR) to the market by implementing the Standard Malaysian Rubber (SMR) Scheme. Since then other natural rubber producing countries have followed suit, e.g., Indonesia with Standard Indonesian Rubber (SIR) and Thailand with Standard Thailand Rubber (STR).

The technical specification provides the rubber producers a guide on how to conform to important technical parameters, such that the rubbers have good consistency in quality, require minimum storage space, and are clean and easy to handle. Since its introduction, the demand for TSR in the form of block rubber has been encouraging, and has prompted other NR producing countries to switch their product from conventional rubbers to TSR.

The processing of field latex involves the following operations: reception, bulking, chemical addition, coagulation, milling, size reduction, drying, baling, testing, grading and packing. A combination of machines such as crushers, crepers, hammermills and shredders are used. The popular grades of TSR produced in the form of block rubber, are SMR 10 and SMR 20, SMR GP, SMR 10 CV and SMR 20 CV. Selection and blending are a prerequisite before further processing. The other steps involved are pre-cleaning, initial size reduction, crepeing, intermediate size reduction, crepeing and final size reduction. Machines such as slab cutters, granulators, prebreakers, crepers, extruders and shredders are generally used. The individual processors select different types and numbers of machines for the same purpose for the purpose of increasing productivity and meeting the required specifications.

The block production method has reduced processing time to less than 24 hours. Besides the technical specifications, deep bed drying at a temperature 100 to 120°C allows the drying to be completed in less than 4 hours. The dried rubber biscuit of crumb is weighed and baled using a hydraulic press.

TSR specifications were developed according to the requirements of the consumer, emphasizing consistency and certain primary features. For example, SMR L production essentially focuses on color with the addition of bleaching agent, 0.04% sodium metabisulfite to the fresh latex. In the case of SMR CV production, 0.15% hydroxylamine neutral sulfate is added to the fresh latex before coagulation to stabilize the Mooney viscosity of the rubber.

Coinciding with the advancement in the rubber product manufacturing industry,

specifications in the Standard Malaysian Rubber were revised in 1970, 1979, and 1991 to further improve the quality of the rubbers. In the 1991 revision several low volume grades such as SMR WF and SMR 50 were deleted from the scheme. The SMR specifications revised in 1991 are given in Table 8.⁸³

	SMR CV60	SMR CV50	SMR L	SMR 5°	SMR GP	SMR 10CV	SMR 10	SMR 20CV	SMR 20
Parameter		Latex		Sheet Material	Blend	Fiel	d Grade	Materia	I
Dirt retained on 44 $\mu$ aperture, % wt, max	0.02	0.02	0.02	0.05	0.08	0.08	0.08	0.16	0.16
Ash Content, % wt, max	0.50	0.50	0.50	0.60	0.75	0.75	0.75	1.00	1.00
Nitrogen, % wt, max	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Volatile Matter, % wt, max	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Wallace Rapid Plasticity, minimum	-	-	35	30	-	-	30	-	30
PRI, %, minimum⁵	60	60	60	60	50	50	50	40	40
Lovibond Color: Individual value Range, max	-	-	6.0 2.0	-	-	-	-	-	-
Mooney viscosity M _L (1'+4') 100°C [♭]	60±5	50±5	-	-	65 (+7, -5)	с	-	с	-
Cure⁴	R	R	R	-	R	R	-	R	-
Color coding marker	Black	Black	Light Green	Light Green	Blue	Magenta	Brown	Yellow	Red
Plastic wrap color: T= Transparent	Т	Т	Т	т	Т	Т	Т	Т	Т
Plastic strip color: Or = orange Op = opaque W = white	Or	Or	Т	Op and W	Op and W	Op and W	Op and W	Op and W	Op and W

 
 Table 8: Standard Malaysian Rubber Specification Scheme (Mandatory From October 1991)

a. Two sub-grades of SMR 5 are SMR 5RSS and SMR 5ADS which are prepared by direct baling of ribbed smoked sheet (RSS) and air-dried (ADS), respectively.

b. Special producer limits and related controls are also imposed by the RRIM to provide additional safeguards.

c. The Mooney viscosities of SMR 10CV and SMR 20CV are, at present, not of specification status. They are, however, controlled at the producer end to 60(+7, -5) for SMR 10CV and 65(+7, -5) for SMR 20CV.

d. Rheograph, delta torque, optimum cure time and scorch are provided with the material certification.

## Packaging and Handling^{84,85}

Traditionally, TSR blocks are wrapped with polyethylene film and packed in wooden crates, each weighing 33.33 kg. Blocks are transported in 1.2 ton units for practical reasons. However, wooden crates have several drawbacks. These include damage to the wooden frames caused by rough handling or poor timber quality, un-reusability, contamination of the rubber by wood fragments, and insect infestation of the wood. An alternative method is the use of shrinkwrapping, in which the rubber blocks, resting on a wooden pallet, are held together tightly by a polyethylene shrink film. This reduces the amount of wood used. More recently, reusable metal crates (Goodpack Metal Box) are also being used to pack rubber blocks for shipment. The crates are made of steel with a rigid structure and constructed in an inverted truncated pyramid. To further improve the packing system, RRIM has designed a collapsible metal crate for packing TSR. This crate facilitates easy packing and unpacking, and allows higher packing density.

In the past, palletized rubber was mostly shipped in the holds of ocean-going vessels. Now more shippers are exporting their palletized rubber in containers. The rubber is protected from the elements and other contaminants, so quality is ensured during transit.

#### Factors Influencing Quality of TSR

The types of contamination in TSR include: dirt, ash, volatile matters, and nitrogen content. If the rubber material is free from contamination, dirt and ash can be kept at a reasonable low level. For other parameters, processing conditions need to be strictly controlled.

*Dirt* - High dirt content in latex grade TSR may be due to poor field cleanliness, poor quality water used in dilution, improper sieving, or contamination from containers and utensils. High dirt content in field grades may be due to contamination from processing equipment, dirt from factory or field, insufficient pre-cleaning processes, and poor water quality.

*Ash* - High ash content is mostly related to dirt content. However, there are cases where the problem is due to the latices having high calcium content or the use of water with high mineral salt content.

*Volatile Matter (VM)* - Highly ammoniated latices may give high VM content to the rubber. In addition, insufficient shear during crepeing, insufficient crumbling, variation in crumb sizes due to inefficient equipment or a faulty drier with uneven temperature distribution, may also give rise to high VM content. In most cases, high VM content is due to the presence of wet spots, commonly known as "fish eyes", virgin rubber or "knuckles". The combination of enzyme treating and steam coagulation produces rubber with very low VM content.

*Nitrogen* - The aim of the nitrogen specification is to prevent the adulteration by skim rubbers, which have a high nitrogen content. Apart from this, rubber from certain clones may contain an intrinsically high level of nitrogen. The use of fractionated crepe may also contribute to the high nitrogen level.

*Color* - Color can be a characteristic feature of certain clones. Latices produced during the wintering period, latices washed out during rainy days, and latices from high intensity tapping areas tend to give darker color to rubbers. Darkening of rubber can also occur due to enzymatic action. This can be reduced by the use of

sodium metabisulfite. The presence of high levels of ammonia or formaldehyde tends to darken the color of rubbers. Lighter rubbers can be obtained by higher dilution with water before coagulation, higher pH of coagulation, or steam coagulation. Excessive maturation, drying, and insufficient washing also tend to give darker color to rubbers.

Mooney Viscosity or Plasticity - Viscosity or plasticity is closely related to the gel formation and crosslinking reaction in the rubber. The value of this parameter therefore depends on the amount of reactive abnormal functional groups present in the rubber, which varies with the clonal origin of the rubber. In addition, acid coagulation produces lower viscosity than biologically assisted or auto-coagulation. Higher dilution of the latex contamination by metals such as copper, treatment with hydroxylamine, and prolonged drying can reduce the viscosity of rubbers. On the other hand, prolonged latex maturation, and high baling temperature could increase the viscosity of the rubbers.

*Plasticity Retention Index (PRI)* - Generally, a high level of ammonia preservation (more than 0.5%) tends to reduce the PRI value, particularly in low DRC latices. METHYL TUADS (TMTD)/ZnO should not be used to preserve rubber for SMR production. Acid coagulation gives the highest PRI, followed by biologically assisted and auto-coagulation. However, if the formic acid is contaminated by sulfuric acid, the PRI will decrease. High dilution, excessive maturation, prolonged drying, exposure of dry rubber to sunlight, and contamination by pro-oxidant metal such as copper, can reduce the PRI value. Certain chemicals such as phosphoric acid, oxalic acid, and thiourea are known to increase the PRI value of the rubbers.

## Specialty Rubbers

## SP/PA (Superior Processing/Processing Aid) Rubber

This rubber is produced by blending vulcanized and raw natural rubber. The vulcanized rubber is derived from prevulcanized latex, using a conventional sulfur vulcanization system. The blending is carried out in latex form to ensure a homogenous mixture. There are five grades of SP/PA rubber on the market, as indicated in Table 9. Grades vary according to the amount of vulcanized rubber. The SP 20 is divided into four sub-grades, depending on the physical form of the rubber. PA 57 is an oil-extended version of PA 80, with an 18.7% maximum extrusion die-swell value, and an acetone extract value of 27.5 to 35.0%. Mooney viscosity and dispersibility data are also normally included for reference in the material certification. SP/PA rubber can be masticated in a two-roll mill or internal mixer. It improves the flow behavior of a rubber compound, resulting in higher output, dimensional stability, better surface finish and reduction in die swell, particularly in unfilled or lightly filled compounds. It also improves the green strength of mixes, which leads to an improvement in the feeding behavior of a strip (particularly gum compounds) in the extruder or injection molding machine. It is therefore suitable for making refrigerator gaskets, adhesives, car window seals, hoses, surgical tubing and other types of tubing.

Grade	Vulcanized Rubber	Raw Rubber	Process Oil (phr)	Form
SP 20 (HC)	20	80	0	Block
SP RSS	20	80	0	Sheet
SP Crepe	20	80	0	Crepe
ADS	20	80	0	Sheet
SP 40	40	60	0	Block
SP 50	50	50	0	Block
PA 57	80	20	40	Block
PA 80	80	20	0	Block

Table 9: Grades of SP/PA Rubber

### Heveaplus MG Rubber

This rubber is produced by grafting the NR molecule with polymethylmethacrylate (MMA). Commercial MG 49 rubber contains 49% PMMA. *Heveaplus MG* doesn't exhibit thermoplastic rubber properties, and its tensile strength decreases drastically after mastication because of the low number of grafting points per chain. In addition, it contains a large proportion of ungrafted rubber and homopolymer. A recent study indicates that the low grafting efficiency of PMMA is due to the formation of secondary particles in the aqueous phase, in which homopolymer is formed.⁸⁶ The grafting efficiency of a monomer can be greatly enhanced when the monomer is highly hydrophobic, and all the monomer diffuses into the rubber particles, with no secondary particles being formed.

# Deproteinized Natural Rubber (DPNR)

DPNR is a type of purified natural rubber with low nitrogen and protein content. Because the natural rubber proteins tend to hold mineral components, DPNR normally has a low ash content as well. To prepare the rubber, the latex is first stabilized with surfactant, and the rubber proteins are then normally hydrolyzed with protease enzyme. The latex is coagulated with acid or steam. The coagulum is converted into small crumbs and washed extensively with water to remove the hydrolyzed proteins, surfactant, and other non-rubber materials. The crumbs are dried in hot air at 90°C, then baled and packed to SMR standards. There are two grades of DPNR; namely, DPNR and DPNR-CV. The specifications and typical values are shown in Table 10.⁸⁷

	DPNR		DPN	NR-CV
Parameters	Spec	<b>Typical Value</b>	Spec	Typical Value
Dirt, %	0.01 max	0.003	0.01 max	0.003
Ash content, %	0.15 max	0.09	0.15	0.09
Nitrogen content, %	0.12 max	0.08	0.12	0.08
Volatile matter, %	0.30 max	0.17	0.30	0.17
Mooney viscosity (M _L 1+4 @ 100°C)	-	84	60-70	64
ΔP	-	-	8 max	4
Wallace plasticity	35 max	46	-	-

Table 10:	Specifications	and Typical	Values of DPN	R and DPNR-CV
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This rubber has low creep and stress relaxation, low water absorption, but high damping properties. These make it a suitable material for making seals, mounts, electrical insulators and shock absorbers. The low nitrogen content makes it useful for food and pharmaceutical applications.

## Liquid Natural Rubbers (LNR)

LNRs are low molecular weight versions of natural rubber that are produced by chemical chain scission of the rubber molecule, forming rubbers with molecular weights below 100,000. Chain scission can be performed on both latex and dry rubber. LNR is available in several grades, which differ in viscosity. Grades with higher viscosity have a higher molecular weight. Typical properties of several LNR grades are given in Table 11. ⁸⁸

Parameter	LNR Grade 40	LNR Grade 75	LNR Grade 400
Viscosity Poise @ 28°C	400	750	4,000
Flash point (°C)	246	255	271
Specific gravity @ 25°C	0.92	0.92	0.92
Tg (°C)	-65	-65	-65
Molecular weight	40,000	45,000	80,000
Unsaturation (mol %)	98	98	98

### Table 11: Typical Properties of LNR

LNR is used to increase the processing flexibility and performance of natural rubber. The conventional method of reducing the viscosity of natural rubber is by mastication. The process is not only time and energy consuming, it may require peptizers or other chemicals, and be difficult to control. A small addition of LNR can reduce the viscosity of the rubber within a short period of time. Since LNR is chemically identical to NR, it can be easily incorporated into the rubber matrix upon curing.

LNR is particularly suitable for both heat-cured vulcanizates and two-part room temperature systems. LNR's good fluidity and compatibility make it a good wetting agent for reinforcements and non-compatible fillers, such as fiber. LNR also supports higher carbon loading without the softening, weakening and fugitive nature of process oils. In summary, the advantages of using LNR in the processing of NR include higher loading, reduced scorch, lower processing energy, improved mold flow, lower viscosity, non-volatility, non-extractability, and increased green strength.

#### Epoxidized Natural Rubber (ENR)

This latex is produced by epoxidation of natural rubber latex followed by steam coagulation, as described in the latex section. Rubbers with a degree of epoxidation of 10 to 50% are commercially available. ENR has several improved properties such as oil resistance, gas impermeability, and higher damping than NR. Despite these, the commercial acceptance of this material has been slow.

#### Chlorinated NR

Chlorinated NR can be prepared in solution or latex form. LNR can also be converted into chlorinated NR. Chlorinated NR is a white thermoplastic material with improved ageing properties, flame retardance, and adhesion to various substrates. It is widely used in the paint and lacquer industries.

### Oil-extended Natural Rubber (OENR)

This natural rubber contains 5 to 30% naphthenic or aromatic oil. When a winter tire is made with OENR, its wet grip is similar to that of oil-extended SBR (OESBR). Below 0°C, the grip is much better than that of OESBR.

#### Thermoplastic NR (TPNR)

This rubber is produced by blending NR with polypropylene. There are several grades available on the market. It can be used to make impact resistant car components such as bumpers. Other applications, such as car radiator grills, and cattle feeding hoppers, have also been reported.

### World NR Production and Consumption

World NR production in 2007 was 9.685 million tons, i.e., comparable to 9.680 million tons in 2006. By 2020, the total production is expected to be around 13.6 million tons.⁸⁹ The total production of synthetic rubber in 2007 was 13.31 million tons, compared to 12.762 million tons in 2006. Thailand remained the largest producer of natural rubber in 2007, followed by Indonesia and Malaysia. The demand for NR depends on technology development, composition of the end uses, and price ratio of NR over synthetic rubbers.

Country	2001	2002	2003	2004	2005	2006	2007
Thailand	2320	2615	2876	2984	2937	3137	3056
Indonesia	1607	1630	1792	2066	2271	2637	2791
Malaysia	783	805	909	1098	1061	1284	1215
India	632	641	707	743	772	853	767
China	478	527	565	573	510	533	577
Vietnam	313	331	364	419	469	554	608
Sri Lanka	86	91	92	95	104	109	120
Brazil	88	89	94	101	107	108	111
Cambodia	42	43	45	43	45	64	68
Other	979	560	589	626	606	401	372
Totals	7328	7332	8033	8748	8882	9680	9685

#### Table 12: Natural Rubber Production ('000 tons)*

* Source: IRSG Rubber Statistic Bulletin 62, March/April 2008

The rubber production of the major natural rubber producing countries is expected to decline as they gradually move towards industrialization. This process is accelerated by the fact that the producing countries are moving to other crops such as oil palm, as well as by the continual decrease in the capital inflow required to develop natural rubber's processing industry. In addition, the

domestic consumption of NR in these countries will increase faster than the production of NR in other countries. Nevertheless, some countries are slowly moving to become rubber producers. These include Ethiopia, Zambia and Guinea. In addition, some countries like Vietnam, the Philippines and Mexico are expanding their NR cultivation. The production of latex concentrate in Malaysia is already insufficient to meet domestic demand, requiring Malaysia to import latex concentrate from neighboring countries. As a result, the world could face shortages of raw rubber in the near future. In Malaysia, several steps are being taken by the Malaysian government to sustain the rubber industry in the long term. These include the allocation of additional funds for replanting, the adoption of Low Intensity Tapping Systems (LITS) and the encouragement of other supplementary economic activities for smallholders. Nevertheless, the anticipated shortage in the forecast done in 2006 did not occur as shown in Table 13.90 This is because many areas planted with rubber trees have been left idle in the past due to unattractive pricing. Once there is a high demand, these rubber trees will be tapped again to meet the demand. With the implementation of the rubber forest plantation system, the supply can be regulated according to the demand.

Natural Rubber	2006	2007	2008
Expected Supply	8.890	9.040	9.340
Expected Demand	9.150	9.510	9.880
Expected Surplus/Deficit	-260	-470	-540
Actual Surplus/Deficit	464	-30	50**

Table 13: Forecast vs. Actual World Supply/Demand of NR*

* IRSG Economist Intelligence Unit (2nd Oct 2006) ** Figure for half year

Polymer	2000	2001	2002	2003	2004	2005	2006	2007
Natural Rubber								
Production	6,762	7,328	7,332	8,033	8,748	8,882	9,680	9,685
Consumption	7,340	7,333	7,628	8,033	8,715	9,082	9,216	9,715
% All rubber	40.4	41.7	41.6	41.4	42.4	43.3	42.5	42.4
Balance	-578	-5	-296	0	33	-200	464	-30
Synthetic Rubbe	er							
Production	10,870	10,483	10,882	11,390	12,019	12,155	12,762	13,310
Consumption	10,830	10,253	10,692	11,371	11,839	11,895	12,446	13,188
Balance	40	230	190	19	180	260	316	122
All Rubber								
Production	17,632	17,811	18,214	19,423	20,767	21,037	22,442	22,995
Consumption	18,170	17,586	18,320	19,404	20,554	20,977	21,662	22,903
Balance	-538	225	-106	19	213	60	780	92

Table 14: World Rubber Production and Consumption ('000 Tons)*

* Source: International Rubber Study Group (IRSG)

Before the Second World War, natural rubber was the only commercial elastomer in use. Since the initial production of SBR the consumption of synthetic rubber has rapidly increased. In 1978 the consumption of NR as a percentage of the total elastomer market reached its lowest level at 29.8%, but has since

slowly increased to above 40% (Table 14). The increase is mainly due to the conversion from bias-ply tires to radial ply tires, and the improved performance of natural rubber in off-the-road tires.

Country	2003	2004	2005	2006	2007
China	1485	1630	1826	2400	2550
USA	1079	1144	1159	1003	1018
Japan	784	815	857	874	888
India	717	745	789	815	851
Malaysia	421	403	386	383	449
South Korea	333	352	370	364	377
Others	3214	3626	3695	3377	3582
Totals	8033	8715	9082	9216	9715

Table 15: Natural Rubber Consumption ('000 tons)*

* Source: International Rubber Study Group (IRSG); Rubber Industry Report

World NR consumption is expected to increase over the next 5 years, with strong demand in the Asia-Pacific region and recovery of the rubber industry in the former Soviet Union and Central and Eastern Europe.

## **Uses of Natural Rubber**

More than 70% of natural rubber is used in tires and automotive products. Other major applications of natural rubber are latex products, industrial and engineering goods, footwear and adhesives.

## Tires

In passenger car cross-ply tires, natural rubber is used in the carcass because of its good tear resistance, building tack and ply adhesion. In radial ply tires, natural rubber is also widely used in the sidewalls due to its lower heat generation and better fatigue resistance. In the treads of passenger car tires in the USA, Western Europe and Japan, virtually no natural rubber is used except in winter tires.

In commercial vehicles, the natural rubber content increases with the size of the tire. In large truck and off-the-road tires, which require low heat generation and high cutting resistance, almost 100% natural rubber is used.

## Latex Products

The main applications of natural rubber latex are in dipped goods such as gloves and condoms. Other major products made from natural rubber latex are foam, carpet backing, latex thread and latex adhesives. Recently there has been a sharp increase in the use of NR examination gloves by medical personnel as a preventive measure against the spread of blood-borne viral diseases such as AIDS. Natural rubber gloves are preferred mainly because of their superiority in barrier protection properties, tensile and tear strength, fit and tactile sensitivity.

## Industrial Goods

These include a host of products such as conveyor belts, hoses, rubber linings, rubberized fabrics and components for the consumer and industrial markets.

# Engineering Products

In recent years, the unique properties of natural rubber that make it a good engineering material have begun to be appreciated. Applications such as bridge bearing pads, seismic bearing pads, dock fenders, springs, anti-vibration mountings and vehicle suspension systems now account for more than 3% of the natural rubber market.

# **Recent Development**

# Latex Protein Allergy

Three types of adverse reactions are associated with latex products: irritant contact dermatitis (non-allergic), Type IV chemical hypersensitivity (cell-mediated allergy), and Type I latex protein hypersensitivity (IgE mediated allergy). Of the three, Type I is the most serious. It is caused by certain residual water-soluble proteins in NR latex products. However, the prevalence of this type of allergy among the general population is less than one percent.⁹¹

Latex allergens that have already been registered by International Union of Immunological Societies (I.U.I.S.) and the World Health Organization (W.H.O.) are shown in Table 16.

Name	Trivial Name	Predicted Physiological Roles
Hev b 1	Rubber elongation factor	Rubber biosynthesis
Hev b 2	Beta-1,3-glucanases	Defense-related protein
Hev b 3	Small rubber-particle protein	Rubber biosynthesis
Hev b 4	Microhelix component	Defense-related protein
Hev b 5	Acidic latex protein	-
Hev b 6.01 Hev b 6.02 Hev b 6.03	Prohevein, Hevein preprotein Hevein, Prohevein C-terminal fragment	Defense-related protein (latex coagulation)
Hev b 7.01 = Hev b 13 (renamed Hev b 7.02)	Patatin homologue from B-serum, Patatin homologue from C-serum	Defense-related protein inhibitor of rubber biosynthesis
Hev b 8	Latex profilin	Structural protein
Hev b 9	Latex enolase	Glycolytic enzyme
Hev b 10	Mn-superoxide dismutase	Destruction of radicals
Hev b 11	Class I endochitinase	Defense-related protein
Hev b 12	Lipid transfer protein	Defense-related protein
Hev b 13 = Hev b 7.01	Latex esterase, Early Nodule Specific Protein (ENSP)	Defense-related protein

Table 16: Registered Natural Rubber-Latex Allergens

Of these, four allergens, i.e. Hev b 1, 3, 5, and 6.02, have been known to be present in latex products and contribute significantly to the total allergenicity. The sum of these allergens has been shown to correlate well with the human IgE-based ELISA-inhibition, a validated and standardized immunological test.⁹² The classification of allergen level for medical glove is given in Table 17.

Sum of four allergens content, µg/g	Category
Below 0.03	Very low
0.03 - 0.15	Low
0.15 - 0.30	Moderate
0.30 - 1.15	Moderate to High
Above 1.15	High

 Table 17: Classification of Sum of Four Allergens of Medical Gloves

In 2008, ASTM has adopted the sum of four allergens test in the ASTM D 7427-08 test method. This is in addition to the ASTM D 6499-07 test method which involves an immunological method to determine the amount of antigenic protein in natural rubber and its products using rabbit antisera specific for natural rubber latex (NRL) proteins, introduced in 2007 and the ASTM D 5712 - 05e1 standard test method for analysis of aqueous extractable protein in natural rubber and its products using the modified Lowry method.

Recognizing the seriousness of this problem, many gloves manufacturers in Malaysia were striving to reduce the extractable protein (EP) content of their products. Their efforts include the adoption of an improved leaching process system (as recommended by the RRIM), the use of low protein latices, chlorination, and polymer coating.⁹¹ In addition, the Standard Malaysian Glove (SMG) scheme, a plan to ensure consistency in the quality of gloves produced in Malaysia, was launched in 1998,⁹² and revised in 2004.⁹³ Besides setting a limit on the EP content, the scheme also includes specifications that control powder content, water leakage and physical properties. The Standard Malaysian Glove (SMG) scheme is recognized by the US Food and Drug Administration (FDA) and permission has been given to certified glove producers to label their glove cartons with the SMG logo.

Despite these advances, the continued concern has created opportunities for other synthetic gloves to be marketed as alternatives. These include polyurethane, nitrile, polychloroprene, styrene-isoprene block copolymer, and polyisoprene gloves.⁹⁴

### Energy and the Environment

Carbon dioxide, particularly from the combustion of fossil fuels, is a major constituent of greenhouse gases. The fast disappearance of forests, particularly tropical rain forests, is of great concern because they are a vital natural sink for carbon dioxide. Planted rubber trees can substitute for the depleted natural forest, and play an important role in removing the excess carbon dioxide from the atmosphere at a rate comparable to that of natural forest. The total carbon sequestration in rubber trees has been estimated to be 135 tons/ha/30 year

cycle, compared with 195 tons/ha/60 year cycle for a forest project. ⁹⁵ However, in a rubber plantation, carbon is sequestered in plant parts, products, litters, debris and soil. The total carbon sequestration has recently been revised to between 235 tonne/ha/30 years and 574 tonne/ha/30 years for a rubber plantation. ⁹⁶

It is estimated that the amount of energy required to collect and process natural rubber is 7 to 11 times less than that required for synthetic rubbers.⁹⁵ The price of crude oil has increased from below US \$20 in 1998 to more than US \$140 per barrel in 2008 but has since dropped to about US\$40 per barrel due to the world economic slump. The price is not expected to come down due to limited oil reserve in world. In fact the oil output is falling in 60 of the 98 producing countries and the production has been flat since 2005. This, together with the growing concern over the environment, is an impetus for more research to improve the properties of natural rubber, so that it can replace synthetic rubber wherever possible. One such example is the Enasave 97 car tire which is made from 97% renewable resources. The elastomers used are a blend of NR and Ekoprena, a commercial epoxidized NR produced by the Malaysian Rubber Board. The 3% non-renewable resources are chemicals used as the anti-degradants and in the curing package. This is very low compared to 56% non-renewable resources by weight used in a standard car tire. The tire also reduces rolling resistance by 35% compared with a standard tire, contributing to improved fuel efficiency. This is also a new generation of eco-tire that can reduce CO₂ emissions at each stage, from production and use to disposal.97,98

## Recycling or Reuse and the Environment

About 75% of natural rubber is used in the manufacture of tires, and their disposal has become a problem. Many countries face the problem of tire disposal. Tires harbor mosquitoes, and are very hazardous when a tire dump catches fire. The recent trend is to extend tire life by increasing their durability, and wear resistance, and to dispose of them by incineration with energy recovery, or by recycling scrap tires to make other products. Retreading truck and aircraft tires is still a common practice. However, retreading passenger tires is becoming less popular, due in part to the availability of inexpensive new tires from countries with depreciated currencies, such as Indonesia, Malaysia and Thailand. There are several new methods to dispose of scrap tires. One of them employs bacteria to decompose the sulfur link in the rubber. Adding shredded scrap tires to the soil in landfills improves permeability by allowing leachate and gas to migrate from refuse, without contributing to airborne dust and fumes. Scrap tires are also used in the preparation of rubberized asphalt, to improve soil texture for better plant growth, in artificial reefs, and as fenders to prevent collision damage to barges and boats.94,99 Other applications include liquid fuel as a feedstock for gasoline or diesel,¹⁰⁰ wood substitute.¹⁰¹

Vulcanized natural rubber can be devulcanized using the "de-link" method where it involves the use of zinc salts of thiocarbamates and 2-mercaptobenzothiazole or their derivatives.^{102,103} However, the system leads to shorter scorch delays, making it difficult to handle. Other methods of reclaiming natural rubber have also been reported.¹⁰⁴

#### Transgenic rubber tree

Through genetic engineering, animals, such as sheep, goats and cows, have been able to produce foreign proteins of therapeutic properties in their milks. Like transgenic animals, plants can too be genetically transformed to produce pharmaceuticals, or other proteins of high commercial value. Transgenic rubber tree of *Hevea brasiliensis* origin can provide a non-destructive system for harvesting the target proteins that are synthesized in the latex continuously as the tree can be tapped every other day for its latex for 25 to 30 years. Other advantages for producing through this system are: (1) the products are non-animal origin, (2) easily produced through the horticultural practice of bud-grafting, (3) low cost, and (4) ecologically friendly. Some progress has been made in the genetic transformation of natural rubber tree.^{105,106} Other genetic transformations of *Hevea brasiliensis* have also been carried out to increase the tree's tolerance to tapping panel dryness and environmental stress.¹⁰⁷

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## SYNTHETIC POLYISOPRENE

# by Jerry Bush, Greg Cox, Harold Marsh and Gordon Schorr

Goodyear Chemical Division The Goodyear Tire & Rubber Company Akron, OH

Synthetic polyisoprene represents one of the important classes of polymers produced in a solution medium. The successful development of a stereospecific catalyst system has permitted the production of a synthetic analog of natural rubber with improved uniformity and processing.

## Introduction

Modern synthetic polyisoprene is designed to be similar to natural rubber in structure and properties. Although it still demonstrates lower green strength, slower cure rates, lower hot tear and lower aged properties than its natural counterpart, synthetic polyisoprene exceeds the natural types in consistency of product, cure rate, processing and purity. In addition, it is superior in mixing, extrusion, molding, and calendering processes.

Synthetic polyisoprene is currently being used in a wide variety of applications requiring low water swell, high gum tensile strength, good resilience, high hot tensile strength and good tack. Gum compounds based on synthetic polyisoprene are being used in rubber bands, cut thread, baby bottle nipples, and extruded hose. Black-loaded compounds find use in tires, motor mounts, pipe gaskets, shock absorber bushings and many other molded and mechanical goods. Mineral-filled systems find applications in footwear, sponge, and sporting goods. In addition, recent concerns about allergic reactions to proteins in natural rubber have prompted increased use of the purer synthetic polyisoprene in some applications.

Consumption of synthetic polyisoprene stabilized in the early 1990s as polyisoprene's availability was limited by manufacturing capacity and monomer availability. Recent increases in capacity, concerns about the stability of the price of natural rubber, and the mandate to move away from natural rubber in certain applications provide avenues for future growth in the industry. Table 1 shows the consumption of synthetic polyisoprene over the past forty years, based on numbers from IISRP and SRI.^{1,2}

	1965	1970	1975	1980	1985	1990	1995	2000	2005	(est.)
North America World*	41 80	81 165	67 196	66 222	47 129	56 143	62 137	78 147	78 154	

Table 1:	Consumption	of Synthetic	Polyisoprene	(Metric Tons,	'000s)
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* World consumption excludes Eastern Europe

#### Historical Background

The successful synthesis of stereoregular polyisoprene (IR) fulfilled a goal sought by polymer chemists for nearly a century. Researchers knew that isoprene was the building block for natural rubber, and through the years, many attempts were made to synthesize materials with similar properties. Initially, the resulting polymers failed to exhibit some of the desired aspects of natural rubber because of differences in microstructure, which plays an important role in polyisoprene's physical properties. The polymer chains in the early synthetics contained mixtures of all possible molecular configurations joined together in a random fashion. Specifically, they lacked the very high *cis*-1,4 structure of the natural rubber backbone that gives it the ability to undergo strain crystallization.

In the mid 1950s, researchers discovered and developed new types of catalyst systems that could selectively join together monomer units in a wellordered fashion. Shortly after Karl Ziegler's breakthroughs in catalyst systems to polymerize ethylene, similar catalysts were developed for use with isoprene. These "stereospecific" catalysts allowed polymerization to a nearly pure *cis*-1,4 structure, and in doing so, the production of a synthetic natural rubber.³

The first commercialization of a stereoregular, low *cis*-1,4 IR (90% to 92%) was achieved in 1960 by Shell Chemical Company, with the introduction of Shell Isoprene Rubber, produced with an alkyl lithium catalyst (Li-IR). The level of purity was still not sufficient, however, to achieve natural rubber's important crystallization properties.

In 1962, Goodyear introduced Natsyn[®], a Ziegler-Natta (titanium-aluminum) catalyzed IR (Ti-IR) with a *cis*-1,4 content of 98.5%, which finally allowed some of the benefits of crystallization to be realized. Goodrich-Gulf introduced another Ti-IR polymer about three years later, but withdrew from the market in 1978. The manufacture of high *cis* IR has since been undertaken elsewhere, primarily in Russia and Japan.

In addition to the cis-1,4 configuration, several other IR microstructures have been reported. A high *trans*-1,4 structure was developed by Polysar, and is now being produced by Kuraray. This polymer has significant crystallinity at room temperature and is a synthetic analog of the naturally occurring Balata. An amorphous IR with a predominantly 3,4 structure can be prepared by adding polar modifiers to the alkyl lithium catalyst system. In contrast, a semi-crystalline 3,4 IR can be prepared with a Ziegler-Natta catalyst.^{4,5} Since the *cis*-1,4 configuration most closely mirrors the properties of natural rubber, and is the most important commercially, it will be the focus of this article.

#### Chemistry

From the preceding discussion, it can be seen that many chemical structures (microstructures) are possible, and that different catalyst systems result in specific microstructures with different physical properties.

The polymerization of isoprene monomer can proceed in a 1,2-; 3,4-; or 1,4manner to give the structures shown in Figure 1.





Furthermore, the monomer units can be linked in head-tail, head-head, or tailtail arrangements, as shown in Figure 2.



random linkages

Figure 2: Head-tail and Head-head, Tail-tail 1,4- Linkages

The highly stereoregular IRs (natural rubber and Balata) have only head-tail linkages. The presence of head-head and tail-tail linkages is thought to be highly disruptive to crystallinity, since they involve chain reversals.⁶ Representative microstructure statistics for the *cis*-1,4-IRs are shown in Table 2.

The *cis, trans*, and 3,4- results were determined by ¹³C-NMR, and the headhead and tail-tail data are from a metathesis procedure.⁷ The metathesis results are consistent with ozonolysis⁸ and NMR results where head-head and tail-tail linkages are seen for Ti-IR, but not for NR.

NR	Ti-IR	Li-IR
100	98.5	90.0
0	1.0	5.0
0	0.5	5.0
0	1.0	0.7
0	0.5	0.6
100	≥97.0	≥88.7
94	>99.0	>99.0
	NR 100 0 0 0 100 94	NR         Ti-IR           100         98.5           0         1.0           0         0.5           0         1.0           0         0.5           100         297.0           94         >99.0

Table 2: Microstructures of Cis-1,4-Polyisoprene Rubber (%)

Stress crystallization in *cis*-1,4 IR leads to important physical properties such as green strength, tear strength, and gum tensile strength. Research has shown that there are major differences in the ability of the *cis*-1,4-IRs to crystallize, depending on the level and nature of the *cis* microstructure in the polymer. Li-IR x-ray diffraction patterns have indicated some crystallinity in stretched specimens, but no crystallinity is seen in the unstretched state. Ti-IR and NR both undergo crystallization in the unstretched state at -25°C, but the rate of crystallization is greater for NR. (Crystallization half-lives at -25°C are 2 to 16 hours for NR vs. 10 to 110 hours for Ti-IR) Ti-IR and NR stress crystallizing at a somewhat lower elongation than Ti-IR.

While the non-rubber components in natural rubber (approximately 6%) are known to contribute to its superior crystallization behavior, melting point (Tm) tests performed on solution grown crystals of NR and Ti-IR demonstrate the role of microstructure.⁹ After the removal of proteins, mixed fatty acids, and bound fatty acids from NR, its Tm is still higher than that of Ti-IR by about 1 degree C.

### Manufacturing Process

Figure 3 depicts a simplified flow diagram for an isoprene polymerization process. Before entering the reactors, the solvent, catalyst, and isoprene monomer must be free of chemical impurities, moisture, and air - all of which are catalyst poisons. The purified streams first enter a chain of reactors into which the catalyst is injected, and the polymerization begins.

After the desired extent of polymerization has been attained, a short-stop or catalyst deactivator is added to the cement so no further linkage of monomer or polymer takes place. A nonstaining antioxidant is then added to protect the polymer during finishing and storage.

In the next step, the cement mixture is put through a stripping operation

whereby the solvent is recovered and the polymer cement converted to a crumb by hot water and steam. The crumb slurry is processed through extruders to remove water before it is cooled, baled, packaged, and placed in storage for shipment.



**Figure 3: Polymerization Process** 

# **Polymer Properties**

The typical properties of the raw polyisoprene polymer and its vulcanizate are listed in Table 3. The vulcanizate properties are similar to the values obtained for natural rubber. Natural rubber and synthetic polyisoprene both exhibit good inherent tack, high compounded gum tensile, good hysteresis, and good hot tensile properties.

The very specific nature of synthetic polyisoprene provides a number of differences from natural rubber. There is minimal variance in physical properties from lot to lot. Polymerization conditions are narrowly controlled to ensure that the polymer is highly specific chemically. There is a low level of non-polymer constituents as compared to natural rubber.

Synthetic polyisoprene's ease of processing is important where consistency and quality are major considerations. Since less mechanical work and breakdown are required, shorter mix cycles and the elimination of pre-massing are possible when it is used as a direct replacement for natural rubber. The end results are time and power savings as well as increased throughput. In addition, synthetic polyisoprene exhibits greater compatibility than natural rubber in blends with solution SBR and EPDM. Synthetic polyisoprene's uniformity is a factor where the need for consistent quality is paramount, as is increasingly the case in many industries which emphasize precise dimensional control in processing.

Polymer Properties	Measurement
Color Density Mooney Viscosity, ML 4´ at 100°C Antioxidant Volatile Matter, % Extractable, % Ash, % <i>Cis</i> -1,4 Content, % Glass Transition Temperature, °C Weight Average Molecular Weight Number Average Molecular Weight	White 0.91 Mg/m ³ 70 to 90 Nonstaining, Nondiscoloring 0.50 maximum 3 maximum 0.6 maximum 98.5 -72 955,000 350,000
ASTM D 3403 Formula for Vulcanizate*	phr
Natsyn 2200 IRB #7 Carbon Black Stearic Acid Zinc Oxide VANAX® NS Accelerator Sulfur	100.00 35.00 2.00 5.00 0.75 2.25
Total	145.00
ODR @ 160°C, 1° Arc, 1.7 Hz, 30 min., Range 50 M _L (dN·m) M _H (dN·m) Minutes to 1 pt. rise t' 50 (min) t' 90 (min) Original Physicals	6.1 to 9.1 33.0 to 38.2 2.8 to 4.4 4.4 to 6.8 6.7 to 9.1
Hardness, Shore A 300 % Modulus, MPa Tensile, MPa, minimum Elongation, %	59 10.5 24.4 580

Table 3: Typical Properties of Natsyn 2200

*Banbury mix in two passes, with sulfur and accelerator added in the second pass.

## Processing

Synthetic polyisoprene rubbers undergo chain scission upon heating or during hot and cold mastication, as does natural rubber. This is inherent in the polyisoprene molecule. Polyisoprene polymers are likewise resistant to crosslinking or gelation upon heating. Breakdown characteristics of the two are similar.

Because of the lower raw polymer viscosity of synthetic polyisoprene, some or all of the breakdown step normally used for natural rubber should be eliminated. If the synthetic polymer is directly substituted for natural rubber, without altering the mixing cycle, compounds can be overmixed with a resulting loss in physical properties.
The following are recommended procedures for Banbury[®] and mill processing:

- 1. Banbury (Two-Pass)
  - a. Add half the polymer, stearic acid, zinc oxide, antioxidant, approximately half of the pigments, and the remaining polymer.
  - b. After batch starts to work, add the remainder of the pigments, and the plasticizer.
  - c. Mix to time or temperature.
  - d. Dump.
  - e. Add accelerator and sulfur on second pass (Banbury or Mill).
- 2. Mill (One-Pass)
  - a. Band polymer on mill.
  - b. Add antioxidant.
  - c. Add stearic acid and zinc oxide.
  - d. Add pigments and plasticizers.
  - e. Add sulfur.
  - f. Add accelerator.

It is important to add the antioxidant to the polyisoprene as soon as it is banded on the mill. This will inhibit oxidative chain scission of the polymer, and permits only chain scission caused by the shear action of the mill roll. Only the desired breakdown of high molecular weight polymer therefore occurs.

Synthetic polyisoprene compounds at the same plasticity of natural rubber will have less die swell because of having less nerve. Also, at the same plasticity, the synthetic polymer will have significantly faster extrusion rates.

In calender operations, warm-up of synthetic polyisoprene stocks should be kept to a minimum. Calendering roll temperatures should be approximately 12°C (20°F) cooler for synthetic than for natural rubber.

### **Compounding and Curing**

Unlike natural rubber, synthetic polyisoprene has a very high rubber hydrocarbon content, and contains no fatty acid. It will require a minimum of 1.5 phr of fatty acid for cure activation and the development of optimum vulcanizate properties. The synthetic polymers can also contain catalyst deactivator complexes, which act as basic accelerators. Each synthetic polyisoprene should therefore be studied for acceleration requirements and the best state of cure. In gum and in black compounds, 1.5 to 2.0 phr of sulfur are recommended. With high levels of non-black loading, 3 phr are generally used.

Synthetic polyisoprene compounds can be adapted to cure in any conventional molding operation, whether compression, transfer, or injection. Transfer and compression molding are usually done in the temperature range of 135 to 175°C (275 to 350°F). Normally, no special compounding considerations are necessary beyond what is required to meet the applicable specification.

Injection molding cycles are generally run at higher temperature, 190 to 220°C (375 to 425°F), and shorter times, so certain compounding practices should be observed. In synthetic polyisoprene as with natural rubber, sulfur is the primary

cause of reversion in overcured compounds. To avoid reversion, low levels of sulfur are generally used with sulfenamides as the preferred accelerators. Low levels of METHYL TUADS[®] (TMTD) are used as secondary accelerators. In addition to low sulfur, higher levels of zinc oxide (10 to 15 parts) may provide better heat protection. VANFRE[®] AP-2 (polymer processing lubricant) and VANPLAST[®] R (neutralized sulfonate of high molecular weight in a paraffinic oil) are useful in improving rates of extrusion.

Synthetic polyisoprene is very well-suited to injection molded compounds. Because of its uniform cure rate, exact time/temperature press cycles can be established with the assurance that all pieces will be uniformly cured. In addition, the Mooney viscosity of synthetic polyisoprene reduces injection pressures and provides shorter injection times, with a resultant increase in output.

### Formulations

Synthetic polyisoprene gum stocks can be compounded to give high tensile strength, high modulus, a high degree of resilience and excellent compression set. Table 4 lists a typical gum compound, along with properties which can be used as starting points in formulations to make rubber bands, thread, and gum sheeting.

Ingredients	phr
Natsyn 2200	100.0
Zinc Oxide	1.5
Stearic Acid	1.5
Wingstay [®] S Antiozonant (nonstaining)	0.5
Low MW Polyethylene	0.5
Sulfur	1.5
ALTAX® (MBTS) Accelerator	0.5
VANAX DOTG Accelerator	0.4
Total	106.4
ODR @ 150°C	
M₋ (dN⋅m)	4.6
M _H (dN•M)	21.8
t₁ (min)	6.2
ť 90 (min)	10.3
Original Physicals, Press Cured 20 min. @ 150°C	
Hardness, Shore A	38
300% Modulus, MPa	1.4
500% Modulus, MPa	2.6
Tensile, MPa	22.7
Elongation, %	765
Comp. Set, Method B, 22 hrs. @ 70°C, %	9.8
Tear, Die B, kN/m	41.8

### Table 4: Gum Compound

Furnace blacks perform as basic accelerators, so their contribution to the cure

system must be considered. Table 5 sets forth a typical N330 (HAF) furnace black compound. The physical properties are approximately equal to those obtained with natural rubber.

Ingredients	phr
Natsyn 2200	100.0
Zinc Oxide	3.0
Stearic Acid	2.0
Wingstay 29	1.0
N330 Carbon Black	40.0
Light Process Oil	5.0
AMAX [®] Accelerator	1.0
Sulfur	2.0
Total	154.0
Mooney Scorch, SR @ 132°C	
Viscosity	23
Minutes to 5 pt. rise	17.2
ODR @ 150°C	
M₋ (dN⋅m)	7.7
M _H (dN·m)	40.5
t _s 1 (min)	6.6
ť 90 (min)	13.3
Original Physicals, Press Cured 25 min. @ 150°C	
Hardness, Shore A	59
300% Modulus, MPa	11.3
Tensile, MPa	31.9
Elongation, %	585
Compression Set, Method B, 22 hrs. @ 70°C, %	13.7
Tear, Die B, kN/m	86.6

Table 5	: Furnace	Black	Compo	ound
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Thermal blacks have less cure activation than the furnace blacks. Table 6 shows a 40 phr thermal black compound.

	I	
Ingredients	phr	
Natsyn 2200	100.0	
Zinc Oxide	3.0	
Stearic Acid	2.0	
Wingstay 29	1.0	
N990 Carbon Black	40.0	
Light Process Oil	5.0	
AMAX	1.0	
Sulfur	2.0	
Total	154.0	

Table 6:	Thermal	Carbon	Black	Compound
Table 0.	merman	Carbon	Diack	Compound

	I ( )
Ingredients	phr
Mooney Scorch, SR @ 132°C	
Viscosity	22.0
Minutes to 5 point rise	19.7
ODR @ 150°C	
M₋ (dN⋅m)	7.9
M _H (dN·m)	37.6
ts1 (min)	8.7
ť 90 (min)	14.3
Original Physicals, Press Cured 25 min. @ 149°C	
Hardness, Shore A	59
300% Modulus, MPa	10.4
Tensile, MPa	26.6
Elongation, %	547
Compression Set, Method B, 22 hrs. @ 70°C	11.8
Tear, Die B, kN/m	68.8

Table 6: Thermal Carbon Black Compound (continued)

Clay has a retarding effect on cure because of its acidity. This necessitates increased acceleration. Table 7 shows a 100 part hard clay compound. Scorch control can be obtained by varying the primary and secondary acceleration ratios.

Ingredients	phr	
Natsyn 2200	100.00	
Zinc Oxide	5.00	
Stearic Acid	3.00	
Wingstay L	1.00	
DIXIE CLAY [®] Hydrated Aluminum Silicate, Hard Kaolin	100.00	
Process Oil	5.00	
AMAX	1.25	
METHYL TUADS (TMTD)	0.10	
Sulfur	3.00	
Total	218.35	
Mooney Scorch, SR @ 132°C		
Viscosity	16	
Minutes to 3 pt. rise	9.4	
ODR @ 149°C		
M₋ (dN⋅m)	5.7	
M _H (dN•m)	28.3	
ts2 (min)	4.6	
ť 95 (min)	16.4	
Original Physicals, Press Cured 20 min. @ 149°C		
Hardness, Shore A	63	
300% Modulus, MPa	4.6	
500% Modulus, MPa	10.5	
Tensile, MPa	18.3	
Elongation, %	630	

Table 7: Hard Clay Compound

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# by John M. Long

Lion Copolymer Baton Rouge, LA

The most widely used rubber in the world is SBR, a copolymer of styrene and butadiene. At present, SBR constitutes about 40% of the total synthetic rubber consumed in the United States. The history of its development from an interesting research material into the dominant commercial rubber in use today is a reflection of the political and social events of the twentieth century.

### **History of Development**

The ability of emulsion systems using free radical catalysts to produce both high polymerization rates and high molecular weight products was first recognized in the 1920s. During the following decade, the German government stimulated research into synthetic rubbers in an effort to free itself of dependence on foreign sources of raw material. The first butadiene-styrene copolymer from an emulsion system (Buna S) was prepared at the research laboratories of I. G. Farbenindustrie by Bock and Tschunker. This was followed shortly thereafter by the analogous butadiene-acrylonitrile copolymer (Buna N).

These products were of poor quality compared to natural rubber. Nevertheless, with considerable improvement and modification, the technology formed the basis for synthetic rubber production in the United States.

Foreseeing shortages of natural rubber due to the spreading war in the Far East, the U.S. Government in 1940 established The Rubber Reserve Company to accumulate a stockpile of natural rubber and start a synthetic rubber research and development program. The program was expanded when the United States entered World War II. Arrangements were made for interested rubber, oil and chemical firms to exchange technical knowledge and coordinate research programs. Polybutadiene was rejected as unsatisfactory, and a styrene-butadiene copolymer made in emulsion with a charge ratio of 25% styrene and 75% butadiene was chosen as the best possible general purpose rubber for development during the emergency.

Production of GR-S (as SBR was then called) in a government plant began in mid-1942. By 1945, production exceeded 820,000 long-tons. To achieve this production level, the U.S. Government financed construction of fifteen SBR plants, two butyl rubber plants, sixteen butadiene monomer plants and five styrene plants. Between 1946 and 1955, these plants were sold to various private companies. Today, there are only three emulsion-based plants in the United States: Lion Copolymer, ISP, and Goodyear Chemical, which produce SBR, BR and NBR of varying types in clear, oil-extended, and black masterbatch forms. The decline in number has come about because of either plant shutdowns or consolidation.

#### Raw Materials

The main raw materials required to manufacture SBR are butadiene and styrene. Other materials required in smaller amounts are the various emulsifiers, modifiers (e.g., thiols), catalysts, shortstops, coagulating agents, antioxidants, and antiozonants.

#### Butadiene

Present butadiene design capacity in the United States is approximately 5-6 billion pounds per year. The major part of the butadiene capacity is produced as a co-product from steam crackers, which produce primarily ethylene. Less than 5% of U.S. butadiene production comes from plants which dehydrogenate butane or butenes. Butadiene for SBR amounts to about 55% of the total monomer production. Crude butadiene, either produced by the dehydrogenation of butylene or obtained as co-product, must be extracted from other olefins or saturated hydrocarbons before it is used. Extractive solvents such as dimethylacetamide, dimethylformamide, acetonitrile, N-methyl pyrrolidone, and furfural are used.

A. By-Product Production of Butadiene

- The cracking of hydrocarbons (e.g., naphtha fractions, gas oil, condensate and ethane/propane, and even crude oil) is widely used to manufacture ethylene. Butadiene is one of the co-products obtained. The yield of butadiene co-product is dependent on the severity of the cracking operation as well as the feed used. Gas oil and naphtha feedstocks for ethylene produce the highest levels of co-produced butadiene.
- 2. Heavy petroleum distillates can be coked to yield butadiene-containing gases along with naphtha, gas oils, and petroleum coke.
- B. Dehydrogenation of Butenes

n-Butenes are used as the exclusive feed for butadiene where the nbutenes are obtained from a  $C_4$  cut (from catalytic or steam cracking of gases), which has been treated for isobutylene and butanes removal. Dehydrogenation of the n-butenes to butadiene is effected catalytically using Dow Type B catalyst (chromium oxide-stabilized calcium nickel phosphate) or Shell Catalyst 205 (ferric oxide, chromium oxide, and potassium oxide).

#### Styrene

The U.S. nameplate production capacity for styrene is currently about 8.5 billion pounds per year, of which about 4.5% is used in SBR manufacture. At one time, SBR dominated the use of styrene, but the maturity of the tire market and the increased use of styrene in packaging have changed this dramatically.

At present, all U.S. styrene plants catalytically dehydrogenate high purity ethyl benzene in the vapor phase to produce styrene. High yields of up to 90% are reported. Ethyl benzene is obtained largely by alkylating benzene with ethylene; some is obtained by fractionating mixed xylene streams (20 to 30% ethyl benzene) which result from the catalytic reforming of naphtha.

In the second method of producing styrene (i.e., as a co-product of propylene

oxide manufacture), ethyl benzene is oxidized to its hydroperoxide, which is then reacted with propylene to yield propylene oxide and the co-product, methyl phenyl carbinol. The carbinol is then dehydrated to styrene. Adequate future raw materials for styrene manufacture seem to be available; however, since aromatics are an important ingredient for upgrading gasoline octane rating (nolead or low lead gasoline), it seems likely that spot shortages and gradual price increases are to be expected.

# Polymerization

Polymerization of butadiene ( $CH_2 = CH - CH = CH_2$ ) occurs by addition of one butadiene unit to another, repeated several thousand times over. Because there are two double bonds in the monomer, additions may be of three varieties known as *cis*-1,4; *trans*-1,4; or vinyl (also called 1,2). The structures are shown in Chapter 1. These additions can all occur randomly in the same chain.

In SBR, there are styrene (CH₂ = CH – C₆H₅) units in the chain as well as the three butadiene forms listed above. These copolymers of styrene and butadiene may be randomly dispersed mixtures of the two monomers, blocks (where large segments of each kind follow one another SSSSBBBBSSSBBBB) or grafts (where the segments dangle from the main chain). SBR made in emulsion usually contains about 23% styrene, randomly dispersed with butadiene in the polymer chains. The structure of the butadiene units is about 18% *cis*, 65% *trans*, and 17% vinyl (percent of the butadiene portion only). SBR made in solution can contain the same amount of styrene or different levels. Both random and block copolymers have been made in the solution process. The solution polymers have widely varying *cis, trans*, and vinyl contents.

Among the newer, synthetic rubbers, a general purpose solution rubber, of medium vinyl polybutadiene, has properties almost identical to those of SBR. By adjusting the vinyl content of polybutadiene between 35% and 55%, one can obtain elastomers that have glass transition temperatures between -70 and -50°C, and these elastomers reportedly have some properties which closely match SBR.

Two methods of polymerization are in widespread use today produce SBR. They are:

- 1. Emulsion Polymerization (for standard SBR)
- 2. Solution Polymerization (for the newer polymers)

# Emulsion Polymerization

It is likely that this method originated from observations by pioneering investigators of natural latices or plant exudates. Natural rubber latex was probably the principal model for these scientists, and its composition was studied in great detail in laboratories around the world. The first successful efforts to produce a synthetic rubber latex occurred in Germany in the early part of the century, just prior to World War I (1914). It was not until the advent of World War II (1939) that this technology was developed to the point that emulsion

polymerization could be considered a preferred method for synthetic rubber manufacture.

In this process, the monomer is emulsified in a medium such as water with the aid of emulsifying agents such as soaps and synthetic emulsifiers. The monomer is present initially as emulsion droplets dispersed in the continuous aqueous phase. Early investigators thought that the polymerization occurred within the emulsion droplets, but subsequently it was shown that the droplets play only a minor role in this type of polymerization. Later it was suggested that polymerization occurred primarily in the aqueous phase and not in the monomer droplets. It is now believed that polymerization begins in the monomer solubilized in the much smaller swollen soap "micelle" of the aqueous phase.

In a homogeneous (solution or bulk) system with free radical initiators, the maximum degree of polymerization (i.e., the chain length) attainable is too low (chain lengths less than 10⁴) for elastomer use unless the rate of polymerization is exceedingly slow. If the free radical concentration is high enough to give appreciable reaction rates, the competition for monomer is so keen that termination occurs before growth to a high degree of polymerization.

This limitation does not apply to emulsion systems for which both high propagation rate and high molecular weight are simultaneously possible because the emulsion physically isolates each growing radical and prevents them from terminating one another.

Other advantages for emulsion systems lie in the high rate of transfer of heat of polymerization through the aqueous phase. Because the heat of polymerization amounts to about 18 kcal/mole for dienes, good heat transfer is necessary if temperature control is to be maintained. The emulsion system also allows ready removal of unreacted monomers and remains fluid even though high concentrations of high molecular weight polymer are present.

The reaction is initiated by free radicals generated by the decomposition of a peroxide or a peroxydisulfate (persulfate) in the emulsion systems. Because the rate of formation of free radicals by the initiator is temperature-dependent, the earliest free radical emulsion polymerizations were carried out at about 50°C or higher, in order to obtain reasonable polymerization rates. Subsequent research led to the discovery of other oxidation reduction reactions (redox) capable of generating radicals in sufficient numbers for adequate polymerization rates at temperatures as low as -40°C.

Commonly employed initiators include potassium peroxydisulfate ( $K_2S_2O_8$ ), benzoyl peroxide, cumene hydroperoxide, p-menthane hydroperoxide, and pinane hydroperoxide. A combination of potassium peroxydisulfate with a mercaptan of varying chain lengths (8 to 16 C atoms) is used to polymerize butadiene and styrene. In hot recipes the mercaptan has the dual function of furnishing free radicals through reaction with the peroxydisulfate, and also of limiting the molecular weight of polymer by reacting with, and thereby terminating, a growing chain, while initiating the growth of another chain. This use of mercaptan as a chain transfer agent or modifier is of great commercial

importance in the manufacture of SBR and polybutadiene in emulsion systems, since it allows the toughness of the product to be controlled, which affects processibility in the factory.

A standard polymerization recipe agreed on for industrial use became known as the "mutual," "standard," "GR-S," or "hot" recipe. Today the original recipes have been modified; typical ones are shown in Table 1.

	Hot SBR 1000	Cold SBR 1500	Cold SBR 1502		
Composition, parts	/hundred mond	omer			
Butadiene Styrene Potassium peroxydisulfate	71 29 0.3	71 29 	71 29 		
p-menthane hydroperoxide (PMHP) n-dodecyl mercaptan (DDM) t-dodecyl mercaptan (TDM)	 0.5 	0.12  0.2	0.12  0.18		
Emulsifier m	akeup, phm				
Water (monomer/water ratio adjusted 1:2) Disproportionated tall oil rosin acid soap Hydrogenated tallow fatty acid soap Potassium chloride DARVAN® WAQ (secondary emulsifier) Versene Fe-3® (iron complexing agent) Sodium dithionite (oxygen scavenger) pH of solution adjusted to 10-10.5 <i>Sulfoxylate activa</i> Ferrous sulfate heptahydrate Versene Fe-3	200 4.5-5 4.5 0.3   tor makeup, pl 	200 4.5  0.3 0.1 0.01 0.025 hm 0.04 0.06	200 1.35 3.15 0.3 0.1 0.01 0.025 0.04 0.06		
Sodium formaldehyde sulfoxylate (SFS)		0.06	0.06		
Shortstop m	akeup, phm				
METHYL NAMATE [®] Accelerator Diethyl hydroxylamine	0.05 0.015	0.05 0.015	0.05 0.015		
Polymerization conditions					
Temperature, °C Final conversion, % Coagulation Antioxidant (~0.5-0.75 on rubber) Organic acid content, % by weight Styrene content, by weight	50 72 acid/amine (staining) 5-7 24	5 60-65 acid/amine (staining) 5-7 24	5 60-665 acid/amine (non-stain) 5-7 24		
Mooney viscosity ML-4, min at 100°C	48	46-58	46-58		

Table 1:	Typical	SBR	Recipes
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At 50°C, conversion to polymer occurs at 5 to 6% per hour. Polymerization is terminated at 70 to 75% conversion, since higher conversions lead to polymers with inferior physical properties, presumably because of cross-linking in the latex particle to form microgel or highly branched structures. The termination

is affected by the addition of a "shortstop" such as hydroquinone (about 0.1 part by weight), which reacts rapidly with radicals to prevent the formation of new chains. The unreacted monomers are then removed: first the butadiene, by flash distillation at atmospheric pressure and then at reduced pressure; then the styrene, by steam-stripping in a column. A dispersion of a staining antioxidant is added (1.25 parts) to protect the product from oxidation. The latex is partially coagulated with dilute sulfuric acid or aluminum sulfate. The coagulated crumb is washed, dried, and baled for shipment. This general procedure is basic for the present-day production of all emulsion polymers. Although many variations and refinements have been developed which make possible products with distinct and special properties, the underlying procedure remains the same. One of the first major improvements in the basic process was the adoption of continuous processing, shown schematically in Figure 1.



Figure 1: The Production of Styrene-Butadiene Rubber

The styrene, butadiene, soap, initiator, and activator (an auxiliary initiating agent) are pumped continuously from storage tanks into a series of reactors. Constant temperatures, flow and adequate agitation are maintained to ensure

a desired degree of conversion before the latex exits the last reactor. Shortstop is then added, the latex is warmed by the addition of steam, and unreacted butadiene is flashed off. Excess styrene is then steam-stripped off and the latex is finished, often by blending with oil, creaming, coagulating, drying and baling, as shown in Figure 1. Common antioxidants or stabilizers are 6PPD for staining grades, and VANOX MBPC for non-staining grades.

# Solution SBR Polymerization

Solution SBR (SSBR) is produced by alkyl lithium-based catalyst systems, which are the only stereo-specific catalysts that have been found to copolymerize styrene and butadiene. These products have received worldwide acceptance for use in tires and rubber goods, as impact modifiers in plastics, and as thermoplastic elastomers. This widespread use reflects the special or optimum properties resulting from the ability of these catalysts to provide precisely designed polymer structures. The underlying features allowing for such control are:

- 1. Almost instantaneous initiation
- 2. Little termination
- 3. Little chain transfer
- 4. Controlled microstructure of the butadiene portion of the polymer
- 5. Variable styrene and butadiene ratios

The combination of these features gives the polymer producer a broad range of possible products. For example, the polymers can have a linear chain of narrow molecular weight distribution or, just as easily, a highly branched broad distribution. The copolymers can be produced with a block structure, such as is required for the thermoplastic elastomers, or as a random copolymer, as is generally used for tire applications. In addition, because of the lack of termination, it is possible to react the chain ends, which can significantly change the rheological or chemical properties of the polymer. For example, chain end functionalized polymers can be produced which can affect the interaction of the polymer with fillers, thereby influencing the hysteretic properties of the rubber compound. Although random SBR copolymers have long been made by the emulsion process previously described, solution SBR offers the advantage of optimized polymer structure, as well as being essentially pure rubber hydrocarbon, since no soaps are required. Emulsion SBRs (ESBR) typically contain 4 to 7% of non-rubber emulsifier residues. Solution SBR polymers were first commercialized by Firestone (Duradene® random copolymers and Stereon[®] block polymers), Shell (Cariflex[®] random and Kraton[®] block polymers), and Phillips (Solprene®). The random copolymers are rubbery and similar to emulsion SBR, but with several improved properties. The block polymers are discussed in the section on thermoplastic elastomers. The random solution SBRs have narrower molecular weight distribution, less chain branching, higher cis content, lighter color, and (usually) fewer non-rubber constituents than the emulsion SBRs. They are reported to have better flex, higher resilience, and lower heat buildup than the emulsion rubbers. Tensile, modulus, and elongation are comparable. Several solution SBR polymers are offered in oil-extended versions from 5 to 50 phr. The Solution SBR Polymerization Process is shown schematically in Figure 2.



Figure 2: Solution SBR Polymerization Process

Because of the wide range of products that can be produced using this manufacturing process, and the excellent control of macro- and micro-structure that is only possible through this route, it is not surprising that strong interest has developed in these products.

Solution SBR's have become very popular in tread compounds for tires because of the ability of producers to manipulate the micro structure and chain end modification to change the balance between traction and rolling resistance that is not possible with emulsion SBR. This is especially true when silicas are used as a reinforcing pigment.

#### **Physical Properties**

The glass-transition temperature (Tg) is the temperature at which a soft viscous polymer changes to a glass-like hardness. Thermodynamically it is a second-order transition, characterized by small changes in refractive index, specific volume, thermal expansion coefficient, sound velocity, etc. In addition to the determination of Tg by the measurement of these quantities, a simple relation was found between the glass-transition temperature and the Gehman low-temperature torsion flex test (ASTM D 1053). The Tg is dependent on the structure and order of the polymer. For SBR copolymers prepared by emulsion polymerization at 50°C, the glass-transition temperature can be calculated from the bound styrene content (S = weight fraction of styrene) by:

$$T_g = (-87 + 135S) / (1 - 0.5S)$$

For a similar copolymer prepared at 5°C, Tg is given by:

Viscosity measurements in dilute solution are often used to estimate molecular weights of polymers using the Kuhn-Mark relation:

$$(\eta) = KM^a$$

Where ( $\eta$ ) is the intrinsic viscosity (dl/g.), M is the polymer molecular weight, and K and a are experimentally determined constants. The values of K and a for SBR prepared at 50°C are 5.4 x 10⁻⁴ and 0.66, respectively, when the viscosity measurements are made in toluene at 30°C.

### Improvements in Production

As indicated previously, one of the first major improvements in the production of emulsion polymers was the adoption of continuous processing. Other major improvements included:

- 1. Production of "cold" SBR polymers
- 2. Preparation of carbon black masterbatches
- 3. Use of particulates and powders

# **Cold Rubber**

The use of more active radical-initiating systems around 1947 led to polymerization at 5°C with high rates of conversion. The "cold" SBR polymers produced at the lower temperature, but stopped at 60% conversion, were found to have properties superior to those of "hot" SBR.

At 5°C, 60% conversion to polymer occurs in about 12 hours. The mercaptan and soap perform the same functions as in "hot" recipes. The main difference lies in the initiator systems. The phosphates and the EDTA act as buffers, and also complex with ferrous ions, thereby limiting the concentration of the free ions. Initiation results from the radicals generated by the reaction of the iron and hydroperoxide.

In many "cold" recipes, an auxiliary reducing agent such as glucose or the sulfoxylates has been used. The sugars are no longer in widespread use because of their cost and susceptibility to bacterial attack during storage.

The availability of cold rubbers led to a significant improvement in SBR quality. It was found that gel-free elastomers with a higher than usual molecular weight could be modified by the addition of up to 50 phr of petroleum base oil, thus permitting easy factory handling. Not only do these extending oils improve processing characteristics, but they also do so without sacrificing physical properties. In the commercial polymerization process, the oil is usually emulsified and blended with the latex before coagulation.

The recent trend in SBR production is the manufacture of grades designed for specific uses. Improvements have been made in the color of SBR, which is important in many non-tire uses. This has resulted from the use of lightercolored soaps, shortstops, antioxidants, and extending oils. An example is the substitution of dithiocarbamates for hydroquinone as the process shortstop. Hydroquinone is now rarely used, and only in some hot SBR where dark color is not objectionable. A shortstop such as sodium dimethyldithiocarbamate (METHYL NAMATE[®]) diethylhydroxylamine is more effective in terminating radicals and destroying peroxides at the lower temperatures encountered in preparing cold rubbers. Because sodium dimethyldithiocarbamate can lead to nitrosamines it has been eliminated by many SBR producers and diethylhydoxylamine or isopropyl amine are being used as the sole shortstop.

## Masterbatches

Another improvement directed toward specific end uses has been the preparation of carbon black masterbatches of regular and oil-extended cold SBR. These are of interest to rubber manufacturers who have limited mixing capacity, and to those who wish to avoid factory handling of loose blacks.

The addition of carbon black in masterbatch manufacture is accomplished by forming a slurry of the pigment in water, which may contain an anionic surfaceactive agent. The SBR latex and slurry are then mixed, along with the emulsified extending oil and antioxidant. The resulting intimate blend is then acid-coagulated and vigorously agitated. The creaming step is usually omitted, since it results in the preferential precipitation of an unredispersible black, with resultant poor qualities of finished product. Other methods for black masterbatching include blending the components in a steam jet and coagulation of the latex-black blend.

# **Particulates and Powders**

These products may have carbon black or some other filler incorporated to help maintain the particle separation. Using a filler blended with the polymer ensures that a dry blend can be produced which can be fed directly to a continuous mixer. Many procedures now used in the rubber industry can thereby be eliminated, leading to a more efficient operation. There have been difficulties adopting continuous mixing but work continues to find a practical solution.

### **Commercial Grades**

The International Institute of Synthetic Rubber Producers, Inc. (IISRP) is responsible for assigning numbers to the various commercial grades of Emulsion SBR, butadiene polymers and latices. The numbering system instituted under the

Government Synthetic Rubber program is still, in the main, adhered to by private industry. The Institute numbering system is shown in Table 2:

Series	Product Type
1000	hot polymers
1500	cold polymers
1600	cold black masterbatch with 14 or less phr oil
1700	cold oil masterbatch
1800	cold oil-black masterbatch with more than 14 phr oil
1900	miscellaneous dry polymer masterbatches
2000	hot latices
2100	cold latices

Table 2: Numbering System for SBR, Butadiene Polymers and Latices

There are many types of SBR, but only a portion of these are available from any one manufacturer. Each producer will generally prefix the code number with his distinguishing trade name.

There are no IISRP standards that are applied to the various solution SBR grades. All manufactures of solution SBR's have adopted their own nomenclatures and product descriptions. The microstructure will either be of the whole polymer or of the Bd portion only. It is up to the compounder to make sure what convention is being used by the supplier to avoid erroneous conclusions.

# **Compounding and Processing**

The compounding of styrene-butadiene rubbers for end products is discussed in more detail in other sections of this handbook. Modern styrene-butadiene rubber no longer requires the repeated mixing cycles of earlier products. Its extrusion properties are superior to those of natural rubber, and its stocks have less tendency to scorch in processing. Cold SBR is often preferable to hot SBR for optimum physical properties because of its lower molecular weight and lesser degree of branching. Nevertheless, the use of hot ESBR types, when possible, can contribute to both processing and product improvements. Higher hysteresis and heat buildup, poor abrasion and cut-growth resistance, as well as higher cost, decrease the usefulness of hot ESBR, but highly loaded stocks that are not used in dynamic applications can benefit from its processing advantages.

For many uses, blends of SBR and rubbers such as natural rubber or *cis*polybutadiene are made. Compounding recipes should be proportioned to balance the requirements for each type of rubber used.

In the evolution to even better performing polymers, styrene-butadiene polymers with the most linear and narrowest molecular weight distribution can be produced only by solution polymerization. The macro-structure that gives solution SBR such useful dynamic properties also results in compounds that are harder to process. Solution SBR tends to increase compound Mooney viscosity and produces a compound with little recovery. A variation of solution SBR is the chain-end coupled structure. This procedure introduces a "star" configuration, which can act like long chain branching in its effect on recovery and processing. These polymers seem to work best in compounds with low levels of fillers. Changes in processing conditions must be made to obtain optimum processing with solution SBR.

The processing differences between the various styrene-butadiene rubbers can be attributed not only to their macro-structural differences, but also to the fact that some solution SBR contains a significant amount of block styrene. Newer SSBR's have reduced this blocked styrene content. The blocked styrene is thermoplastic and, at processing temperatures, it softens and smoothes out the compound. Polymers such as Duradene 710 and Solprene 1205 have been used at levels of 10 to 25 phr to improve processing, but can have adverse effects on wear resistance and dynamic properties in applications that operate at elevated temperatures. These polymers can also be used to modify asphalts and roofing cements.

The emulsifiers that are used for polymerization generally have beneficial effects on extrusion, stock flow, and mold release. Processing agents such as VANFRE® AP-2 can be added to solution SBR for these same effects if desired. One little considered aspect when comparing ESBR with SSBR, part for part, is the fact that emulsion SBR contains emulsifiers and that the actual rubber hydrocarbon level will be different which is not accounted for in compounding, and which for many properties penalizes the ESBR.

The processing of SBR compounds is similar to that of natural (or other) rubber. The normal fillers, plasticizers, antioxidants, and activators are used. SBR requires less sulfur than natural rubber and slightly more accelerator. Emulsion SBR is slower curing than solution SBR; thus it often requires the use of a secondary accelerator, which may not be the case with solution SBR. The vinyl content of the butadiene micro-structure also affects the cure rate. In emulsion SBR, the vinyl butadiene content is fixed at 23%. In solution SBR, the vinyl butadiene content is fixed at 23%. In solution SBR, the vinyl butadiene in solution SBR will increase hysteresis at equal raw polymer Mooney viscosity. EV and semi-EV cure systems are often used with SBR. These types of cure systems provide excellent aged properties, but do not penalize un-aged flex properties, as is the case with natural rubber.

The ingredients for SBR compounds can be mixed in internal mixers or on open mills, and may then be extruded, calendered, molded, and cured in conventional equipment. Mixing procedures vary with the compound.

Natural rubber is often plasticized mechanically or chemically to aid its processibility. Chemical peptizers have little or no effect on SBR. Emulsion SBR is sometimes pre-masticated in an internal mixer before other ingredients are added. This will drop the Mooney viscosity of emulsion SBR, but will have no effect on solution SBR. Although mixing procedures do vary, the general procedure is to mix the rubber, zinc oxide, antioxidant, and stearic acid, then add the carbon black in portions with the softener or oil (this is considered a black masterbatch). It may be desirable at this point to dump, sheet out, and cool the masterbatch. The second phase now includes mixing in all the other ingredients, with the accelerator and sulfur being added last. Mixing is then continued until the sulfur is well-dispersed.

There is little difference between emulsion SBR and solution SBR with regard to mixing times, temperatures, or levels of dispersion. Remilling can reduce the Mooney viscosity of emulsion SBR, but has only minimal effect on solution SBR. Both emulsion and solution SBR have oil-extended versions which can be used to help adjust viscosities.

The processibility of SBR compounds is extremely formula-dependent. In many cases the broader molecular weight emulsion polymer is helpful in carrying the solution polymer through the system. Generally, the higher the compound Mooney viscosity, the more difficult it is to process. On breakdown and warm-up mills, these compounds can build up heat very quickly. An extra 10% to 25% scorch time is recommended for higher viscosity compounds. These compounds also have a tendency to mill-bag. This can be alleviated by adjusting cooling water to the mill, adjusting the friction ratio, or reducing the mill gap. Cold feed extruders are becoming very popular because they bypass milling difficulties.

Extrusion rate and extrudate appearance are also formula-dependent. Fatty acids are excellent metal-to-rubber release agents, and small amounts added to the compound can improve the extrusion process. Dual extrusion of two or more components is becoming popular as a means of overcoming the low green tack of SBR compounds. Addition of small amounts of natural rubber will also improve green tack.

SBR does not have the green strength and green tack combination of natural rubber. Although some solution SBR has been developed to address this problem (e.g., Duradene 775), some natural rubber is still required for radial tire carcasses. Some SBR does have the ability to retain excellent shape in extruded goods and is used in continuous vulcanization applications such as hose.

Molding and vulcanization can be accomplished by compression, transfer, or injection methods. All three methods yield satisfactory products. Molding times are generally short in comparison with some specialty polymers, but are about the same or slightly longer when compared to natural rubber. Other types of satisfactory vulcanization procedures are open steam curing, continuous cure systems (such as continuous steam), and liquid salt trains. Microwave curing is also used.

The formulations for large volume tread stocks usually do not require remilling of the masterbatch to achieve satisfactory extrusion conditions on the tread tubing machine. Common mixing procedures compare as follows (after the tread stock is allowed to cool, and is warmed again on 84 inch mills prior to feeding to the tubing machine):

Natural Rubber	Styrene-Butadiene Rubber
Plasticize or Peptize (by mechanical methods)	Black Masterbatch
Finish	Finish

The masterbatches of certain synthetic tread stocks must be remilled prior to the finishing step in which the vulcanizing ingredients are added, but this is equally necessary for certain natural rubber tread stocks. On an overall basis, the processing of synthetic tread stocks requires less milling time than natural rubber tread stocks, because one step is eliminated.

A typical comparison of the time required per 1,000 lbs. of finished stock, using a No. 11 Banbury at 30 rpm, would be:

Natural Rubber Tread	30 min.
SBR Tread	20 min.

These times have been considerably reduced with the use of higher rotor speeds and higher ram pressures.

The power requirements for synthetic stocks are somewhat higher. They vary with the particular formulation, but loads on the Banbury motor may be 20% higher for synthetic than for natural rubber stocks.

In tubing operations, the rates of extrusion of synthetic and natural rubber tread stocks are comparable in terms of output per hour. Synthetic stocks will break down somewhat more quickly than natural rubber stocks. Thus, if warm-up capacity is the limiting factor, total output of the tubing machine can sometimes be increased with synthetic stocks.

One of the major defects in SBR stocks is the lack of green tack. For this reason, a layer or cushion of natural rubber cement is applied to at least one of the surfaces (usually the tread base) that are to be joined. This is done mechanically at the extruding stage.

When using SBR in stock for coating fabric on a calender, it is necessary to use slightly more crown on the calender roll which forms the gum sheet in order to achieve uniform gauge across the sheet. The greater crown required is .001 to .002 of an inch thick, depending on the diameter of the roll.

If the stock being calendered has a synthetic rubber content in excess of one third of the total rubber hydrocarbon, a thin layer of natural rubber cement is normally applied to the surface of the coated fabric to obtain satisfactory green adhesion. After this point in the manufacturing of passenger tires or belts, there is no difference in processing that can be attributed to the type of stock employed, whether it is natural or synthetic.

DuPont's "Delphi Forecast", made in the early 1970's, the predicted that by 1980, dry blends of powdered rubber and compounding ingredients would be used for 20% of all domestic extruded rubber. The rubber industry, in all its operations, would be much more highly automated and continuous. New forms of materials, especially pellets and powders, would be displacing elastomers supplied in the familiar bales. Many fabricators, especially smaller ones, would be buying their materials either fully or partially pre-formulated. As of 2009 this has not happened, even though polymers and black masterbatches are available in particulate or powdered form.

Hot polymerized, emulsion SBR products are still used in a variety of rubber applications; the foremost of which is solvent-based adhesives. These polymers include an extensive and unique product line that is available in both bale and crumb form (1006, 1011, 1012, and 1013), with additional polymer variations in

molecular weight, bound styrene, and pre-crosslinked or linear polymer chain configuration.

Particularly noteworthy is that some of these products are offered in a freeflowing crumb form that greatly simplifies the manufacturing process of rubberbased adhesives and sealants. These crumb products eliminate the need for milling, cutting or grinding the rubber, so that they can be added directly to a mixer with other ingredients.

The pre-crosslinked products 1009 and 4503 are two popular and essential ingredients for construction adhesives, such as panel adhesives, tile mastics and various sealants. The cross-linking in these products provides unique rheological characteristics that enable the adhesives to be caulked or trowelled with ease. The adhesives maintain their applied shape, enabling a proper contact and bonding of the substrates to take place.

#### Compounds

The following are suggested as good starting point compounds; slight adjustments may be needed depending on the equipment available.

Ingredients	phr	phr
SBR extended with Aromatic Oil	137.5	
SBR extended with Carbon Black		162.5
Zinc Oxide	4.0	4.0
Stearic Acid	2.0	1.0
Antioxidant	2.0	2.0
Sulfur	1.8	1.8
VANAX [®] NS Accelerator	1.5	1.5
METHYL TUADS [®] (TMTD) Accelerator	0.4	
Carbon Black	70.0	
Aromatic Oil	10.0	
Totals	229.2	172.8

# **High Quality Conveyor Belt Cover**

#### Medium Quality Conveyor Belt Cover

Ingredients	phr	phr
SBR extended with Aromatic Oil	137.5	
SBR extended with Oil and Carbon Black		245.0
Carbon Black	100.0	
Aromatic Oil	40.0	
Zinc Oxide	4.0	
Stearic Acid	2.0	2.0
AGERITE [®] SUPERFLEX [®] Antioxidant	1.0	1.0
6PPD Antiozonant	1.0	1.0
Sulfur	2.0	2.0
VANAX NS	1.6	1.6
METHYL TUADS (TMTD)	0.6	0.6
Totals	289.7	253.2

# Automotive Mat

Ingredients	phr	
SBR extended with Naphthenic Oil	150.0	
Zinc Oxide	4.0	
Stearic Acid	4.0	
AGERITE SUPERLITE® Antioxidant	1.5	
VANWAX [®] H Special Protective Wax	3.0	
Glycol Activator	2.0	
McNAMEE® CLAY Hydrated Aluminum Silicate, Soft Kaolin	200.0	
Calcium Carbonate	100.0	
Naphthenic Plasticizer	30.0	
AMAX [®] Accelerator	2.0	
METHYL TUADS [®] (TMTD) Accelerator	0.4	
Sulfur	4.0	
Silica	25.0	
Totals	525.9	

# Shoe Sole

Ingredients	High Quality	Medium Quality
SBR (45-55 ML4)	100.0	100.0
Naphthenic Oil	5.0	5.0
Zinc Oxide	4.0	4.0
Stearic Acid	2.0	2.0
VANOX MBPC Antioxidant	1.0	1.0
ALTAX [®] (MBTS) Accelerator	1.5	2.0
UNADS [®] Accelerator	0.5	0.5
Glycol Activator	2.0	2.0
Sulfur	2.0	2.5
Silica Filler	50.0	40.0
Pliolite [®] S6-B		25.0
DIXIE CLAY® Hydrated Aluminum Silicate, Kaolin		120.0
Totals	168.0	304.0

# Flooring or Cove Base

Ingredients	phr
35% Styrene SBR	100.0
AGERITE SUPERLITE	1.0
Calcium Carbonate	100.0
MCNAMEE CLAY	250.0
Petroleum Resin	10.0
Zinc Oxide	5.0
Stearic Acid	5.0
Sulfur	6.0
AMAX	2.0
METHYL TUADS (TMTD)	0.4
Naphthenic Plasticizer	30.0
High Styrene Resin	15.0

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The American Society for Testing and Materials (ASTM) has published a "Standard Classification for Various Types of Petroleum Oils for Rubber Compounding", ASTM Designation: D 2226, which is shown below in Table 3:

Types	Asphaltenes Max. %	Polar Compounds Max.%	Saturated Hydrocarbons %	Common Name
101	0.75	25	20 max.	Highly Aromatic
102	0.5	12	20.1 to 35	Aromatic
103	0.3	6	35.1 to 65	Naphthenic
104	0.1	1	65 min.	Paraffinic

Table 3: Classification of Oil Types

Type 104 oils are further classified into two subtypes 104A and 104B for SBR polymers only (paraffinic oils are not recommended for SBR compounding). Type 104B oils are those that have a viscosity-gravity constant up to 0.820, while Type 104A oils are those that have a viscosity-gravity constant greater than 0.820. The classifications highly aromatic, aromatic, naphthenic, and paraffinic correspond to the ASTM classification of Types 101, 102, 103, and 104, respectively.

The EU has mandated that only oils with low levels of PAH's (Poly Aromatic Hydrocarbons) be allowed in tires manufactured or imported into the EU after 1 January 2010. In Europe and other parts of the world MES (Mild Extraction Solvate) and TDAE (Treated Distillate Aromatic Extract) are available to meet this criteria. In the USA very little of either oil is available and heavy naphthenic oils are being used. IISRP has proposed two different specifications for the heavy naphthenic oils one for 1900-2500 SUS @ 100F and one from 2900 – 3500 SUS @ 100F. With either the MES or heavy naphthenic oil reformulation or use of a 32% Bound Styrene with slightly lower oil content than 1712 are required to achieve properties roughly equivalent to 1712 which has 23.5% bound styrene and aromatic oil.

Table 4 compares ASTM Designation: D 1765 ("Standard Classification System for Carbon Blacks Used in Rubber Products) to the Industry Type for most of the major commercial Carbon Blacks:

Industry	ASTM	Industry	ASTM
Types	Classification	Туре	Classifica
SAF	N110	HAF-HS/HM	N351
ISAF	N220	HAF-EHS	N358
ISAF-LM	N231	FEF	N550
ISAF-HS	N234	GPF-HS	N650
ISAF-HS/HM	N299	GPF	N660
HAF-LS	N326	SRF-LS	N754
HAF	N330	SRF-LM	N762
HAF-HS	N339	SRF	N774
HAF-HS	N347	MT	N990

Table 4: Nomenclature for Carbon Blacks

#### POLYBUTADIENE

# by Judy Douglas*, PhD and Ron LaFlair**, PhD

*LANXESS Corporation Orange, TX

> "Bayer, Inc. Sarnia, ON. Canada Retired

Polybutadiene (BR) is a homopolymer of 1,3-butadiene usually produced by a solution process. Various controlled microstructure polymers are made, of which the largest by far in volume is high *cis*-1,4-polybutadiene, which is produced with Ziegler-Natta Catalysts. It is widely used in truck and passenger tires, where its very low glass transition temperature gives excellent resilience and excellent abrasion resistance. High *cis*-1,4-polybutadiene does not have good traction properties, so the tread portions of a tire must also contain a second elastomer with a higher glass transition. This is either natural rubber (NR) or styrene-butadiene rubber (SBR). SBR can be produced by either the emulsion (ESBR) or solution process (SSBR).

Medium *cis* polymers with a mixed microstructure are produced in solution with *n*-butyl lithium (*n*-Bu Li) initiators. These are used for some tire specialties and in the production of high impact polystyrene. In the high impact polystyrene (HIPS) application Li-BR shares the market with Cobalt-BR, as well more recently Neodymium-BR, mainly because these systems can achieve the high purity required. Li-BR with an elevated vinyl content is also produced for special applications, due to its miscibility with natural rubber. Special grades of Li-BR with a highly branched structure are produced for applications where easy mixing and high loadings are required. Star-branching gives very low viscosity, which can greatly aid the processing of bead and chafer compounds.

Some emulsion BR is produced, as well as small amounts of other stereoregular and partly crystalline polybutadienes (syndiotactic 1,2-BR and *trans*-1,4-BR).

Polybutadiene is not resistant to oil. This excludes it from some industrial applications, but means that it can be oil-extended for some applications. Oxygen, ozone and sunlight rapidly attack unprotected polybutadiene, but BR can have a very long service life when protected with a combination of antioxidants, antiozonants and carbon black.

#### Historical Background

The synthetic rubber industry had its commercial beginning in the 1930s when monomers such as butadiene, styrene and acrylonitrile were polymerized by free radical systems in emulsion.

Emulsion polybutadiene was at first hard, tough and difficult to process, and had inferior product properties. However, the polybutadiene emulsion copolymers with styrene (E-SBR) and with acrylonitrile (NBR) could be easily processed and were very successful in tire and oil resistant applications, respectively. The

growth of these businesses was greatly accelerated by the Second World War.

After the war, emulsion products were improved by using low temperature redox systems. The goal was to duplicate desirable properties of natural rubber (*cis*-1,4-polyisoprene) with its stereospecific structure, good green strength, building tack and low glass transition temperature. This work benefited from the development of Ziegler-Natta processes in the mid-1950s, which enabled the manufacture of high *cis*-1,4-polyisoprene and high *cis*-1,4-polybutadiene. Plants to make these two polymers were built in the early 1960s, but the scarcity and high cost of isoprene delayed the development of polyisoprene. Some polyisoprene is produced in the former Soviet Union.

The availability and cost of butadiene were much more favorable, so the high *cis*-BR business grew rapidly. The high *cis*-BR product was found to give high resilience and low heat buildup, and tires made with it had good tread wear. Tire compounders learned how to blend high *cis*-BR, E-SBR and natural rubber to provide the balance of properties needed for specific tire applications.

The concurrent development in the 1960s of anionic polybutadiene using n-Bu Li produced another family of polybutadienes. Sodium catalysts had been used in the 1930s by I.G. Farben and the Russians, but these anionic systems give a product with a high vinyl content, which results in a high glass transition temperature and less desirable properties. The process used was also rather complicated. The soluble n-Bu Li made possible a much simpler process in a hydrocarbon solvent. It also gave a lower vinyl content and hence a lower glass transition temperature and better properties.

The 1960s also saw development of improved emulsion BR technology. These products are still available today as clear polymers and also in oil-extended and black masterbatch form, but for most applications the high *cis*-1,4 solution product is preferred.

Recent research on polybutadiene has been directed at finding new Ziegler catalysts. Some improvement in product performance and in processing has been achieved.

### **Monomer Production**

Several different routes have been used for the commercial synthesis of 1,3-butadiene. These include dehydrogenation of butanes and butenes, oxidative dehydrogenation of butenes and direct cracking. However, the world's major source of 1,3-butadiene is as a by-product of the production of ethylene from the cracking of petroleum-derived hydrocarbons. The products and their yields depend on the nature of the feedstock and the cracking conditions. The C4 stream from the cracker contains, in addition to the 1,3-butadiene, a wide range of similar molecules: butene-1, *cis*- and *trans*-butene-2, isobutylene, acetylenes, 1,2-butadiene and other materials.

The separation is a complicated process because of very similar boiling points, and is usually carried out by extractive distillation. Even parts per million of acetylenes or of 1,2-butadiene can alter the polymerization, so a very pure butadiene product is required.

Butadiene dimerizes with time and forms peroxide easily. Refrigeration is used to reduce dimer formation, and oxygen is excluded to prevent the formation of hydroperoxide. Monomer stabilizers are added to prevent the free radical side reactions which can lead to explosions or "popcorn". This uncontrolled reaction in the monomer can generate crosslinked polymer with tremendous power to expand and bend pipes and exchangers with very serious consequences.

# **Polymer Structure**

The properties of polybutadiene are influenced by several factors:

- 1. Molecular weight and molecular weight distribution
- 2. Microstructure
- 3. Crystallinity (if present)
- 4. Branching

The glass transition temperatures in turn depend on the polymer's microstructure.

The 1,3-butadiene can enter the growing polymer molecule in one of three isomeric forms, as shown in Figure 1. The pendant vinyl group along the polymer chain may be entirely on one side (isotactic), on alternating sides (syndiotactic), or on both sides with no regularity (atactic or heterotactic).



Figure 1: Microstructure of Polybutadiene

*Cis*-1,4-polybutadiene has a T_g of -109°C and is the most resilient polymer used in tires. The *trans*-polybutadiene polymer has a similar T_g, but material with a *trans* level above ~70% crystallizes very easily and can be used only in blends.

High *cis*-polybutadiene can be produced with various catalyst systems, the most important of which are shown in Table 1. Mixed lanthanides are also used in China.

Although the differences in the *cis*-1,4 content of the various products are small, the more linear and higher *cis* product from the Neodymium (Nd) catalyst system results in improved flex fatigue properties, resistance to abrasion and crack growth, and lower hysteresis.

The mixed microstructures produced by emulsion and lithium solution BR are shown in Table 1. The addition of polar additives to the anionic polymerization with n-Bu Li can increase the 1,2-polybutadiene to any desired level up to ~80%, at which point it has  $T_g$  of -20°C. These so-called vinyl BRs are available for special applications. High vinyl BR is of special interest because it is miscible with natural rubber, and improves its resistance to reversion. There is also extensive interest in high vinyl contents in the related field of solution SBR, because such polymers have lower rolling resistance in tread formulations. A syndiotactic 1,2-polybutadiene, which is partly crystalline, has been produced for some years and is used as a flexible thermoplastic.

				-	
	Cis-1,4	Trans-1,4	Vinyl	Tg, ℃	Comments
<i>Medium cis</i> n-Bu Li	38	52	10	-93	Very linear
High cis					
Cobalt	96	2	2	-107	Slightly branched
Nickel	96	2	2	-105	Slightly branched
Titanium	92	4	4	-105	Slightly branched
Neodymium	97-98	1-2	1	-109	Very linear, gel free
Emulsion BR	14	69	17	-80	Branched, some gel

Table 1: I	Microstructure	Content of Pol	ybutadienes (	(%)
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# **Ziegler-Natta Polymerization**

High *cis*-polybutadiene is made with Ziegler-Natta catalysts and is a major tire elastomer. In contrast to single site catalysts, the Ziegler-Natta catalysts are produced in solution by the reaction of transition metal salts in combination with aluminum alkyls. The Lewis acidity and reduction power of the aluminum alkyls has to be adapted to the transition metal and the final catalyst structure. Therefore the aluminum alkyls can also be used in mixtures or in combination with reactive additives, like alcohols or water. Furthermore, the catalyst can contain modifiers, including donor molecules, which influence the microstructure of the resulting polymer. The active catalyst structure of Ziegler-Natta systems is very sensitive to impurities such as water, alcohols and oxygen. In some cases the catalysts are also unstable and have to be stabilized by the coordination of the monomer during the polymerization.

The first system used titanium and was developed in 1954. The titanium catalyst consist of soluble titanium salts, iodine and aluminum alkyls (Phillips Petroleum Co., GB 848.065, 1956). This was quickly followed by cobalt (Goodrich-Gulf Chemicals, Inc. US 2.977.349, 1955) and nickel catalyst systems (Bridgestone Tire Co. DE-AS 1.213.120, 1959). The cobalt catalyst is a combination of soluble cobalt carboxylates and aluminum alkyl halides that could be modified with small amounts water or other donors. The nickel catalyst consists of nickel carboxylate, boron trifluoride and aluminum alkyl. At the beginning of the 1960s the first high *cis*-polybutadiene could be produced industrially in large scale with these typical Ziegler-Natta systems.

In recent years, there has been a move toward lanthanide catalysts, especially to neodymium (Bayer AG, EP 0.007.027, 1978). The neodymium catalyst consists of soluble neodymium salts, like carboxylates, aluminum alkyls and chlorides.

Each system has its own individual characteristics in terms of the polymerization conditions and the resultant product.

The use of the titanium system has declined in recent years because it works best in benzene and toluene, two environmentally undesirable solvents. Cobalt and nickel systems can be run in a variety of solvents. Due to environmental concerns modern processes with these catalytic systems have been changed from aromatic to aliphatic solvents. Neodymium systems only run in aliphatic solvents. One of the advantages of the neodymium catalyst is its high activity at high temperatures, so that it can be run adiabatically.

Each catalyst system tends in practice to give a fairly fixed microstructure. The system is controlled to produce the desired molecular weight. Polymers with the highest *cis* and the lowest *vinyl* content offer advantages, with the more linear and higher *cis* neodymium polymer providing improved flex fatigue and abrasion resistance, and lower heat buildup. In some cases, the degree of branching may be controlled and reactor design, feed addition and backmixing may influence the molecular weight distribution. The control of gel formation is very important for products meant to improve the impact resistance of polystyrene. However, minor levels of gel are not usually a concern in tires.

### Anionic Polymerization of Butadiene

I. G. Farben first carried out the anionic polymerization of butadiene using the BUNA (Butadiene [Bu] Sodium [Na]) process. The polymer produced contained about 65% vinyl, and therefore had a high glass transition temperature. When lithium alkyls became available, it was possible to simplify the process by using simple hydrocarbon solvents, producing polymers containing only 10% vinyl and having a much lower glass transition temperature. Polymerizations can be carried out with any alkali metal (Li, Na, K, Rb, Cs), but the simplicity and flexibility of lithium has made it the preferred system.

When n-Bu Li is used to initiate a simple batch polymerization of butadiene, a living polymerization ensues. Rapid initiation takes place and a butadiene anion is formed with its associated lithium cation. These ions are preserved at the end of the chain throughout the polymerization, as long as the system is kept free of impurities. Each monomer unit adds to the previous anion and forms a new anion. As the polymerization proceeds, the number of active anions is constant, and each forms one polymer molecule. When polymerization is completed, a product with a narrow molecular weight distribution is formed. With some restrictions, a second monomer can be added to form a block polymer, or postpolymerization chemistry can be used to couple polymers, add end groups or functionalize the backbone.

The polymerization will be living only if impurities (water, oxygen, CO₂, alcohols, etc.) are not present and if the temperature is kept low enough to avoid side reactions. The block polymers and solution SBR products that can be made with this system are beyond the scope of this article. Most Li-BR applications do not seem to need end groups, or narrow molecular weight distribution. It is therefore made by a continuous, adiabatic process. This process may not even be truly living, but nonetheless makes an excellent product with high purity, good color and low levels of gel. This is one of the preferred polymers for the production of high impact polystyrene.

The production of polybutadiene with elevated vinyl content can be carried out with the above process by adding polar chemicals such as ethers or diamines. The vinyl content is a function of the additive chosen, its concentration and the temperature of the polymerization. These additives must be chosen with care, since they can also promote side reactions that reduce the living nature of the polymer and can cause problems in the solvent recovery and waste water control systems.

Star-branched Li BR polymers are produced as a specialty because of their exceptionally good processing. They mix very easily and can accept very high levels of carbon black. They are therefore often used in bead and chafer compounds.

### **Polymerization Process**

In any solution polybutadiene plant, much of the process involves not the polymerization itself but the steps that precede or come after it. All of the solution processes are very sensitive to water, oxygen and many other impurities. The process usually begins by removing the t-butyl catechol stabilizer from the monomer followed by the complete removal of any water present. The solvent and monomer are then charged into the reactor. Figure 2 shows a generalized schematic of a typical BR manufacturing unit.



Figure 2: Generalized Schematic of a Polybutadiene Manufacturing Unit

After polymerization, the reaction is shortstopped and antioxidants are added to protect the product. The pH may also have to be adjusted. The removal of solvent and any excess monomer is usually achieved by mixing steam, water and polymer solution in a coagulating vessel, where the solvent and monomer are stripped off with steam, leaving a slurry of rubber. When all the remaining solvent and monomer have been stripped away, the water is then removed by a series of screens, dewatering extruders and tunnel driers. The dry rubber can then be baled and packaged. The reprocessing and purification of the solvent and any residual monomer then completes the cycle.

Attempts to directly devolatilize the solvent and monomer have been tried but with relatively little success. The viscosities are high, and removal of residual monomer to meet the tight specifications expected today is difficult. It is also hard to remove catalyst residues and adjust pH without a water wash step.

If desired, oil and/or carbon black can be added to the product. The oil allows higher molecular weight polymers to be processed, and the addition of the carbon black at this stage simplifies the compounding and allows the customer to operate in a cleaner environment. The oil and black must be added before the rubber is recovered from the solvent.

### Processing

In comparison to E-SBR, which tends to be fairly uniform in processing, regardless of the grade or supplier, the processing of BR is very much dependent on the specific grade and producer.

The various products vary not only in Mooney viscosity but also in

molecular weight distribution, branching, low molecular weight components and microstructure. These factors can influence mill behavior and extrusion characteristics. BR polymers are somewhat difficult to process on their own. They are less thermoplastic, and there are major differences in green strength and green tack among BR grades. Insufficient tack is often a problem with compounds high in BR. In some cases it is necessary to add a second polymer in order to increase the tack. Neodymium BR gives compounds improved tack, and is preferred where the polymer is used alone, or in blends containing a high proportion of BR.

Since BR is used primarily in blends, these differences may not be hugely significant, but the processing differences can still require changes in mixing conditions and extrusion dies if the polymer is changed.

### Compounding and Curing

BR, SBR and NR are all unsaturated materials which can be vulcanized by a variety of sulphur accelerator systems. These three polymers are the dominant tire polymers, and can be used in different ratios for the various components of the tire. They may be extended with oils and filled with reinforcing fillers such as carbon black and silica.

Few polymer combinations are truly miscible on a molecular scale. The properties of a vulcanized article made with two or more polymers will depend on the nature of the polymers themselves, the amount of oils and fillers present, the nature of the vulcanization and the nature of the phases formed. It is desirable to find mixing conditions which give very small phases. However, even after good mixing, the phases may coarsen during the early stages of the cure process.

It is relatively easy to use different combinations of BR, NR and SBR, in spite of the miscibility problems, since these three polymers all are reasonably similar in compatibility and cure rate. Where greater differences of polarity or cure rate exist, i.e., BR and nitrile rubber (NBR), BR and polychloroprene (CR), BR and butyl rubber (IIR), or BR and ethylene propylene diene terpolymer (EPDM), the polymers cannot be used together and are termed as incompatible. However, blends with lower amounts of BR are used successfully on a commercial scale to help with cost and/or processing. For example, BR (i.e., up 10 phr) is blended with CR to help with processing of conveyer and automotive belts. BR can also be blended with NBR to reduce the cost of hose and seals where oil resistance can be slightly sacrificed.

Black masterbatch BR grades are also available commercially which include oil and carbon black, or simply BR with oil. The benefit to the compounder is the removal of free oil from the mix, improved incorporative mixing with potential for reduced mixing cycles and cycle times, as well as faster throughput rates.

#### Producers

Producers of high *cis*-1,4-polybutadiene are shown in Table 2. Producers of lithium polybutadienes are shown in Table 3. In addition to the mixed microstructure polymer shown in Table 1, special polymers with higher vinyl content are produced by a few suppliers, as are some star-branched materials.

	-		
Producer	Country	Trade Name	Catalyst
North America			
LANXESS Corp.	USA	Buna CB ¹	Co, Nd
Firestone Synthetic Rubber	USA	Diene	Ni, Nd
Goodyear Chemical	USA	Budene®	Ni
LANXESS Elastômeros do Brasil S.A. ²	Brazil	Buna CB ³	Nd
Europe/Russia			
Arak Petrochemical Co.	Iran		Co
LANXESS Deutschland GmbH	Germany	Buna CB	Nd, Co
Schkopau (Dow)	Germany	Buna cis	Ni
Efremov Synthetic Rubber	Russia	SKD	Ti
Polimeri	Italy, UK	Europrene [®] , Neocis [®]	Ti, Nd
Michelin	France	Cisdene	Ti
Nizhnekamskneftekhim	Russia		Nd
Petkim	Turkey	Pet Cis	Co
Voronezhsyntezkachuk Co.	Russia	SKD	Ti, Nd
Courth Africa (Australia (Asia			
South Africa/Australia/Asia	China		NI
Choi Moi Corp	Taiwan	Kibipol	Nd
Daguing Conoral Potrochomical	China	Кіріроі	Ni
Gaogiao	China		Ni
Hyundai Petrochemical	S Korea	Sector	Ni
Indian Petrochemical Corp	India	Cisamer	Co Ni
linzhou Petrochemical Corp.	China	Cisamer	Ni
Japan Synthetic Rubber	lanan	ISR® BR	Ni
Karbochem (Dow)	S Africa	Neodene [®]	Nd
Korea Kumbo	S Korea	Kosyn [®] Kumho [®]	Ni
I G Polymer	Korea	Robyin , Runno	Ni
Nippon Zeon	Japan	Nipol®	Co
Qilu Petrochemical	China	. upoi	Ni
Quenos	Australia	Austrapol	Co
Taiwan Synthetic	Taiwan	Taipol	Co
BST Elastomers	Thailand	BSTE	Co
UBE	Japan	Ubepol [®] BR	Co
Yanshan	China	F -	Ni
Yueyang	China		Ni
Xiujiang	China		Ni

Table 2: High Cis Polybutadiene Producers

"Buna CB" grades from LANXESS Corporation in Orange, TX were formerly named "Taktene[®]"
"Elastômeros do Brasil S.A." was formerly "Petroflex Industria e Comercia S.A."
"Buna CB" grades from Elastômeros do Brasil S.A. were formerly named "CoperflexBR" from Petroflex

Producer	Country	Trade Name
North and South America LANXESS Corp. Firestone Synthetic Rubber Goodyear Tire & Rubber Co. LANXESS Elastômeros do Brasil S.A. ²	USA USA USA Brazil	Buna CB ¹ Diene Budene [®] Buna CB ³
Europe/Russia LANXESS Elastomeres S.A.S. Schkopau (Dow) Polimeri Efremov	France Germany Italy, UK Russia	Buna CB SE PB Intene® SKD
South Africa/Australia/Asia Asahi Chemical Chi Mei Hyundai Petrochemical Japan Elastomers Japan Synthetic Rubber Karbochem (Dow) Kumho Nippon Zeon	Japan Taiwan S. Korea Japan Japan S. Africa S. Korea Japan	Asadene Kibipol Seetec® Asaprene® JSR Afdene Kosyn® Nipol®

**Table 3: Lithium Initiated Polybutadiene Producers** 

¹ "Buna CB" grades from LANXESS Corporation in Orange, TX were formerly named "Taktene®"

² "Elastômeros do Brasil S.A." was formerly "Petroflex Industria e Comercia S.A."

³ "Buna CB" grades from Elastômeros do Brasil S.A. were formerly named "CoperflexBR" from Petroflex

### Applications

**Tires** use by far the major portion of the polybutadiene manufactured. Components containing polybutadiene include sidewalls, body plies, treads, chafer and bead compounds. These components make use of the high resilience, abrasion resistance and good flex fatigue characteristics of polybutadiene.

High and medium *cis*-polybutadienes impart excellent abrasion resistance and low rolling resistance, but have very poor wet traction characteristics. Elastomeric polybutadienes have poor tear resistance that limits their use in areas where this property is important (i.e., off-road tires). Special lithium polymers with starbranching are used for bead and chafer compounds, and vinyl BR is used to improve the reversion resistance of NR.

BR is traditionally blended with SBR to optimize rolling resistance, traction and abrasion resistance in tire tread compounds. Tires manufactured for the original equipment (OE) industry are typically made with solution SBR (SSBR) whereas the after-market tire industry incorporates emulsion SBR (ESBR) due to its lower cost and longer history. Table 4 presents a generic ESBR carbon black based tread compound. The global trend is to move away from highly aromatic oils (or DAE distillate aromatic extract) toward low polycyclic aromatic hydrocarbons (PAHs) as mandated in Europe and Japan by 2010. Examples of oils which meet the low PAH requirement are MES (mild extraction solvate), RAE (residual

aromatic extract), TDAE (treated distillate aromatic extract), TRAE (treated residual aromatic extract) and naphthenic oils.

Ingredients	phr
Buna SE 1712	89.4
Buna CB 24 (High <i>cis</i> BR)	35.0
N 234 Carbon Black	75.0
Process Oil	7.0
Stearic Acid	2.0
Vulkanox [®] 4020 (6PPD)	2.0
AGERITE [®] RESIN D [®] (TMQ) Antioxidant	2.0
Zinc Oxide	4.0
Wax	2.5
Sulfur	1.9
DURAX® (CBS) Accelerator	1.5
Total	222.3

Table 4: ESBR Carbon Black Tread Compound

Although the after-market tire industry generally compounds to improve treadwear while maintaining traction, reduction of rolling resistance is typically the focus for the OE tire manufacturer. The polymer, filler and oil types have a large influence on rolling resistance. A typical carbon black filled low rolling resistant tread compound is presented in Table 5. Please note the use of naphthenic oil and carbon black type.

Table 5: Carbon Black Low Rolling Resistance Tread Compound

Ingredients	phr
Buna VSL 2525-0 (SSBR)	70.0
Buna CB 25 (High <i>cis</i> BR)	30.0
N339 Carbon Black	60.0
Naphthenic Oil	20.0
ZnO	3.0
Stearic Acid	1.5
Vulkanox 4020 (6PPD)	1.0
AGERITE RESIN D (TMQ)	1.0
Wax	1.0
Sulfur	2.5
DURAX CZ (CBS)	1.0
Vulkacit [®] DZ (DCBS)	1.0
Total	192.0

Iotal

The use of silica fillers to reduce rolling resistance has become more common and an example is shown in Table 6. This test formulation incorporates the use of a high vinyl SSBR blend with BR, silane and DPG as an accelerator. SSBR products are available in different Mooney viscosities to optimize the balance between processing and tire performance. Many polymer producers have introduced functionalized SBRs which can strengthen the interaction between reinforcing filler and the polymer matrix which also reduces rolling resistance.

Ingredients	phr
Buna VSL 5025-2	96.3
Buna CB 24 (High <i>cis</i> BR)	30.0
Vulkasil [®] S (Silica)	80.0
Si 69	6.4
Process Oil (TDAE)	11.3
Stearic Acid	1.0
Zinc Oxide	2.5
AGERITE RESIN D (TMQ)	1.0
Vulkanox 4020 (6PPD)	1.0
Sulfur	1.8
DURAX (CBS)	2.0
VANOX® DPG Accelerator	1.8
Total	235.0

Table 6: Silica Low Rolling Resistance Tread Compound

Blends of natural rubber and polybutadiene are used in tire sidewalls, where a 50:50 blend, as shown in Table 7, is typical. The polybutadiene imparts particularly good resistance to crack initiation.

Ingredients	phr
Taktene [®] 1203G1 (High <i>cis</i> BR)	50.0
Natural Rubber (SMR5)	50.0
N660 Carbon Black	50.0
Naphthenic Oil	10.0
Zinc Oxide	3.0
Stearic Acid	2.0
Sunproof Improved Wax	2.0
Vulkanox 4020 (6PPD)	2.0
AGERITE RESIN D (TMQ)	2.0
Sulfur	1.8
VANOX NS (TBBS) Accelerator	1.0
Total	173.8

# Table 7: Black Sidewall Compound

Another example where a 50:50 blend of BR and NR is advantageous is with the tire's rim strip (see Table 8). The rim strip contains a higher loading of high surface carbon black (N330) for better abrasion resistance as it acts like a cushion between the exterior rim and interior tire components.

Ingredients	phr
Buna CB 24 (High <i>Cis</i> -BR)	50.0
Natural Rubber (SMR5)	50.0
N330 Carbon Black	75.0
Process Oil	9.0
Zinc Oxide	4.0
Stearic Acid	2.0
Protector Wax	1.0
Process Aid	2.0
Tacktifier	3.0
Vulkanox 4020 (6PPD)	2.0
AGERITE RESIN D (TMQ)	1.0
Sulfur (80%)	3.4
DURAX (CBS)	2.0
Total	204.4

Table 8: Rim Strip/Cushion Formula

Medium- and high-vinyl polybutadienes are used almost entirely in tire tread applications. High-vinyl polybutadienes confer good wet traction and low rolling resistance, but have very poor abrasion resistance. Medium-vinyl polybutadiene tends to have reasonable traction characteristics and low rolling resistance, along with good abrasion resistance.

**High Impact Polystyrene (HIPS)** and **Mass Acrylonitrile Butadiene Styrene** (**M-ABS**) are made by polymerizing the styrene (and acrylonitrile) in the presence of polybutadiene to improve impact resistance. Grafting takes place and the rubber exists as domains within the polystyrene or SAN matrix. The choice of elastomer is dictated primarily by the need for purity and low gel; special grades of Li-BR, Co-BR and Nd-BR have been produced for this purpose. Formulas and mechanical properties of HIPS based on different polybutadiene rubbers are shown in Table 9. Whereas low viscosity polymers like Co-BR and Li-BR, which have a somewhat higher vinyl content, provide inherently smaller rubber particle sizes (rps), the Nd-BR polymer leads to superior mechanical properties (i.e., Izod and elongation at break).

Initiation	Peroxide Grafting		
Polymer Type	Co-BR	Li-BR	Nd-BR
Buna Grade	CB 1406	CB 529 T	CB 728 T
Weight, % Polymer	6.0	6.0	6.0
Physical Data			
Rubber particle size (rps), µm	1.68	2.02	4.88
Izod Impact @ 23°C, Mean Value, kJ/qm	67.4	92.4	135.6
Izod Impact @ -40°C, Mean Value, kJ/qm	47.0	54.4	71.7
Orginal Physicals, @ 23°C			
Elongation at break, %	47.3	51.1	66.0
E-Modulus, N/mm ²	1689	1809	1662

Table 9: Characterization of HIPS Based on Different BR Catalysts

For M-ABS applications, star-branched Li-BRs are widely used because such rubber type leads to resins combining improved gloss behavior with good mechanical properties.

**Solid Core Golf Balls** use high *cis* polymers. The development of highly resilient polybutadiene and compound core technology has favored solid core construction at the expense of wound golf balls. High performance solid golf balls typically have 3 to 4 piece layers in their construction, i.e., single or dual core(s) with dual covers. Common cover materials are ionomeric ethylene copolymers containing acid groups neutralized by using various metal salts and polyurethanes.

For high performance golf balls, it is recommended that the polybutadiene have a high *cis* (>95%) and low vinyl (<2%) microstructure, high molecular weight, high linearity, low and consistent moisture content, incorporate a peroxidefriendly antioxidant and is easy to process. In this application, the resilience is accentuated by a very tight crosslinking network, achieved using a peroxide in the presence of a difunctional monomer such as zinc diacrylate. Table 10 displays a typical golf ball formulation.

Ingredients	phr
High <i>Cis</i> -BR	100.0
Zinc Diacrylate	25.0
Zinc Stearate	10.0
Zinc Oxide	5.0
VAROX DCP-40C Peroxide	1.0
Total	141.0

Table 10:	Typical	Golf Ball	Core	Formulation
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**Other Applications** such as **Hose, Conveyor Belts** and **Roll Covers**, take advantage of the polybutadiene's flexibility at low temperature and good abrasion resistance. Blends of BR, NR and ESBR are used for low cost, abrasion resistant conveyor belts. BR is also used in shoe sole applications where abrasion resistance and flex fatigue are needed. Although it is rare for BR to be used 100% in any application other than golf balls, substituting a BR polymer for the NBR polymer in the ASTM D 3187 test formulation does provide a good test formulation for those interested in benchmarking their BR suppliers.

### **Future Developments**

The unique combination of polybutadiene's low cost and low glass transition temperature, together with its ability to improve the tear resistance, wear characteristics, resilience, and low rolling resistance of tires, likely assures its dominant position in the tire industry. However, the tire industry is aggressively seeking further improvements, mainly through functionalization of the current polymers, either by end-group, backbone or coupling reactions. Functionalized SSBR polymers are produced to reduce rolling resistance by reducing filler-
filler interactions and there is a hope to make similar improvements to high *cis*-BR polymers. However, the chemistry of the Ziegler-Natta catalyst systems is particularly complicated, and a satisfactory result is thus problematic.

In addition, it is highly desirable that all new developed technologies fit into established processes. The tire industry is highly resistant to significant investments in totally new processes (i.e., gas phase EPDM). However, it is very likely that new or revised metallocene and Ziegler-Natta catalyst systems will be explored to polymerize 1,3-butadiene in a more economically feasible manner (i.e., Vanadium-BR)

The future of BR seems to be one of incremental developments, such as improved processing grades, reduced cost, improved uniformity, and environmentally friendlier oil extended polymers. Only a major change in tire technology would threaten the current markets for BR. Work continues to produce new elastomers for other applications, even to duplicate natural rubber, but success in these areas is unlikely to detract from current BR applications.

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# by James V. Fusco* with additions by Ilan Duvdevani

ExxonMobil Chemical Company Baytown, TX *Deceased

Commercial isobutylene-based elastomers include polyisobutylene homopolymers, isobutylene/isoprene copolymers and their halogenated derivatives, and brominated isobutylene/p-methylstyrene copolymers. These isobutylene-based polymers owe their commercial success to a unique set of properties which includes exceptionally low permeability to gases, excellent vibration damping and good to excellent heat, chemical, ozone and oxidation resistance. The consumption of these elastomers ranks fourth in total volume among all synthetic rubbers consumed in the world today.

Butlerov and Gorianov¹ noted the formation of oily polymers when isobutylene was treated with boron trifluoride late in the 19th century. In the 1930's high molecular weight polyisobutylenes were produced that showed rubber-like properties. Their saturated hydrocarbon structure precluded vulcanization with sulfur vulcanization systems. W. J. Sparks and R. M. Thomas of the Standard Oil Development Company (later to become the Exxon Research & Engineering Company) produced the first vulcanizable isobutylene copolymer in 1937 by incorporating a small amount of a diolefin into the macromolecule, first butadiene and later isoprene, which came to be known as "butyl rubber".¹⁻⁵ Development of this new polymer was fostered by the United States government during World War II due to the desperate need for synthetic rubber. ExxonMobil Chemical Company built the first commercial butyl rubber facility in cooperation with the Office of Rubber Reserve in 1942. ExxonMobil Chemical purchased the commercial butyl plants from the government in 1956.

Industrial consumption for the isobutylene-based elastomers grew from about 100 ktons in the post WW II period to about 902 ktons in 2008, with the halobutyls dominating in market share. There are three major worldwide producers, as shown below. The industrial consumption of isobutylene-based elastomers has been dominated by tire-related applications, which consumed ~85% of the total, the remaining ~15% going into various non-tire applications.

Producer	IB Based Elastomers	Production Capacity Share*
ExxonMobil Chemical Co. & Producing Partners	butyl and halobutyl	~52%
Lanxess	butyl and halobutyl	~28%
Russia and Others	butyl	~20%

* IISRP Publication Worldwide Rubber Statistics (2008)

### BUTYL RUBBER

### **Process and Manufacture**

A typical butyl process schematic is shown in Figure 1. The feed, which is a 25% solution of isobutylene (97-98%) and isoprene (2-3%) in the diluent methyl chloride, is cooled to  $-100^{\circ}$ C in a feed tank. At the same time, aluminum chloride is dissolved in methyl chloride. Both of these streams are then continuously injected into the reactor. Because the reaction is exothermic and is practically instantaneous, cooling is very important. To remove the heat of reaction, liquid ethylene is boiled continuously through the reactor cooling coils, maintaining the reaction at  $-100^{\circ}$ C. As the polymerization proceeds, a slurry of very small particles is formed in the reactor. This slurry overflows into a flash drum that contains copious quantities of hot water. Here the mixture is vigorously agitated, during which time the diluent and unreacted hydrocarbons are flashed off overhead.



Figure 1: Flow Plan for Butyl Rubber Manufacture

At this point, an antioxidant and zinc stearate are added to the polymer slurry. The antioxidant is added to prevent breakdown of the polymer in the subsequent finishing section. Zinc stearate is added to prevent the agglomeration, or sticking together, of the wet crumb. The slurry is then vacuum-stripped of residual hydrocarbons.

In the finishing operation, the butyl rubber slurry is dewatered in a series of extruders to reduce the water content in the rubber to 5-10%. Final drying is

accomplished in the last extruder by allowing the compressed polymer melt to expand through a die to form an exploded crumb. The crumb is air-conveyed to an enclosed fluidized bed conveyor, where water vapor is removed and the crumb is cooled and baled.

Most of the world production of isobutylene-based elastomers is made by the low temperature slurry process using methyl chloride as the polymerization medium and aluminum chloride as the initiator. One Russian plant uses a solution process with an alkane solvent and alkyl aluminum halide initiator.

### **Properties of Commercial Butyl Grades**

The commercially available butyl rubbers are copolymers of isobutylene with isoprene, and are described in Table 1. Grades are distinguished by molecular weight (Mooney viscosity), and isoprene content is reported as mole % unsaturation. The mole % unsaturation value is the moles of isoprene per 100 moles of isobutylene. Figure 2 compares the structure of butyl rubber with that of natural rubber. Natural rubber contains an olefinic bond for each monomer repeat unit. In contrast, a butyl rubber with a mole % unsaturation value of 1 mole % would have a molecular weight between olefinic units of over 5,000. Butyl rubber was the first example of a limited olefinically functional elastomer, containing a controlled small amount of double bonds to permit vulcanization, in an otherwise essentially saturated copolymer.

The unsaturation level of butyl is measured by nuclear magnetic resonance (NMR).⁶ The isoprene unit enters the chain randomly in a *trans*-1,4 configuration; chemical analysis shows no evidence for 1,2 and 3,4 modes of entry at the unsaturation levels present in commercial grades of butyl.



#### Figure 2: Comparison of Unsaturation of Butyl and Natural Rubber

Typical Range For	Mole %	Suppliers and Grades	
Mooney Viscosity ML-125°C	Average Range	ExxonMobil Chemical	Lanxess Corporation
29-35	0.8-1.3 ^b	Exxon™ Butyl 065	
46-56	1.5-2.0°		Lanxess Butyl 101-3
29-35	1.3-1.7 ^b	Exxon Butyl 165	
46-56	1.5-2.1 ^b	Exxon Butyl 268	Lanxess Butyl 301d
52-62	1.5-1.9 ^b	Exxon Butyl 269	
29-37	2.0-2.6 ^b	Exxon Butyl 364	Lanxess Butyl 402 ^e
^a = 1+8 min. ^b = Nonstaining antio	vidant	^d = Russian equiva	alent grade BK-1675

Table 1: Commercial Butyl Rubber Grades

Nonstaining antioxidant

Russian equivalent grade BK-2045

° = No antioxidant added

A low-molecular-weight, semi-liquid variety of butyl rubber (40,000 viscosity) was developed by ExxonMobil Chemical⁶ and is available as Kalene[®] from Royal Elastomers in Belleville, New Jersey. This polymer is used primarily in coatings and sealants applications. An aqueous dispersion of butyl (55% to 65% solids) using an anionic emulsifier, also developed by ExxonMobil Chemical⁸, is available from the Lord Corporation of Pompano Beach, FL. The latex is also used in adhesives and coatings. Partially crosslinked varieties of butyl listed in Table 1 are available from the Lanxess Corporation, and under the trade name Kalar® from Elementis Specialties, for use in sealant/tape applications.

### Vulcanization

The very low levels of unsaturation in butyl rubber require more active accelerators, particularly the thiuram sulfides and dithiocarbamates. These are generally used with elemental sulfur to effect crosslinking in acceptable cure times. Vulcanizates of excellent quality result when 1.0 to 1.5 phr of these accelerators are combined with 1.0 to 2.0 phr of sulfur. Butyl can also be crosslinked with dioxime and related dinitroso compounds, and with polymethylolphenol resin cure systems.

Sulfur-based Cures - Table 2 shows the range of ingredients in an accelerated sulfur cure. To activate the organic accelerators, butyl compounds normally require zinc oxide at the 5 phr level, which also contributes reversion resistance. Stearic acid or other fatty acids are not required for vulcanizing butyl compounds, but are often used as processing aids. Table 3 shows the more conventional sulfur formulations for butyl rubber, while Table 4 describes some special accelerator systems.

The normal range of curing temperatures for butyl rubber is 149 to 171°C, but fast curing combinations will give good cures in longer times at temperatures as low as 100°C. Temperatures above 171°C do not harm the butyl polymers and can be used to give shorter cure times. To cure thick items, temperatures of 182°C or higher are suggested. The most heat-stable sulfur donor, quinoid, and resin cures are suggested for such applications. The temperature coefficient of vulcanization for carbon black-sulfur formulations has been estimated as 1.4 for 6°C. That is, the vulcanization time is multiplied by 1.4 for every 6°C decrease in curing temperature.

Ingredients	phr
Butyl Elastomers	100.0
Zinc Oxide	5.0
Sulfur	0.5-2.0
Thiuram or Dithiocarbamate Accelerator	1.0-3.0
Modifying Thiazole Accelerator	0.5-1.0

	Table 2:	Sulfur-Accelerator	Formulations
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*The Resin Cure* - The crosslinking of butyl rubber (and other elastomers containing olefinic unsaturation) by this system depends on the reactivity of the phenolmethylol groups of reactive phenol-formaldehyde resins:



Two mechanisms involving the isoprenoid unit have been postulated. One involves reaction with allylic hydrogen through a methylene quinone intermediate, and the other an actual bridging of the double bond. The low levels of unsaturation of butyl require resin cure activation by adding halogen-containing materials such as SnCl₂, or halogen-containing elastomers such as Neoprene in combination with ZnO. The series of curves in Figure 3 illustrates the activating effect of stannous chloride and the resistance of the resultant crosslink to reversion upon prolonged heating. This feature of the resin cure is used in the fabrication of tire-curing bladders.

Acceleration System	on phr	Processing Safety (Scorch)	Cure Rate	Maximum Serviceable Intermittent Temperature	Comments	Major Application
Sulfur TeDEC MBTS	1.5 1.5 1.0	Safe	Fast	121-135°C (250-275°F)	Good dynamic properties	General Purpose
Sulfur TMTD SeDMC	2.0 1.0 1.0	Safe	Fast	100-121°C (212-250°F)	White loaded compounds Cures under 300°F	General Purpose
Sulfur TMTD MBT	1.5 1.0 0.5	Very Safe	Moderate	100-121°C (212-250°F)	General purpose	Innertubes
Sulfur TeDEC TMTD MBT	2.0 0.5 0.5 0.5	Very Safe	Slow	121-135°C (250-275°F)	High loading, low plasticizer compounds	Extruded
Sulfur TeDEC TMTD MBT	1.0 1.0 1.0 1.0	Safe	Moderate	100-121°C (212-250°F)		General Purpose
Sulfur TeDEC TMTD ZnMBT	1.5 1.0 1.0 1.0	Safe	Fast	121-135°C (250-275°F)	Excellent steam cure	Extruded
Sulfur TeDEC CuDMC MBTS	1.5 1.0 1.0 1.0	Safe	Fast	121-135°C (250-275°F)		General Purpose
Sulfur TeDEC TMTD CuDMC MBTS	1.0 1.5 1.0 0.5 1.0	Safe	Very Fast	121-135°C (250-275°F)	High modulus	Corner Molding

Table 3: Conventional Sulfur Acceleration for Butyl Rubber

Acceleration System	phr	Processing Safety (Scorch)	Cure Rate	Maximum Intermittent Temperature	Comments	Major Application
DTDM TMTD	2.0 2.0	Very Safe	Slow	135-149°C (275-300°F)	Substitute TeDEC for TMTD to improve heat aging	Molded
Sulfur TeDEC	0.5 3.0	Scorchy	Very Fast	143-160°C (290-320°F)	Low compression set	Molded
Sulfur TeDEC MBTS	0.5 3.0 1.0	Safe	Fast	143-160°C (290-320°F)	Safer than Sulfur/TeDEC	Molded
Sulfur TeDEC CuDMC	0.5 1.5 1.5	Safe	Fast	143-160°C (290-320°F)	Safer than Sulfur/TeDEC	Molded
BAPFR	12.0	Safe	Slow	177-204°C (350-400°F)	Good heat stability	General Purpose & Curing Bladder
MPFR Halogenated Polymer	12.0 5.0	Safe	Slow	177-191°C (350-375°F)	Good heat stability	General Purpose & Curing Bladder
MPFR SnCl ₂	12.0 2.0	Scorchy	Very Fast	191-232°C (375-450°F)	No Zinc Oxide	Molded & Curing Bladder
GMF MBTS Sulfur	2.0 4.0 1.0	Safe	Fast	149-185°C (300-365°F)	Good electrical properties	General Purpose

Table 4:	Special Acceleration	Suctor	o for But	Dubbor
Table 4:	Special Acceleration	System	s for Buty	Rubber

Accelerator Abbreviations for Tables 3 and 4

BAPFR	Bromomethyl alkylated phenol formaldehyde resin
CuDMC	Copper dimethyldithiocarbamate (METHYL CUMATE®)
DTDM	4,4'-Dithiodimorpholine (DTDM)
GMF	p-Quinone dioxime
MBT	2-Mercaptobenzothiazole (CAPTAX®)
MBTS	Benzothiazyl disulfide (ALTAX®)
MPFR	Methylol phenol formaldehyde resin
SeDMC	Selenium dimethyldithiocarbamate (METHYL SELENAC®)
TeDEC	Tellurium diethyldithiocarbamate (ETHYL TELLURAC®)
TMTD	Tetramethylthiuram disulfide (METHYL TUADS®)
TMTD	Tetramethylthiuram disulfide (METHYL TUADS®)
ZnDEC	Zinc diethyldithiocarbamate (ETHYL ZIMATE®)
ZMBT	Zinc salt of 2-mercaptobenzothiazole (ZETAX®)

A more reactive resin cure system, requiring no external activator, is obtained if some of the hydroxyl groups of the methylol group are replaced by bromine. A commonly used resin is Schenectady Chemical's SP-1055[®].



Figure 3: Rates of Cure and Reversion of Resin and Sulfur-Cured Butyl

## Antiozonants

Butyl polymers are inherently ozone resistant because of their low unsaturation. This natural resistance can be significantly reduced, however, by the effects of other compound ingredients. In compounds which have higher filler loading or are subjected to severe exposure, it is usually advantageous to incorporate an antiozonant. Either staining or nonstaining systems may be used. A nonstaining system which provides good resistance consists of 3.0 phr of microcrystalline wax (VANWAX[®] H) and 1.0 phr of either nickel dibutyl dithiocarbamate (VANOX[®] NDBC antioxidant/antiozonant) or nickel di-isobutyl dithiocarbamate (ISOBUTYL NICLATE[®] antioxidant/antiozonant). Another method of improving ozone resistance with a nonstaining ingredient is to substitute 15 to 25 parts of Vistanex[™] MML-120 polyisobutylene for 15 to 25 parts of butyl rubber in the compound. A staining system which gives excellent resistance in steam-curing rubber parts contains 0.5 to 2.0 phr of VANOX 6PPD antiozonant and 2 to 5 phr of VANWAX H.

### Processing

The chemically inert nature of butyl rubber is reflected in the lack of significant molecular weight breakdown during processing. This allows operations such as heat treatment or high-temperature mixing to alter the vulcanizate characteristics of a compound. Hot-mixing techniques promote pigment-polymer interaction in compounds containing carbon black. This heat treatment alters the shape of the stress-strain curve of the vulcanizate to reflect a more elastic network. Heat treatment has resulted in more flexible vulcanized compounds for a given level of carbon black. More flexible butyl rubber compositions have also been prepared with certain types of mineral fillers such as reinforcing clays, talcs and silicas that contain appropriately placed hydroxyl (-OH) groups in the lattice. This enhancement of pigment-polymer association has usually been accomplished by the addition of chemical conditioners such as VANAX PY.

Banbury mixing in conventional formulations does not require longer mixing

times than other natural and synthetic elastomers. There is, of course, no premasticating operation to produce a degree of molecular weight breakdown, as in the case of natural rubber, but pre-warming the butyl rubber prior to mixing reduces mixing times.

## **Properties and Applications**

The molecular characteristics of low levels of unsaturation between long polyisobutylene segments produce unique elastomeric qualities that find application in a wide variety of finished rubber articles. These special properties can be listed as (1) low rates of gas permeability, (2) thermal stability, (3) ozone and weathering resistance, (4) vibration damping and higher coefficients of friction, and (5) chemical and moisture resistance.

## Gas Permeability

The permeability of elastomeric films to the passage of gas is a function of the diffusion of gas molecules through the membrane, and the solubility of the gas in the elastomer. The polyisobutylene portion of the butyl molecule provides a low degree of permeability to gases, which leads to its preferred use in inner tubes. For example, the air permeability of SBR at 65°C is about 80% that of natural rubber, while butyl allows only 10% permeability on the same scale. The difference in air retention between a natural rubber and a butyl innertube can be demonstrated by data from controlled road tests on cars driven at 96 km/h (60 mph) for 161 km (100 miles) per day. Under these conditions (Table 5), butyl retained air at least 8 times better than did natural rubber. Other gases, such as helium, hydrogen, nitrogen, and carbon dioxide, are equally well retained by a butyl bladder membrane. This property of non-permeability is also important in air barriers for tubeless tires, air cushions, pneumatic springs, accumulator bags, air bellows and the like. A typical formulation for a passenger tire inner tube is given in Table 6.

Innertube	<u>Original Pressure</u> kPa (psi)	<u>Air Pr</u> 1 Week	<u>essure Loss</u> 2 Weeks	s <u>, kPa (psi)</u> 1 Month
Natural Rubber Butyl	193 (28) 193 (28)	27.6 (4.0) 3.4 (0.5)	55.0 (8.0) 6.9 (1.0)	114.0 (16.5) 13.8 (2.0)
	Table 6: Butyl Inne	ertube Forr	nulation	
Ingredients				phr
Exxon Butyl 268 N660 Carbon Blacl Paraffinic Process Zinc Oxide Sulfur METHYL TUADS ( CAPTAX (MBT)	k Oil TMTD)			100.0 70.0 25.0 5.0 2.0 1.0 0.5

Table 5:	Air Loss	of Innertubes	during	Driving	Tests

Total

203.5

Cure range: 5 min. @ 177°C (350°F), and 8 min. @ 166°C (330°F)

#### Thermal Stability

Butyl rubber sulfur vulcanizates tend to soften during prolonged exposure to elevated temperatures of 150 to 200°C. This deficiency is largely the result of the sulfur crosslink, coupled with low polymeric unsaturation, which allows no compensating oxidative (crosslinking) hardening. However, certain crosslinking systems, specifically the resin cure of butyl, provide vulcanized networks of outstanding heat resistance. This cure has found widespread use in the expandable bladders of automatic tire-curing presses.

Examples of tire-curing bladder formulations are given in Table 7. In compound 1, the Neoprene serves as a halogen-containing activator, while compound 2 uses a partially brominated resin that does not require an external source of halogen. Butyl rubber passenger tire-curing bladders have a life of 300-700 curing cycles at steam temperatures of 195°C or higher, at approximately 10 minutes per cycle. Other applications are conveyor belting for the handling of hot materials, and high temperature service hoses.

Ingradiants	1 (phr)	2 (phr)
ingreatents	(piii)	(piii)
Exxon Butyl 268	100.0	100.0
Neoprene GN	5.0	
N330 Carbon Black	50.0	50.0
Process Oil	5.0	5.0
Zinc Oxide	5.0	5.0
SP-1045 [®] Reactive Phenol Formaldehyde Resin	10.0	
SP-1005 Brominated Phenol Formaldehyde Resin		10.0
Totals	175.0	170.0

### Table 7: Tire-Curing Bladder Compounds

#### Ozone and Weathering Resistance

The low level of chemical unsaturation in the polymer chain produces an elastomer with greatly improved resistance to ozone when compared to polydiene rubbers. Exxon Butyl 065 has the lowest level of unsaturation, and provides high levels of ozone and weather resistance, which is also influenced by the type and concentration of vulcanizate crosslinks. Thus, Exxon Butyl 065 is preferred for electrical applications needing ozone resistance, and in rubber sheeting for roofs and water management systems. A typical butyl rubber sheeting compound is given in Table 8.

Butyl rubber is useful in high quality electrical insulation because of its ozone resistance and the moisture resistance of its essentially saturated hydrocarbon structure. A cable insulation formulation for use up to 50 kV employs the lowest unsaturated butyl and the p-Quinone dioxime (GMF) cure system, as shown in Table 9.

Table 8:	Butyl	Sheeting	Compound
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Ingredients	phr
Exxon Butyl 065	100.0
N330 Carbon Black	48.0
N774 Carbon Black	24.0
Zinc Oxide	5.0
VANFRE® M Process Aid	3.0
VANWAX H Special	4.0
Sulfur	1.0
ETHYL TELLURAC	0.5
CAPTAX (MBT)	0.5
METHYL ZIMATE®	1.5
Total	187.5

Table 9:	Cable	Insulation	Formu	lation

Ingredients	phr
Masterbatch mixed @ 149°C (300°F)	
Exxon Butyl 065	100.0
Zinc Oxide	5.0
Calcined Clay	100.0
Pb ₃ O ₄	5.0
VANWAX H Special	5.0
Low MW Polyethylene	5.0
N774 Carbon Black	10.0
Added as a separate, cooler mix	
ALTAX (MBTS)	4.0
p-Quinone dioxime	1.5
Total	235.5

### Vibration Damping

The viscoelastic properties of butyl rubber are a reflection of the molecular structure of the polyisobutylene chain. This molecular chain with two methyl side groups on every other chain carbon atom possesses greater delayed elastic response to deformation. The damping and absorption of shock have found wide application in automotive suspension bumpers. An elastomer with higher damping characteristics also restricts vibrational force transmission in the region of resonant frequencies.

In the region of resonance, where the impressed frequency of vibration is equal to the natural frequency of the system, the more highly damped butyl compositions more effectively control vibrational forces. These frequencies are in the region of vehicular body vibration and, as a result, butyl compositions are employed in the fabrication of automotive body mounts. In theory, more highly damped systems will less effectively isolate vibration at very high frequencies. However, in practice, dynamic stiffness becomes a controlling factor governing transmissibility. Transmissibility is the ratio of output force to input force under impressed oscillatory motion. This dynamic behavior can be greatly influenced by compounding variations, as well as by the size and shape of the molded part. For this reason, it is difficult to provide a typical butyl body mount compound, but the one shown in Table 10 can be considered representative of a 50 Shore A hardness vulcanizate.

The higher damping behavior of an elastomer can be associated with higher coefficients of friction between a rubber and a surface with a measurable degree of roughness or undulations. This property of butyl has the potential to improve the coefficient of friction of tire tread materials against a variety of road surfaces.

Ingredients	phr
Exxon Butyl 268	100.0
N330 Carbon Black	45.0
N990 Carbon Black	15.0
Paraffinic Oil	20.0
Zinc Oxide	5.0
ETHYL CADMATE [®] Accelerator	2.0
ALTAX (MBTS)	0.5
Sulfur	1.0
Total	188.5

## Table 10: Butyl Body Mount Compound

### Chemical and Moisture Resistance

The essentially saturated hydrocarbon property of butyl imparts moisture resistance to compounded articles. Moisture resistance is beneficial in applications such as electrical insulation and rubber sheeting for outdoor use. The saturated hydrocarbon property also provides useful solubility characteristics that are used in a variety of protective and sealant applications. The solubility characteristics can be expressed as a solubility parameter ( $\delta$ ) of 7.8 for butyl rubber. This value is similar to the solubility parameters of aliphatic and some cyclic hydrocarbons ( $\delta$  = 7 to 8), but very different from those of more polar oxygenated solvents, ester-type plasticizers, vegetable oils and synthetic hydraulic fluids ( $\delta$  = 8.5 to 11.0).

Thus, while butyl vulcanizates will be highly swollen by hydrocarbon solvents and oils, they are only slightly affected by oxygenated solvents and other polar liquids. This behavior is used in elastomeric seals for hydraulic systems using synthetic fluids, as Figure 4 demonstrates.

The low degree of olefinic unsaturation in the saturated hydrocarbon backbone also imparts mineral acid resistance to butyl rubber compositions. After 13 weeks of immersion in 70% sulfuric acid, a butyl compound experiences little loss in tensile strength or elongation. Under similar conditions, natural rubber or SBR will be highly degraded.



Figure 4: Swell of Vulcanizates in Phosphate Ester Fluids

## HALOGENATED BUTYL

Halogenated butyl or halobutyl is an isobutylene-isoprene copolymer containing reactive halogen. Both the chlorinated and brominated versions (commonly called chlorobutyl or bromobutyl) are commercially available.

Because halogenated butyls have the predominantly saturated polyisobutylene backbone, many of their properties are related to those of the parent butyl rubber: superior impermeability to the passage of air, gases and moisture, vibration damping, and resistance to aging and weathering.

The introduction of halogen, chlorine or bromine, into the butyl molecule allows new crosslinking chemistry and increased crosslinking activity. In particular, it provides the ability to covulcanize with, and adhere to, highly unsaturated general-purpose elastomers. The latter property is vital to halobutyl's major application in tubeless tire innerliners. Halogenated butyl contributes the required level of covulcanizability and adhesion to the high-unsaturation tire elastomer components necessary for the development of the radial tubeless tire with butyllike air retention.

Chlorobutyl and bromobutyl exhibit similar vulcanizate stability and, in many vulcanization systems, are superior to sulfur-vulcanized conventional butyl. The main differences between chlorobutyl and bromobutyl arise from the difference in the chemical reactivity of the two halogens. The lower C–Br bond energy predicts that bromobutyl should be more reactive than chlorobutyl, giving faster cures, more versatility in vulcanization and better covulcanization with general purpose rubbers. On the other hand, chlorobutyl generally gives longer scorch times and better storage stability in fully compounded stocks.

The major application of halobutyl is in tubeless tire innerliners; bromobutyl is generally used in 100% halobutyl truck tire inner liners; while chlorobutyl is used in blend innerliners for passenger tires. Tire sidewalls and heat resistant truck tire innertubes are also important applications for halobutyl, as is conveyor belting, mainly for high temperature conditions. Halobutyl's ability to be rapidly crosslinked with curative combinations results in very low extractable residues, making it an elastomer of choice for pharmaceutical closures. Other applications include chemically resistant tank linings and vibration control items.

#### Historical

Crawford, Morissey and co-workers at The B.F. Goodrich Company first reported the modification of butyl with small amounts of halogen.⁹⁻¹³ Goodrich commercialized a brominated butyl (Hycar[®] 2202) in 1954. The material produced by a bulk batch halogenation technique was withdrawn in 1969. ExxonMobil Chemical developed a practical and cost effective chlorination process and commenced commercial production of chlorobutyl in 1961.¹⁴⁻¹⁷ Bromobutyl was commercially introduced by Polysar Limited of Canada in 1971¹⁸ and by ExxonMobil Chemical Company in 1980.

### **Halobutyl Manufacturing Process**

Halobutyl is produced in hydrocarbon solution, commonly in hexane, using elemental chlorine or bromine at 40 to 60°C. A schematic flow plan of the halogenated butyl rubber process is given in Figure 5. The hydrochloric or hydrobromic acid generated by the halogenation substitution reaction is neutralized with dilute aqueous caustic. The halogenated cement is then stabilized against oxidative breakdown and dehydrohalogenation with antioxidant, calcium stearate and, in the case of bromobutyl, with epoxidized soybean oil. Commercial grades of halobutyl rubber are shown in Table 11.



Figure 5: Schematic Flow Plan of Halogenated Butyl Rubber Process

	Mooney Viscosity,	
Supplier Grade	ML 1+8 at 125°C	Halogen, wt. %
Exxon Chlorobutyl 1066	33-43	1.2-1.3
Exxon Chlorobutyl 1068	45-55	1.2-1.3
Lanxess Chlorobutyl 1240	34-42	1.2-1.3
Exxon Bromobutyl 2211	27-37	1.9-2.3
Exxon Bromobutyl 2222	27-37	1.8-2.2
Exxon Bromobutyl 2235	34-44	1.8-2.2
Exxon Bromobutyl 2244	41-51	1.9-2.3
Exxon Bromobutyl 2255	41-51	1.8-2.2
Lanxess Bromobutyl X2	42-50	1.6-2.0
Lanxess Bromobutyl 2030	28-36	1.6-2.0
Lanxess Bromobutyl 2040	35-43	1.6-2.0

Table 11: Commercial Grades of Halobutyl, Typical Inspections*

* Prior to 2008

All halobutyl grades contain nonstaining antioxidants at about 0.1 wt %. They also contain calcium stearate to protect the polymer from dehydrohalogenation. All bromobutyl grades contain epoxidized soybean oil to provide additional protection from dehydrohalogenation. Exxon Bromobutyl 2211, 2235 and 2244 are fast curing grades.

## Halobutyl Rubber Structure

The reaction of a solution of butyl in hexane with elemental halogen in the dark at conventional process temperatures (~50°C) is an ionic substitution reaction taking place at the isoprenoid unit, proceeding by the well-established chloronium (or bromonium) ion mechanism. This leads to a double bond shift and the formation of an exomethylene alkyl halide, the halogen being of the secondary allylic type^{15,19}, as shown below in the Type II structure for bromobutyl.

In the case of *bromobutyl*, analysis by nuclear magnetic resonance (NMR) indicates that up to 80% of the resulting brominated units exist as the exomethylene allylic bromide isomer (Type II). Other allylic bromide structures make up most of the remaining species, and very little, if any, of the original butyl rubber unsaturation is lost.^{20,21} The most important minor isomer is the bromomethyl allylic isomer (Type III). The Type III structure is formed under specifically defined high temperature conditions or by isomerization of the Type II structure. It has been shown that the two brominated isoprenoid isomers (Types II and III) have distinct vulcanization behavior. For example, the Type III structure has higher activity than the Type II structure in zinc oxide based cures, but is inactive in free radical type crosslinking.²²



Type II

Type III

*Chlorobutyl*, by NMR analysis, shows similar or higher percentage levels of the predominant exomethylene allylic halogenated structure (Type II) compared to bromobutyl. Isomerization to Type III is very slow in this case and requires catalysis. The *allylic* character of the halogen atom present in the polymeric chain of chloro- and bromobutyl explains the unique cure system activity of halobutyl.

### **Compounding Halobutyl**

As with most elastomer systems, the final properties of a vulcanized halobutyl compound depend upon the nature and degree of crosslinking, as affected by curatives, and the type and concentration of the other compounding ingredients. The latter include fillers (carbon black and mineral fillers), plasticizers, processing aids, tackifiers, and antidegradant agents.

*Carbon Black* - The response of halobutyl to carbon blacks is generally similar to that of butyl and most other synthetic elastomers. A good balance of compound mixing and processing, reinforcement and physical properties is obtained, for example, with N660 carbon black at a loading of 50 to 70 phr. Cured modulus increases with the level of carbon black level up to 80 phr. Tensile strength goes through a maximum at a carbon black level of 50 to 60 phr.

*Mineral Fillers* - Common mineral fillers may be used with halobutyl, but since they vary significantly both in particle size and chemical composition, they have the potential to alter vulcanization characteristics. As a general rule, highly alkaline fillers such as calcium silicate, and hygroscopic fillers, can strongly retard halobutyl cure.

Acidic clays give very fast cures, so that additional amounts of scorch retarders, such as magnesium oxide, may be needed. Hydrated silicas should be used at moderate levels since they promote compound stiffness and strongly affect cure rates because of their tendency to absorb curatives. Talc is semi-reinforcing in halobutyl, without a major effect on cure. Calcium carbonates (whiting) give relatively little reinforcement, but yield good elongation after heat-aging. Calcium carbonates coated with calcium stearate are strongly retarding.

A combination of two or three mineral fillers can lead to a balance of properties and cure rate effects. Figure 6 presents a contour graph for combinations of fumed silica, platy talc (VANTALC[®] 6H) and calcined clay at a constant 60 phr loading. The contour shows that:

- hot tear and hardness increase with silica level,
- clay and talc have about the same effect on the 3 parameters measured, and
- optimum compression set is achieved with lower levels of silica.



Figure 6: Mineral Filler Effects in Bromobutyl

*Silanes* - One way to enhance the interaction between the polymer and silicates, and improve compound properties, is to add small (0.5 to 1.0 phr) amounts of organofunctional silanes. Particularly useful silanes are the mercapto- and amino-derivatives.

*Plasticizers* - Aliphatic and naphthenic mineral oils are preferred plasticizers because their solubility parameters ensure improved solvation. Other useful plasticizers are paraffin waxes and low molecular weight polyethylenes. Adipates and sebacates can be used to improve flex at extremely low temperatures.

*Processing Aids* - Struktol[®] 40 MS and/or Promix[®] 400 function as part of the plasticizer system and, more importantly, enhance cured adhesion to high unsaturation rubber substrates. Materials such as mineral rubber or asphaltic pitch also seem to have this effect.

*Tackifiers* - Hydrocarbon resins such as Escorez[™] 1102 at 4 to 8 phr are used as tackifiers. While they are less effective tackifiers than the phenolic types, they are also less likely to reduce compound scorch safety and are less expensive.

Halobutyl generally does not require the addition of antioxidants or antiozonants, apart from the phenolic type antioxidant added during polymer manufacturing. Amine-type antidegradants such as mercaptotoluimidazole and especially p-phenylenediamines will react with the halogen and affect crosslinking. They should therefore not be added to the masterbatches.

### Vulcanization

The presence of the allylic halogen atom in halobutyl allows a great variety of vulcanization techniques. Zinc oxide, preferably with some stearic acid, can act as the sole curing agent for halobutyl. One proposed mechanism is based on the formation of stable carbon-carbon crosslinks through a cationic polymerization route, catalyzed by zinc chloride or zinc bromide. The necessary initiating amounts of zinc halide are likely formed by the thermal dissociation of some of the allylic halide to hydrogen halide. The hydrogen halide then reacts with the zinc oxide.²³

Both the state of cure and the cure rate obtained with the zinc oxide system can be improved by including other ingredients, of which the following are the most pertinent examples:

- Thiurams and Dithiocarbamates These cure systems produce very stable networks with low compression sets.
- *Polymethylol Phenol Resins* These and their halogenated derivatives are very effective at 1 to 2.5 phr of resin. No halogen-donating catalyst is necessary, in contrast to the use of these resins in regular butyl.
- Alkylphenol Disulfides These are particularly effective in providing high quality vulcanizates in blends of chlorobutyl with high unsaturation rubbers. With bromobutyl, however, these cures tend to be scorchy, even when typical bromobutyl retarders are employed.
- Alkoxyalklthioxy Thiadiazole VANAX 189 provides high hardness and modulus with low compression set and excellent heat aging.

When applying zinc oxide-based cure systems to halobutyl, certain key principles must be considered. Many compounding ingredients alter scorch and cure rate in these cures, in particular acidic and alkaline ingredients. In general, acids will accelerate, and bases will retard, the rate of cure. This is exactly the opposite of their effect in sulfur cures of non-halogenated unsaturated rubbers.

Water is a strong retarder because it complexes with the reactive intermediates. The acidity, basicity and moisture content of all compounding ingredients should therefore be considered.

Scorch Control - The most commonly used scorch improver for halobutyl vulcanization is magnesium oxide. Calcium oxide, magnesium and calcium stearates and other alkaline salts of fatty acids also function as scorch retarders. By the addition of polyethylene glycols or epoxidized oils, it is possible to increase scorch with a reduced effect on cure rate. Other ways to increase scorch times are to reduce the stearic acid and/or sulfur level, or to raise the benzothiazyl disulfide (MBTS) content.

# **Bromobutyl Curing**

Bromobutyl is generally faster curing than chlorobutyl, and moreover, it also shows more versatility in vulcanization. In other words, some cure systems can be used with bromobutyl, which are less active, or in some cases even inactive, with chlorobutyl.

- Bromobutyl can easily be cured without zinc oxide or other zinc-containing accelerators, through the use of amines. A good example is hexamethylene diamine carbonate.
- Bromobutyl can be vulcanized by the sole use of sulfur in the absence of zinc oxide or other curatives. This type of vulcanization appears to be free radical in nature, since it is retarded by phenolic-type antioxidants.
- · Low temperature cures are easier to effect with bromobutyl.
- Peroxide cures, preferably in the presence of a suitable co-agent, are possible with bromobutyl.

A summary of the most common halobutyl cure systems is given in Table 12. A summary of the effect of various compounding ingredients on bromobutyl cure parameters is given in Table 13.

System	Curatives	phr	Cure Rate	Scorch Safety	Characteristics	Applications
Zinc Oxide Stearic Acid	ZnO Stearic acid	3-5 1	Moderate	Very good	Non-toxic. Sensitive to compounding. Good heat resistance.	Pharmaceutical. Food contact.
Dithio- carbamate	ZnO Stearic acid ZnDEC MgO	3 1 1.5 0.5	Very Fast	Fair	Low compression set. Heat- resistant.	Mechanical goods. Injection molding.
Thiram & Thiazole	ZnO Stearic acid MBTS TMTD	3 1 2 1	Fast	Good	Heat-resistant.	Truck innertubes. Conveyor belts.
Sulfur & Thiazole	ZnO Stearic acid Sulfur MBTS TMTD	3 1 0.5 1.5 0.25	Moderate	Very good	Covulcanization with highly unsaturated rubbers.	Tire innerliners.
Dithio- thiadiazole	ZnO VANAX 189	3 2.5	Very Fast	Very good	Low compression set. Heat- resistant.	Mechanical goods. Injection molding.
Resin	ZnO Stearic acid SP-1045	3 1 2	Fast	Good	Sulfur-free.	Pharmaceutical closures.
Phenol disulfide (Chlorobutyl)	ZnO Stearic acid Vultac [®] 5 MBTS MgO	5 1 1.5 1 0.25	Fast	Mod.	Chlorobutyl blends with NR, and blends with GPRs.	Chlorobutyl innerliners. Sidewalls.
Room Temp.	ZnO SnCl ₂ ZnCl ₂	5 2 2	Very Fast	Scorchy	Premix curatives in Vistanex.	Room Temperature cured sheet.
Peroxide	VAROX [®] DCP Stearic acid VANAX MBM	2 1 1	Moderate	Fair	High heat resistance.	Hot air and steam-resistant compounds.
Zinc Free (Bromobutyl)	MgO Diak [™] No.1	3 1	Fast	Scorchy	Low compression set.	Special pharmaceutical closures.

# Table 12: Halobutyl Cure System Summary

Effect of increased amount of	Scorch time (t _s 3 @135°C)	Rheometer cure rate (1 / t' 90)	Rheometer modulus (M _H )
MgO	+	-	+
Carbowax [®] 3350	+	0	0
Sulfur	-	0	+
ALTAX (MBTS)	+	0	0
METHYL TUADS (TMTD)	-	+	+
Phenolic Resin	-	0	0
Hydrocarbon Resin	0	0	-
Stearic Acid	-	+	-
Amine Antioxidants	-	+	+

Table 13: Effect of Compounding Ingredient Levels on Bromobutyl Cure

### **Processing Halobutyl**

The following processing conditions are recommended for both chloro- and bromobutyl.

*Mixing* - Internal mixing is done in two stages. The first stage contains all the ingredients except for zinc oxide and accelerators. The batch weight should be 10-20% higher than that used for a comparable compound based on general purpose rubbers.

The following is a typical internal mixing cycle for a halobutyl innerliner compound:

First stage:	0 min: Halobutyl, carbon black, retarder. 1.5 min: Process aids, plasticizers, fillers, stearic acid. 3.5 min: Dump at 120 to 140°C. (Higher dump temperatures could result in scorching.)
Second stage:	0 min: Masterbatch plus curatives 2.0 min: Dump at 100°C.

Mill mixing on a two roll mill is best accomplished with a roll speed ratio of 1.25 to 1, and roll temperatures of  $40^{\circ}$ C on the slow roll and  $55^{\circ}$ C on the fast roll.

The following sequence of addition is recommended: (1) part of the rubber together with a small amount of a previous mix as a seed; (2) retarder plus one quarter of the filler; (3) remainder of polymer; (4) rest of filler in small increments; (5) plasticizers at the end; (6) acceleration system below 100°C.

*Calendering* - Feed preparation can be done either by mill or by extruder. Halobutyl compound follows the cooler roll, therefore a temperature differential of 10°C between calender rolls is recommended. Starting roll temperatures should be:

Cool roll: 75 to 80°C Warm roll: 85 to 90°C Normal calendering speeds for halobutyl compounds are between 25 to 30 meters/minute. Rapid cooling of the calendered sheet is beneficial for optimal processability (handling) and maximum tack retention.

*Extrusion* - The feed temperature should be 75 to 80°C, while the temperature of the extrudate should be around 100°C. The major problem during the calendering and extrusion of halobutyl compounds is blister formation. The cause of this phenomenon is the low permeability of these polymers, which tend to retain entrapped air or moisture. Preventive action should be taken at all stages of the process, by:

- · ensuring that the stock is well mixed in a full mixer to prevent porosity,
- · avoiding moisture at all stages, and
- · keeping all rolling banks on mills and calender nips to a minimum.

*Molding* - Halobutyl can be formulated to have a fast cure rate, and good mold flow and mold release characteristics. It can therefore be molded into highly intricate designs using conventional molding equipment. Entrapped air can be removed by bumping the press during the early part of the molding cycle.

Halobutyl is also very well-suited for injection molding because of its easy flow and fast, revision-resistant cure. The low molecular weight polymer grades are required for optimum flow and good scorch safety.

## **Properties and Applications**

Chlorobutyl and bromobutyl have proven to be highly useful in many commercial rubber products that benefit from the characteristics inherent in butyl polymers, such as low gas permeability and resistance to environmental attack. In addition, halobutyl offers the advantages of cure versatility, highly heat-stable crosslinks, and the ability to vulcanize in blends with highly unsaturated elastomers. Tire applications for halobutyl are innerliners for tubeless tires, black sidewall, white sidewall and sidewall coverstrip.

### **Tire Component Applications**

Innerliners for Tubeless Tires - The combination of low permeability to gas and moisture vapor (Table 14), high heat resistance, excellent flex resistance, and the ability to covulcanize with high unsaturation rubbers, make halobutyl particularly attractive for use in innerliners for tubeless tires, especially in steelbelted radial tires.^{24,25} The function of the tire innerliner is to provide an effective air barrier and to minimize intracarcass pressure (Figure 7). The latter is a result of the migration of air from the tire cavity into the cord area of the tire and the damming effect of the sidewall and tread exterior.

			_
Polymer	Air	Moisture	
100% NR	8.3	13.3	
100% SBR	6.8	11.0	
60% Chlorobutyl	3.1	3.0	
60% Bromobutyl	3.1	3.0	
100% Chlorobutyl	1.0	1.0	
100% Bromobutyl	1.0	1.0	

Table 14: Relative Air and Water Vapor Permeation Rates at 65°C in aTypical Innerliner Formulation



Figure 7: Intracarcass Pressure Buildup

The reduction of air (and oxygen) in the carcass, provided by using low permeability innerliners based on halobutyl, serves to lessen oxidative degradation of the tire fabric and the carcass/belt rubbers. Intracarcass pressure and oxidation can weaken the body of the tire and cause tire failures through flex fatigue or the loss of adhesion between components. For almost forty years, halobutyl innerliners have enhanced the durability of tubeless tires for passenger cars and commercial vehicles. Chlorobutyl continues to be used for light duty and economy innerliners (often 60-80% chlorobutyl blended with natural rubber) for passenger tires. Examples of chlorobutyl innerliner formulations and their properties are given in Table 15.

Because of its better adhesion to high unsaturation rubbers, bromobutyl finds a major use in 100% halobutyl innerliner formulations for all-steel belted truck tires. The latter require the highest quality because of their severe service conditions. A typical starting point for a bromobutyl innerliner formula is presented in Table 16.

Ingredients	phr	phr	phr
Exxon Chlorobutyl 1066	100.00	80.0	60.00
Natural Rubber		20.0	25.00
SBR 1778			20.60
N660 Carbon Black	60.00	55.0	
N330 Carbon Black			40.00
Omya [®] Whiting			40.00
Phenol Formaldehyde Resin	4.00	8.0	4.00
Struktol 40 MS	7.00	10.0	
Naphthenic Oil	8.00		10.00
Stearic Acid	2.00	2.0	1.00
Magnesium Oxide	0.15		0.50
Zinc Oxide	3.00	3.0	3.00
Sulfur	0.50	0.5	
ALTAX (MBTS)	1.50	1.5	1.00
Vultac 5			1.30
METHYL TUADS (TMTD)			0.25
Totals	186.15	180.0	206.65
Mooney Viscosity, M _L 1+4 @ 100°C	43	52	54
Mooney Scorch			
Minutes to 3 pt. rise @ 135°C	12	12	—
Minutes to 5 pt. rise @ 121°C	_	_	15
Original Physicals, and After Aging in Air 72	hrs. @ 125°C	;	
Press Cure Time, Minutes @160°C	25	25	20
Hardness, Shore A	55/74	63/76	55
300% Modulus, MPa	3.2/8.3	3.6/6.8	5.2
Tensile Strength, MPa	8.1/8.6	10.8/8.7	11.1
Elongation, %	860/330	850/510	520
Tear, Die C, kin/m @100°C	21	25	20
Air Permeability @ 66°C, Q x 10³	3.0	6.0	8.2
Static Peel Adhesion @ 100°C (to General F	Purpose Rubb	er)	
kN/m	4.4 I*	15.0 S/I*	—
Monsanto Fatigue-to-Failure Flex Test			
Extension, %	140	140	100
Kilocycles to Failure	415	434	236

Table 15: Typical Chlorobutyl Innerliner Formulas

* I denotes interfacial separation; S denotes stock tearing

Ingredients	phr
Exxon Bromobutyl 2255	100.0
N660 Carbon Black	50.0
Flexon [®] 876 Paraffinic Oil	8.0
Stearic Acid	2.0
Maglite D	0.5
	7.0
ZIIU Sulfur	3.U 0.5
ALTAX (MRTS)	0.5
Total	172.5
Moonov Viscosity M 1,8 @ 100°C	65
Mooney Viscosity, ML 1+6 @ 100 C	05
Mioutes to 5 pt rise	22
ODP Rheamater @ 150°C	~~
M./M. (dN·m)	2/5
ť 90 (min)	37
Monsanto Tal Tak kPa (20 s. 16az.)	
• to self	240
to 100% NR carcass	125
<ul> <li>to 50/50 NR/SBR carcass</li> </ul>	80
to 25/75 NR/BR chafer	85
Green Strength, MPa x 10 ⁻²	27
Decay Time to 50% of Initial Stress, seconds	32
Original Physicals Properties (Press Cured t 90 @ 150°C) / After Aging in Air 72 hrs	s. @ 125℃)
Hardness, Shore A	44 / 48
100% Modulus, MPa	1.1/1.5
300% Modulus, MPa	3.7/4.8
Flongation %	756 / 687
Tear, Die C, kN/m	40 / 36
Monsanto Fatique-to-Failure Flex Text.	
K cycles, 140% Extension, Mean (Range)	40 (25-55)
Static Peel Adhesion (to 100% NR carcass)	
kN/m (*=Separation with stock tearing)	35*
Permeability to Air @ 65°C	
cm ³ •cm•cm ⁻² •s ⁻¹ •atm ⁻¹ •10 ⁻⁸	3.0
Water Vapor Permeability @ 65°C	
g•cm•cm ⁻² •h ⁻¹ •atm ⁻¹ •10 ⁻⁶	2.5

Table 16: Typical Bromobutyl Innerliner Compound

# **Tire Sidewall Components**

Halobutyls have been used commercially in combination with general purpose tire elastomers in tire sidewall components, specifically white sidewall and cover strip compositions, to provide improved aging and flex resistance without the use of discoloring additives such as the p-phenylenediamine antidegradants.

The substitution of halobutyl, either alone or in combination with an ethylenepropylene terpolymer, for a portion of the high unsaturation polymers commonly used in tire sidewalls, offers a simple and economical means to upgrade the weathering (particularly ozone resistance) and flex resistance of tire sidewall components. These polymer combinations are extensively used in white sidewall compounds, adjacent components and cover strips, as well as in corresponding black sidewall cover strips.

Polymer	Black Sidewalls	White Sidewalls
Chlorobutyl or Bromobutyl	45	60
Vistalon [™] 6505 (EPDM)	10	20
SMR 5 (Natural Rubber)	45	20

Table 17: Starting Point Polymer Blend Compositions for Tire Sidewalls

Properly formulated halobutyl compounds based on these polymer blends exhibit excellent dynamic ozone resistance. Black-filled stocks have exceeded 900 hours in 100 pphm ozone while flexing 0 to 25% at 30 cpm without cracking. In this test, general purpose rubber compounds protected with p-phenylene diamines start to crack in less than 48 hours.

# **Heat Resistant Truck Innertubes**

Chlorobutyl offers improved resistance to heat softening as well as butyl's desirable property of excellent air retention in innertubes. This is particularly important for severe service conditions, where heavy loads or high speeds frequently cause tire service temperatures to exceed 140°C. Ordinary butyl innertubes soften and fail at these temperatures. Chlorobutyl innertubes retain a significant portion of their original properties, as shown in Figure 8. A typical formulation is shown in Table 18.



Figure 8: Chlorobutyl Truck Innertube Performance

Ingredients		phr
Exxon Chlorobutyl 1068		100.0
N660 Carbon Black		70.0
Paraffinic Oil		25.0
Stearic Acid		1.0
Zinc Oxide		5.0
METHYL TUADS (TMTD)		0.2
Maglite D [®] Magnesium Oxide		0.1
(Cure 15 Minutes at 177°C)	Total	201.3

Table 18: Typical Truck Innertube Formulation

(Cure 15 Minutes at 177°C)

#### **Non-tire Applications**

### Pharmaceutical Closures

Halobutyls are extensively used in pharmaceutical closures because of their inherent properties: low permeability to gases and moisture vapor, chemical and biological inertness, low extractables due to cure versatility, resistance to heat, UV and ozone, and adequate self-sealing and low fragmentation during needle penetration.

Halobutyl can be cured with sulfurless cure systems, resulting in very low extractables. A typical cure system is based on zinc oxide combined with 1.5-2.5 phr reactive phenol formaldehyde resin. Bromobutyl has the added advantage of being vulcanizable without zinc, which is useful for some special types of closures.

Calcined clay is the preferred filler, but it can be partially replaced by talc, whiting or carbon black. For improved hot tear resistance, silica can be added. but only in low amounts, since it has a hardening and a cure-retarding effect. All the ingredients should be of the purest grade possible.

Phenolic Resin Cured Chlorobutyl		Sulfurless, Zinc-free Bromobutyl	
Exxon Chlorobutyl 1066	100.00	Exxon Bromobutyl 2211	100.0
Maglite D (MgO)	0.25		
Calcined Clay	90.00	Calcined Clay	60.0
A-C 617 A Polyethylene	5.00	VANTALC R Talc	40.0
Stearic Acid	1.00	Dynamar [®] PPA 790	0.4
Zinc Oxide	3.00	SULFADS [®] Accelerator	2.0
SP-1045	2.00	Maglite D	1.0
Total	201.25	Total	203.4

Table 19:	Formulations	for	<b>Pharmaceutical</b>	Stop	pers
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These compounds, when cured for 10 minutes at 170°C, give a Shore A hardness of approximately 45, with a compression set of less than 30% (22 hours at 70°C), and comply with the extraction specifications of the various pharmacopoeia, e.g., the German DIN 58367.

### Heat-resistant Conveyor Belts

Several types of rubber polymers are used for heat-resistant conveyor belt cover and skim compounds. Bromobutyl provides a good compromise between heat resistance and adhesion to textile.

Ingredients	phr
Exxon Bromobutyl 2244	100.0
N550 Carbon Black	45.0
Maglite D Magnesium Oxide	1.0
Carbowax 3350	1.5
Stearic Acid	1.0
VANOX MTI Antioxidant	1.0
Zinc Oxide	3.0
VAROX DCP-40C	2.0
VANAX MBM Coagent	1.0
Total	155.5
Press Cured 35 min. @ 160°C	
Original Physicals / and After Aging in Air 168 hrs. @ 150°C	
Hardness, Shore A	59 / 64
Tensile, MPa	11.2 / 9.1
Elongation, %	250 / 200

able 20:	Heat Resistant Conve	yor Belt Formulation

## Chemical-Resistant Tank Lining Compounds

The inherent resistance of butyl-type elastomers in contact with normal concentrations of acids and bases is reinforced with the cure versatility of halobutyl. Compositions are available, usually with barium sulfate as a filler for acid resistance, which can be cured either with hot water in 1 to 2 days, or at room temperature. Commercially available adhesive systems are used for adhesion to metal.

### Other Applications

Hose (steam and automotive), gaskets, ball bladders, adhesives and sealants, tire-curing bags, engine mounts, rail pads, bridge-bearing pads, curable contact cements for rubber-to-rubber adhesion and sealant tapes are some of the other applications for halobutyl rubbers.

# POLYISOBUTYLENE

Polyisobutylene is an amorphous polymer, composed of long straight chain molecules having terminal unsaturation only. The high molecular weight polyisobutylenes are capable of strain crystallization when extended. The crystallites have a helical conformation with a repeating length of eight monomer units. Due to the absence of any comonomers, the high molecular weight polyisobutylenes are the only isobutylene-based polymers capable of strain crystallization. The polyisobutylenes have a glass transition temperature of about  $-70^{\circ}$ C.

Commercially available polyisobutylenes are divided into two groups according to molecular weight ranges. The low molecular weight grades are clear, very viscous, tacky semi-solids. The molecular weight range for these polymers is 35,000 to 46,000 viscosity average molecular weight (Flory). The higher molecular weight grades are tough rubbery solids ranging in molecular weight from 900,000 to 5,000,000. They generally have the narrowest MWD of the isobutylene-based elastomers, with  $M_w$  /  $M_n$  slightly above 2.0.

The high molecular weight polyisobutylenes are produced in a process similar to that of butyl rubber. The lower molecular weight polymers are produced in a modified hydrocarbon solution process at a higher temperature, using a similar catalyst system. The major producers of the polyisobutylenes were ExxonMobil Chemical Company, under the trade name Vistanex (BASF acquired this product line in 2003), and BASF Company (under the trade name Oppanol[®]). Worldwide consumption is approximately 20 ktons/year.

The polyisobutylene polymers cannot be vulcanized because they are paraffinic homopolymers with only terminal unsaturation. They are generally inert, resistant to acids, alkalis, oxygen and ozone. They are, in fact, often added to other polymers to improve their resistance to chemical attack. Their permeability resistance to moisture and gases is similar to that of butyl rubbers. Commercial applications of the polyisobutylene polymers include:

- · Impact-strength blending with olefin plastics
- · Adhesives, caulks and sealants
- · Uncured sheeting, i.e. roofing membranes
- · Pipe wrap and electrical tape
- · Wax modifiers
- · Chewing gum base
- · Fluids modification and drag reducers
- · Lube oil modifiers

# STAR-BRANCHED BUTYLS

A new butyl polymer concept was introduced by ExxonMobil Chemical Company in 1989. It altered molecular topology to achieve a unique and different response to the processing of butyl and halobutyls.^{28,29} A broadening of molecular weight distribution was achieved through the use of branching agents in the polymerization to create a bimodal molecular weight distribution. One mode consists of normal linear chains, as previously described. The second mode consists of branches of normal chains connected through a polymeric branching agent added to the polymerization, as illustrated in Figure 9. The amount of branching agent is selected to give the optimal balance of processability and physical properties, i.e., about 87% of the weight is in the normal chains and about 13% is in the star polymer. The new concept was labeled "Star-Branched Butyls" (SBB and HSBB for the halobutyls).



Figure 9: Star-Branched Butyl (SBB)

Star-branched butyl rubbers exhibit a different balance of viscoelastic properties, resulting in improved processability along with higher green strength and faster stress relaxation. For example, a conventional 34 Mooney bromobutyl polymer has a green strength (100% modulus) of about 350 kPa. Increasing the Mooney viscosity to 49 increases green strength to about 425 kPa, but the relaxation time (t 75) increases from about 2¼ sec.⁻¹ to about 5½ sec.⁻¹. A 39 Mooney viscosity star-branched bromobutyl polymer has a green strength of 450 kPa with a relaxation time just over 2 sec.⁻¹. That is, the bromo-star-branched polymer compound has the green strength of the high Mooney conventional grade, but the stress-relaxation time of the low Mooney conventional grade.

The star-branched butyl compounds also exhibit lower running die-swell at various shear rates than do conventional butyl grades. At a shear rate of 40 sec.⁻¹, conventional butyl innertube compounds exhibit a die-swell ~15%; star-branched butyls, less than 10%. At 1,000 sec.⁻¹, the die swell of the regular polymers increases to 25 to 30%, compared to ~15% for the star-branched counterpart.

Compounding and vulcanization of the star-branched butyls are generally similar to that of regular butyls and halobutyls. Physical properties after curing depend on the crosslink density, which may be higher in the star-branched butyls at equivalent levels of unsaturation compared to the standard butyl and halobutyl grades. The star-branched butyl polymers have the following attributes:

- Higher green strength for improved handling and less cold flow.
- Faster stress-relaxation for better shaping tolerances, improved splicing and reduced shrinkage.
- Increased shear-thinning for faster extrusion rates, improved mixing quality and shorter mix cycles.
- Lower capillary die-swell for better extrudate/calender surface quality, less shrinkage of extrudate/calendered products for better dimensional stability.

In summary, the star-branched butyls provide improved processing over the conventional butyl and halobutyls, while preserving the desirable butyl properties.

## BROMINATED ISOBUTYLENE/p-METHYLSTYRENE ELASTOMERS (BIMSM)

A new class of isobutylene-based elastomers, brominated copolymers of isobutylene with p-methylstyrene, was developed by ExxonMobil Chemical Company.³⁰⁻³² These brominated copolymers have been prepared over a broad range of monomer ratios, bromine content and molecular weights. The products are commercially available from ExxonMobil Chemical Company under the trade name Exxpro[™] Elastomers. Bromination is directed to the para-methyl group of the styrenic comonomer in the copolymer, providing a reactive benzylic bromide functionality which is key to this elastomer's vulcanization and modification versatility.

The BIMSM elastomers have a saturated backbone providing complete ozone and oxidation resistance, while the benzylic bromide functionality provides increased latitude for vulcanization and covulcanization with the high unsaturated general purpose elastomers. This new family of elastomers preserves the basic properties of butyl and halobutyl, and offers ozone and heat resistance comparable to EPDM.

### BIMSM Manufacture

The polymerization of isobutylene with p-methylstyrene (PMS) is conducted in methyl chloride at  $-100^{\circ}$ C using a Lewis acid catalyst, i.e. AlCl₃ or alkyl aluminum halides. The resultant hydrocarbon polymer is then brominated in solution at the benzylic position. Polymer recovery after neutralization is similar to that of the halobutyls, in which small amounts of calcium stearate stabilizer are added prior to solvent removal with steam and water in a flash drum. The polymer is separated from slurry, extruder-dried and baled to give the commercial bromo-(isobutylene-co-para-methylstyrene) elastomers denoted as BIMSM by the IISRP.

Commercial products contain about 2.5 to 7 mole percent of PMS. The glass transition temperatures of the BIMSM polymers change very little at PMS concentrations of <15 weight % PMS. Above 20% PMS, the glass transition increases from -60 to +110°C in a nearly linear fashion. ¹³C NMR studies have shown that the PMS preferentially polymerizes with itself. A polymer with IB:PMS ratio of 37 was found to have about half of the PMS as individual mers flanked by isobutylenes -BSB-, and about half as diads -BSSB-.³³ The molecular weights of the copolymers are similar to those given for the butyl rubbers. Their molecular weight distributions, however, are typically narrower, in the range of 2.2 to 3.5.

All the commercially available BIMSM grades contain 5 to 12% of PMS and 0.5 to 1.2 mole % of benzylic bromide. As shown below, not all of the PMS is brominated. The ratio of PMS to bromo-methyl groups to total PMS in the polymer is variable in different grades.



### **Properties**

The fully saturated, predominantly polyisobutylene structure and high molecular weight of the BIMSM elastomers provide high physical strength, excellent resistance to gas and moisture permeability, chemical inertness, good vibration damping and excellent resistance to heat and atmospheric aging. Besides these properties, BIMSM elastomers also provide:

- Enhanced cure activity by virtue of their reactive benzylic bromide functionality. Even though halogen levels may be lower than the halobutyls, cure activity is as good as, or better than, the halobutyls.
- · Covulcanizability with high unsaturation general purpose rubbers.
- Facile functional modification through the benzyl bromide site to introduce other functional groups such as dithiocarbamates, acrylate, carboxy and hydroxy derivatives. In addition, polymers with functional end groups can be grafted onto the benzyl bromide polymer site.

Because of the BIMSM polymer's excellent chemical resistance, oxidative and thermal degradation is extremely slow. An example is high temperature mixing tests conducted at 180°C. Degradation of a butyl polymer occurs after 60 minutes, and crosslinking of halobutyl polymers after 10 to 25 minutes. BIMSM polymer showed little or no degradation or crosslinking, even after 120 minutes at 180°C. The cure response of BIMSM after this heat aging was relatively unchanged. Like other isobutylene based polymers, BIMSM polymers are soluble in nonpolar liquids. They are readily soluble in alkanes and cycloalkanes, less so in benzene, and are insoluble in methyl ethyl ketone.

After heat aging, BIMSM vulcanizates exhibit better retention of tensile strength, elongation, tear strength and flex than do halobutyls. Compared to the EPDM peroxide cured systems, BIMSM vulcanizates give essentially equivalent tensile strength, significantly better elongation retention, and improved resistance to compression set. The BIMSM elastomer's saturated backbone, together with its stable carbon to carbon crosslinking, provides these exceptional heat aging characteristics. Light-colored BIMSM compounds have been shown to be less sensitive to UV attack than other isobutylene polymers by virtue of the p-methylstyrene comonomer in the molecular chain.

### **BIMSM** Compounding

The response of BIMSM elastomer compounds to filler and plasticizer is very similar to that of other isobutylene based elastomers, particularly the halobutyls.

Special attention should be given to mineral-filled BIMSM compounds. In general, the acidic or basic nature of the mineral filler has less influence on the cure of BIMSM compounds than on that of halobutyl compounds. Silica fillers, however, tend to be very retarding, as they are in halobutyls.

Tackifier resins (used at 2 to 4 phr), such as the non-heat reactive phenolformaldehyde types, are the most effective in BIMSM compounds. Hydrocarbon resins are also useful in enhancing tack. Generally, higher concentrations are necessary, since they are less effective than the phenolic types. The major advantage of the hydrocarbon resins is that they are less discoloring in mineralfilled light colored compounds.

Stearic acid is commonly used as a processing aid and release agent in rubber compounding. In BIMSM elastomer systems, however, stearic acid and zinc stearate affect the cure. The alkaline-earth metal stearates that are often used as release agents in rubber compounding will also have a drastic retarding effect on cure response.

Processing aids such as Struktol 40 MS and Promix 400 are especially helpful in BIMSM compounding and processing, as previously discussed in the section on halobutyl.

The mixing of BIMSM compounds in internal mixers and on mills is very similar to that of halobutyls. Again, special consideration should be given to the ZnO and zinc stearate additions during the mix cycle, since they are curatives. They should not be added in the first stage of the mix cycle, but rather added with other curatives, generally at a lower mix temperature, in the second pass. Extrusion, calendering and molding operations are similar to the halobutyls.

# Vulcanization

BIMSM elastomers have been shown to vulcanize via electrophilic addition of the benzylic bromide to the styrene comonomer in the polymer chain.³⁴⁻³⁷ The zinc salts catalyze the crosslinking reaction to form carbon to carbon bonds. BIMSM can also be crosslinked via nucleophilic substitution reactions with bifunctional organic compounds (i.e. Diak No. 4). The Lewis acid salt of the benzylic bromide can undergo subsequent alkylation reactions with olefinic groups, leading to covulcanization with general purpose rubbers.

The benzylic bromide concentration strongly affects network density (cure state). Times to optimum cure are dependent on the benzylic bromide concentration and the specific curative combination employed. The temperature coefficient of vulcanization for carbon black filled compounds is about 1.6 per 10°C.

Several sulfur containing accelerators common to halobutyl vulcanizations systems are equally effective in combinations with the zinc oxide/stearic acid system of BIMSM. The following combinations have been tested with corresponding cure behavior and utility characteristics.

 Sulfur and Thiazoles – The combination of ALTAX (MBTS) and sulfur, with zinc oxide and stearic acid, yields good aging and flex resistance. Typically, the levels of curatives are 2.0 phr each of ZnO and ALTAX (MBTS) and 1.0 phr each of stearic acid and sulfur. Thiazoles used alone are scorchy. Sulfur and sulfenamides are generally inferior in cure rate.

- Thiurams and Dithiocarbamates Ultra accelerators tend to yield very fast but scorchy cures in BIMSM compounds. The control of scorch can be difficult. Thiuram hexasulfide (SULFADS) is a very effective curative for BIMSM, combining thiuram activity with the sulfur donor characteristics of the hexasulfide.
- Alkylation Curatives Polymethylol phenol resins (heat reactive), phenol disulfides, diphenyl p-phenylenediamine (AGERITE[®] DPPD[®] antioxidant) and VANAX PML, in combination with zinc oxide and stearic acid, are very effective curing agents for BIMSM. Combinations of resin with sulfur, ALTAX (MBTS) and triethylene glycol are generally very effective for high heat and compression set resistance.
- HTS A highly efficient cure system for BIMSM uses 1,6-hexamethylenebis(sodium thiosulfate) as the central ingredient.³⁶ The HTS, in combination with zinc oxide, provides highly efficient and heat stable cures even in low functionality BIMSM polymers, down to 0.17 mole % of benzylic bromide. In optimizing the HTS cure, a slight stoichiometric excess of HTS over benzylic bromide is desirable with a larger molar excess of zinc oxide. This cure system yields high states of cure with excellent elasticity and high temperature stability.

Effective scorch retarders for most of the cure systems include calcium stearate, magnesium oxide, and in some cases triethylene glycol. Concentrations of scorch retarders must be carefully controlled for the proper balance of scorch safety and cure rate. Zinc hydroxycarbonate with MgAIOH(CO₃) and with MgO/MgO(OH)₂ is especially effective in providing scorch safety with minimal cure rate interference. The most appropriate curative combinations in different applications for the achievement of specific properties are contained in the following section.

# Applications for BIMSM

The unique combination of butyl-like attributes, together with the complete ozone, oxidation and heat resistance of the EPDM elastomers, provides the basis for a number of industry applications, in both tire and non-tire areas.

### Tires

A number of tire components have been tested using the properties of BIMSM during the development stages. These provide new applications for isobutylene-based elastomers in the tire area³⁹, and include:

• Tire sidewalls for improved ozone and flex resistance in blends with general purpose rubbers without the use of discoloring antidegradants. This application is under development for both a polymer grade and a formulation. A suggested starting point sidewall compound is shown in Table 21. It is expected to offer improved longevity and improved tire appearance compared to conventional compositions with GPR rubbers using discoloring antidegradants.^{40,41}

- Innerliners in severe-off-the-road and large truck tires for improved heat and flex resistance, along with air and moisture impermeability. Innerliner compositions based on BIMSM are similar to the halobutyl formulations shown in Tables 15 and 16, with a cure system of 2 phr each of zinc oxide and ALTAX (MBTS), and 1 phr each of stearic acid and sulfur.
- Curing bladders for improved heat and flex resistance. Two curing bladder compositions are shown in Table 22. The second compound is more reversion-resistant, and has less tendency to grow in size during use.
- Treads with minor amounts of BIMSM in general purpose rubber tread compositions can provide improved traction at low temperature, and reduced rolling resistance with minimum abrasion loss.

Ingredients	phr
BIMSM (Exxpro 3745)	50.00
BR 1207	42.00
SMR-20	8.00
N330 Carbon Black	40.00
Flexon [®] 641 Paraffinic Oil	12.00
Escorez 1102	5.00
SP-1068® Resin	2.00
Struktol 40 MS	4.00
Remill first stage to 160°C, then add in 3rd pass:	
Zinc Oxide	0.75
Sulfur	0.32
ALTAX (MBTS)	0.80
Rylex [®] 3011	0.60
Stearic Acid	0.50
Total	165.97

# Table 21: Starting Point Tire Sidewall based on BIMSM

Ingredients	phr	phr
BIMSM (Exxpro 3035)	100.00	100.00
N330 Carbon Black	55.00	55.00
VANWAX H Special	2.00	2.00
Castor Oil	7.00	7.00
Perkalink [®] 900		0.75
Zinc Oxide	3.00	3.00
SP-1045 Resin	7.00	7.00
Stearic Acid	0.50	0.50
ALTAX (MBTS)	1.20	1.20
DHT-4A2	1.10	1.10
Sulfur	0.75	
Totals	177.55	177.55

# Table 22: BIMSM Curing Bladder Formulations
Non-tire applications of BIMSM are being developed in a variety of mechanical and extruded parts, such as:

- Automotive dynamic mechanical molded goods for improved age resistance, while maintaining butyl-like dynamic properties.⁴²
- Heat-resistant hoses and belting for improved heat and age resistance and blending with other elastomers.⁴³ A typical heat resistant BIMSM compound for a mechanical or extruded goods application is shown in Table 23.
- · Pharmaceutical applications for "clean polymer" sulfur free compounds.
- Adhesives and mastics for good adhesive qualities with excellent age resistance.⁴⁴

Ingredients	phr
BIMSM (Exxpro 3745)	100.0
N330 Carbon Black	55.0
Paraffinic Oil	5.0
A-C 617 Polyethylene	4.0
Stearic Acid	1.0
Zinc Oxide	1.0
ETHYL ZIMATE	2.0
Triethylene Glycol	2.0
DHT-4A2	2.0
Total	172.0
ODR Rheometer @ 180°C           ML (dN•m)           MH (dN•m)           ts2 (min)           t' 90 (min)	1.7 10.5 3.9 9.7
Mooney Viscosity, ML 1+4 @100°C	66.0
Mooney Scorch @ 135°C, Minutes to 5 pt. rise	9.4
Original Physicals / Aged in Air 70 hrs. @ 150°C / 175°C Hardness, Shore A Tensile, MPa Elongation %	57 / 66 / 64 14.9 / 14.7 / 13.3 206 / 220 / 200
Compression Set, Method B, 70 hrs. @ 125°C / 150°C / 175°C No Postcure, % Postcured 2 hrs. @ 165°C, %	20.9 / 25.5 / 37.4 6.6 / 15.0 / 27.9

#### Table 23: Heat Resistant Compound

## Other Modifications of BIMSM

The benzylic bromide functionality in BIMSM allows for a wide range of nucleophilic substitution reactions to convert all or a part of the benzylic bromide to other desirable functional groups. Specific functional modifications include esters and ethers, carboxyl and hydroxyl derivatives, ionomers and a variety of grafted compositions that may be useful for impact modification.^{45,46}

The development of these functionalized derivatives of BIMSM extends the cure and chemical reactivity of the isobutylene-based polymers. The acrylate and methacrylate derivatives can provide a halogen free vulcanizate. A benzophenone modification of the acrylate yields an internally stabilized system. Free radical cures via peroxides or electron beam radiations are possible with the acrylate derivative. These modifications hold the promise of extending the scope and utility of the isobutylene-based elastomers.

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# by Sunny Jacob*, Eric Jourdain**, Brendan Rodgers*

*ExxonMobil Chemical Company Baytown, TX **ExxonMobil Chemical Europe Machelen, Belgium

#### Introduction

Developed in the late 1950's from two simple olefins (ethylene and propylene), ethylene-propylene rubber is one of the most versatile synthetic specialty elastomers. Since its commercial introduction in the 1960's, sales volume has grown to about 1200 kilotons in 2007. The worldwide growth of ethylene-propylene elastomers in the last one-half century is illustrated in Figure 1.¹

Ethylene-propylene rubbers (also called EPM and EPDM rubbers) continue to be one of the most widely used and fastest growing synthetic rubbers, having both specialty and general-purpose applications. Polymerization and catalyst technologies in use today provide the ability to design polymers to meet specific and demanding application and processing needs. Versatility in polymer design and outstanding weathering and heat resistance has resulted in broad rubber applications such as electrical insulation, roofing membranes, rubber mechanical goods, hoses, tubing, belts, plastic impact modification, and motor oil additive applications and various automotive exterior applications like weather-strips and seals, glass-run channels, and thermoplastic vulcanizates applications. This diversity of end-uses ensures that the demand for these polymers will remain strong as the producers, converters and end users of these EPDM elastomers show a continuous growth by continuing to develop new applications and programs to further the value created by these polymers.



WW EPDM Demand (IIRSP source)

#### History of Ethylene Propylene Rubbers

Ethylene-propylene (EPDM) elastomers were first developed in Europe in the early 1950's, utilizing the catalyst technology discovered by Professor K. Ziegler and advanced by Dr. G. Natta for polymerizing alpha-olefins.^{2,3} Ziegler and Natta were honored for their remarkable discoveries when they jointly received the Nobel Prize for Chemistry in 1963. Specifically, the polymerization of two simple olefins, ethylene and propylene, in the presence of a Ziegler catalyst at approximately ambient temperature and atmospheric pressure, produced amorphous and semicrystalline elastic materials. Most manufacturers, including ExxonMobil Chemical, use a solution polymerization process. After commercial introduction, interest in this new, pure hydrocarbon elastomer intensified rapidly because of its unique features: a completely saturated polymer backbone which provided virtually unlimited ozone and weather resistance, good heat resistance, low compression set, low temperature flexibility, and the ability to accept relatively large quantities of low-cost filler and oil compared to other rubbers, while retaining a high level of compounded physical properties. This combination of high quality and cost effectiveness led initially to rapid penetration of the automotive weatherstrip market and has since permitted expansion into many other areas.

Since the first commercial manufacture of ethylene-propylene (EP) rubber in 1962 and ethylene-propylene-diene (EPDM) rubber in 1967 by ExxonMobil Chemical, the ethylene-propylene rubber business has enjoyed a dramatic growth in demand, now exceeded only by those synthetic rubbers used in tire production, butadiene rubber (BR) and SBR rubbers. The EPDM installed capacity is estimated at 1300KT in 2009. Table 1 shows the major global producers of ethylene-propylene rubber, their product trade names and manufacturing locations.^{3,4}

EPDM Producers	Trademark	Plant Location	Capacity (%)
ExxonMobil Chemical	Vistalon	France, US (2)	21
DSM	Keltan	Holland, Brazil	17
Dow	Nordel IP	US	12
Lanxess	Buna EPG, Buna EPT	Germany, US	10
Mitsui	EP	Japan (2)	9
Lion	Royalene	US	7
Polimeri	Dutral	Italy	7
Kumho	KEP	Korea	6
Jilin	KuLun	China	6
JSR	EP	Japan	3
Sumitomo	Esprene	Japan	3
Nizhnekams	Elastokam	Russia	2
SK Chemicals	Suprene	Korea	2

Table 1: Global Producers of Ethylene-propylene Rubbers

In this chapter, the above two classes of elastomers are collectively described as EPDM elastomers, and the terms rubber, elastomer, and polymer are used interchangeably throughout this chapter to describe the ethylene-propylene synthetic rubber. ASTM Standard D 1418 classifies this synthetic elastomer with an "M" designation, meaning that it has a saturated polymer chain of the polymethylene type. Within this classification, there are two basic kinds of rubber: EPM, the copolymer of ethylene and propylene which can only be vulcanized using peroxides; and EPDM, the terpolymer of ethylene, propylene and a non-conjugated diene with residual unsaturation in the side chain (see Figure 2). The E refers to Ethylene, P to Propylene, D to diene and M refers to its classification ASTM Standard D 1418. The residual diene unsaturation in EPDM allows crosslinking of the rubber using a conventional vulcanization agent such as sulfur, the location on a side chain (pendant) prevents the reactive unsaturation from being a site for molecular breakdown. The diene shown is ethylidene norbornene (ENB), the most commonly used diene as the termonomer in EPDM.



Figure 2: Structure of EP and EPDM

The structures of diene (third monomer) comonomers commonly used in the manufacture of EPDM rubbers, 1,4 hexadiene (HD), dicyclopentadiene (DCPD), ethylidene norbornene (ENB) and vinyl norbornene (VNB) are given in Figure 3. A characteristic of the structure of commercially used third monomers is that the two double bonds are non-conjugated, cyclic or bicyclic dienes with a bridged ring system, and one of the double bonds preferentially reacts with the ethylene and propylene monmers, leaving the second less reactive double bond for vulcanization. DCPD, ENB, and VNB are the three diene monomers commonly used for the commercial production of EPDM. Unlike natural rubber and SBR where the unsaturation is on the main backbone, the unreacted double bond in EPDM is pendant to the main chain, contributing to its unique resistance to light and heat.



Dicyclopentadiene (DCPD)



Ethylidene norbornene (ENB)

Vinyl norbornene (VNB)

ĊH₂



1,4 Hexadiene (HD)

# Figure 3: Termonomers Used in EPDM.

## **Properties of EPDM Elastomers**

The EPDM molecule is a saturated hydrocarbon with a random coil configuration. The unique features of crosslinked EPDM elastomers described earlier such as ozone and weather resistance, heat resistance, low compression set, and low temperature flexibility, and the ability to accept relatively large quantities of fillers and oil compared to other rubbers, while retaining a high level of physical properties, benefit a broad range of applications for this technical elastomer. Typical physical constants of EPDM polymers are shown in Table 2. The typical applications of EPDM copolymers are listed in Table 3.

Property	Unit	Value
Specific Gravity	g/cm ³	0.86 to 0.89
Specific Heat Capacity	J/(g•K)	2.22
Thermal Conductivity	W/(m•K)	0.176
Thermal Diffusivity	cm/s	1.9 x 10 ⁻³
Thermal Coefficient of Linear Expansion	1/°C	2.5 x 10 ⁻⁴
Brittle Point	°C	-55 to -65
Glass Transition Temperature	°C	-45 to -60
Air Permeability	cm ² /s•atm	100

Applications	Description
Automotive Parts	Hoses: coolant, heater, brake, A/C and air tubing Radiator seal Multi V-belts Weather strips and sealing systems Molded gaskets and ducts Windshield wiper Mounts Tire & Tube applications (minor component in blends) Tire curing bands
Electrical Products	Insulation and jacketing for low & medium voltage Connectors and tapes
Plastics Blending	Impact modification of thermoplastic polymers Dynamically Vulcanized Alloys
Mechanical Goods	Gaskets Industrial hoses (air, water, steam, hydraulic) Conveyor belts Roll covering O-rings
Oil Additives	Viscosity index improvers
Construction	Single-ply roofing sheet Geomembrane Flooring, sport tracks Window gaskets and profiles Asphalt modifiers

Table 3: Typical Applications of EPDM Rubbers

The mechanical properties of the EPDM elastomer depend on the glass transition temperature ( $T_g$ ), and the level of crystallinity. These properties are related to a number of structural parameters of the copolymer chains: the relative content of comonomer units in the copolymer chain, the way the comonomers are distributed in the chain (more or less randomly), the variation in the comonomer composition of different chains, average molecular weight, and molecular weight distribution, amount and type of unsaturation introduced by the third monomer, and long chain branching. These structural parameters can be controlled via the operating conditions during polymerization and the chemical composition of the catalyst system. For a detailed description of these factors please read the reviews by Gary Ver Strate and Kirk-Othmer.^{6,7} The major polymer parameters that can be varied to meet many processing and end use requirements are:

### Composition and Sequence Distribution

Ethylene–propylene copolymers exhibit elastomeric properties over a broad range of compositions. The ethylene composition of commercial EPDM polymers generally ranges from 45 to 80 weight percentages. Below 45 percent ethylene content, the drop in properties is such that it does not offer attractive industrial applications. The ratio of ethylene to propylene in the elastomer is an important factor that controls the glass transition temperature of the elastomer. The T_g

decreases with increasing ethylene content due to increased flexibility of the chains. Crystallinity is another property that is greatly affected by the ethylene content. In general the crystallinity of the elastomer increases with increasing ethylene content.⁸ The ethylene-propylene ratio also affects the oxidative stability of the elastomers, higher ethylene rubbers have better oxidative stability and resistance to chain scission during free radical crosslinking due to the lower number tertiary hydrogen on the backbone.

EPDM elastomers with low ethylene content (less than about 60 weight percent) are practically amorphous at room temperature. Compared at a given molecular weight, crystalline EPDMs offer higher cold green strength and physical properties, are less tacky (and therefore easy to store in pellet form), and also allow options for higher loading of fillers to lower the compound cost. Another important factor affecting the overall properties is the distribution of the ethylene segment on the backbone of the polymer. Depending on the catalyst system and polymerization conditions used, the ethylene units may tend to group together to form blocky or sequential structures.⁹ The presence of blocky ethylene units adds strength to the EPDM vulcanizates. Such high ethylene EPDMs find lightcolored applications wherein less reinforcing mineral fillers are used. On the other hand, these blocky structures or crystallinity have a detrimental effect on the low temperature rubbery properties of the polymer. The ethylene content and monomer sequence distribution in an EPDM polymer is determined by proton NMR, C¹³NMR or Infra Red spectroscopy (FTIR).^{10,11} Most of the manufacturers use the Infra Red method in accordance with ASTM D 3900-95 to determine the ethylene content of the EPDM polymer. The result is expressed as "weight percent ethylene" for both copolymers and terpolymers, but this is technically only correct for the EPM copolymers. For EPDM terpolymers this ratio or "weight percent ethylene" is more correctly termed "percent ethylene uncorrected for diene content."

## Molecular Weight and Molecular Weight Distribution

Molecular weight of a polymer is a basic molecular parameter that determines the physical properties such as stiffness, strength, viscoelasticity, toughness, and viscosity. The molecular weight of EPDM polymers has to be above a certain critical number for it to be useful in any commercial application. Although lower molecular weight elastomers facilitate easy processability of compounds, they provide lower physical properties and lack the ability to extend with fillers and oils. Similar to the ethylene/propylene ratio, the average molecular weight and molecular weight distribution of elastomers is controlled by polymerization variables such as type of catalyst used, reaction temperature, residence time in the reactor, solubility of polymers in the diluent, etc., of which the catalyst selection has the most significant effect.^{10,12}

The polymer molecular weight properties are generally measured as the average molecular weight by gel permeation chromatography or intrinsic viscosity. The rubber compounder uses Mooney viscosity for practical purposes. The Mooney viscosity of polymers is determined by following the ASTM/ISO test methods D 1646. In general, EPDM elastomers are tested for Mooney viscosity

by the large rotor after one minute pre-heating and four minutes running time at 125°C. Results are reported as ML (1+4) at 125°C. Although Mooney viscosity is a primary indicator of polymer molecular weight, as EPDM grades vary in molecular weight distribution (MWD) and polymer structure, a Mooney Stress Relaxation (MLR) test in ASTM D 1646 (94) is used as an indicator of polymer processability. Mooney stress relaxation is inherently highly sensitive to the presence of higher molecular weights in EPDM polymers. Since longer molecules relax more slowly, the stress relaxation values increases with the Mooney viscosity of the polymer. However, at constant polymer Mooney viscosity, the stress relaxation values of polydisperse EPDM polymers increases further as a result of polymer long chain branching and/or MWD broadens. Therefore, the combination of Mooney viscosity with the stress relaxation gives a more complete characterization of the molecular structure of EPDM polymers. The majority of the commercially available EPDM grades have Mooney viscosity ML (1+4) at 125°C in the range of 15 and 90 Mooney units. Grades with higher molecular weight are generally extended with either paraffinic, or sometimes naphthenic, oil to reduce the apparent Mooney viscosity for processing purposes.

Molecular weight distribution is one of the most important variables that affect the processability and the cure rate of the polymers. It is generally the presence or absence of the highly elastic, high MW components that determines the processability of ethylene-propylene rubbers. The MWD of EPDM elastomers can be narrow or broad depending on the polymerization parameters. Broad MWD and very broad MWD indicate the presence of a significant portion of high and low molecular weight molecules. In narrow MWD polymers, significant amounts of high molecular weight end are absent. Figure 4 shows the molecular weight distribution (MWD) of a narrow and a broad molecular weight distribution EPDM.⁵ In general narrow MWD polymers are advantageous for faster cure rate and higher cure state, good hot and cold compression set, and low die swell. However, they have low green strength, poor mill and calender handling, difficult extruder feeding and higher viscosity at high shear, which could cause rough extrudate surface and edges. On the other hand, broad MWD polymers show good hot green strength, improved extruder feeding, smooth surface extrudate, easier mill and calendar handling, and low compound tack.



Figure 4: MWD Profile of a Narrow vs. Broad EP(D)M Polymer⁵

A macromolecular engineer can design product with tailored MWD by the selection of catalyst systems and polymerization process parameters. The term "tailored" can encompass several MWD variations, including two or more major modes or peaks, and/or significant amounts of high molecular weight molecules. Tailored MWD polymers are used where unusually high amounts of elastic high MW molecules are needed for processability or toughness in the uncured state. Tailored polymers are also referred to as bimodal polymers or bimodal MWD, where overall MWD is narrow with a controlled amount of long chains. Figure 5 depicts a bimodal molecular weight distribution polymer.⁵ Bimodal MWD EPDM elastomers provides the desired combination of properties without blending with another EPDM grade. Bimodal MWD EPDM elastomers exhibit a balance of best cure performance and good processing characteristics. In a bimodal EPDM, the high molecular weight ends tend to increase the viscosity of the overall product. This is compensated for by having the main mode of the distribution at a slightly lower molecular weight than the narrow MWD polymer of equivalent Mooney. Owing to their very high molecular weight fraction, EPDM bimodal polymers generate higher shear stresses at early mixing stages, which translate into faster filler incorporation and finer dispersion in the polymer matrix.



Figure 5: MWD Profile of a Bimodal EP(D)M Polymer⁵

Compared to narrow molecular weight distribution EPDM, bimodal EPDM have a higher viscosity shear thinning effect at small deformations, which explain their better extrudability, and have a higher elasticity at low shear (see Figure 6), providing a better collapse resistance. These properties are related to their unique MWD depicted in Figure 5.



Figure 6: Shear-flow Behavior of Narrow, Branched, and Bimodal MWD EP(D)M rubbers

### Diene content

As described in an earlier Section, the primary role of a diene is to provide crosslinking sites during vulcanization. The type and amount of diene levels greatly influence cure rate and cure state of the vulcanizate. Similar to the

ethylene content the glass transition temperature of the polymer is a function of the diene content. Diene monomers such as ENB and DCPD raise the T_g of polymer whereas 1,4-heaxadiene has very small effect on the  $T_{g}$ .¹⁰ The distribution of the diene moiety along the backbone of the chain is presumably random along the chain, but the actual distribution depends on the structure of the diene. ENB for example has higher reactivity towards ethylene than propylene and low reactivity to itself.^{10,11} Thus the ENB units are individually distributed among ethylene and propylene with ENB usually following an ethylene group. An FTIR technique is used to accurately measure the amount of ENB in a polymer. This methodology has been adopted as ASTM D 6047-96, which is the standard for the EPDM rubber industry. Commercial EPDMs with 5-vinyl-2norbornene (VNB), a precursor in the synthesis of ENB, as third monomer has been developed, aiming at a higher vulcanization yield with peroxide curatives, relative to ENB- or DCPD-containing EPDMs.9,13 Combinations of more than one-third monomer are not typical. The use of low amount of either VNB or DCPD is actually to introduce some branching in the molecular structure.^{14,15}

The amount of third monomer in general purpose grades range from 0.5 to 4 wt% and are termed low diene grades. For fast curing, medium diene level (5-7 wt%) grades are used. For ultra fast curing, high diene grades in the range of 8-11 wt%, are used. Ultra fast curing grades of EPDM can cure at rates closer to other general purpose diene rubbers, and hence can be blended with diene rubber like NR and SBR for tire applications to provide excellent ozone resistance. The type of diene in the EPDM also has a role in the cure rate of compounds. For sulfur-curing the ENB containing EPDM cures almost twice as fast as DCPD containing ones. Almost reverse is the case for peroxide-cured DCPD containing EPDM, which gives a higher state cure due to the higher reactivity to radicals.¹⁶ VNB containing EPDM does not give a high state of cure with sulfur. Table 4 summarizes the dependance of molecular parameters of EPDM on final compounded product properties and processing characteristics of compounds.

Property	Advantage	Disadvantage
Molecular Weight	Tensile and tear strength increase	More difficult to disperse
Mooney Viscosity	<ul> <li>Black / oil loading can increase for lower cost</li> <li>Hot green strength increases</li> <li>Collapse resistance improves</li> <li>Low pressure continuous vulcanization (CV) cure improves</li> </ul>	Extrusion rate and ability to calender decrease
Ethylene Content	<ul> <li>Cold green strength increases greatly</li> <li>Flow at high temperature increases</li> <li>Tensile strength increases</li> <li>High filler / oil loadings possible</li> <li>Easier to pelletize raw polymer and compounds</li> <li>Peroxide cure improves</li> </ul>	<ul> <li>More difficult to mix</li> <li>Poorer low temperature set and flex resistance</li> <li>Higher tension set, less elastic recovery</li> <li>Higher Shore hardness</li> </ul>
Diene Content	<ul> <li>Faster cure rate</li> <li>Better low pressure CV cures</li> <li>More flexibility in selecting accelerators</li> <li>Compression set improves</li> <li>Modulus increases</li> </ul>	<ul> <li>Compound cost may increase</li> <li>Scorch safety decreases</li> <li>Shelf-life decreases</li> <li>Elongation decreases</li> <li>Heat resistance decreases</li> </ul>
"Narrow"	<ul> <li>Faster cure rate</li> <li>Lower die swell</li> <li>Higher cure state</li> <li>Better compression set</li> </ul>	<ul> <li>Lower green strength at all temperatures</li> <li>Poorer extruder feeding and extrudate surface / edges</li> <li>Poorer mill handling (greater adhesion to mill roll)</li> <li>Poorer calendering</li> </ul>
"Broad"	<ul> <li>Improved calendering</li> <li>Improved mill handling</li> <li>Higher green strength, especially when hot</li> <li>Improved extruder feeding at all temperatures</li> <li>Improved collapse resistance</li> <li>Less compound flow and tack</li> </ul>	<ul> <li>Higher die swell</li> <li>Slower cure rate and lower cure state</li> </ul>
"Tailored" (Bimodal MWD)	<ul> <li>Improved mixing consistency</li> <li>Excellent collapse resistance, even at low ethylene content</li> <li>Good balance of processing and physical properties</li> </ul>	

# Table 4: Dependence of Compound Properties and Processing Characteristics on EPDM Molecular Parameters

## Manufacture of EPM/EPDM rubbers

The primary monomers for the synthesis of EPDM polymers are ethylene and propylene, which are aboundantly used in the production of commodity polymers polyethylene and polypropylene, respectively. Ethylene and propylene are produced in the petrochemical industry by steam cracking. Both ethylene and propylene are gases at room temperature and are generally transported to the EPDM production site through pipelines where these gasses may be converted to liquids, under pressure at cryogenic temperatures, before polymerization. The

diene monomers are also prepared from by-products of petrochemical industry. For example, ENB is produced by a two-step process: a Diels-Alder reaction of cyclopentadiene and butadiene; the resulting product VNB is rearranged to ENB through a catalytic isomerization process.^{17,18} DCPD is a petrochemical product. HD is the dimerization product of ethylene and butadiene.¹⁹

elastomers are produced in a continuous EPDM process. The manufacturing processes differ greatly between various suppliers and most of them have highly proprietary process schemes to produce polymer with unique properties. The conventional production technology of EPDM uses Ziegler-Natta catalysts having a common electron deficient metal, a vacant orbital, and a metal-carbon bond in the proper orientation that allows insertion of the monomers during polymerization.^{11,12,21,22} The catalyst is a complex of two main components: a catalyst which is a transition metal halide, such as TiCl₄, VCl₄, VOCl₃, etc., of which VOCl₃ is the most widely used; and a co-catalyst which is a metal alkyl component such as  $(C_2H_5)_2$ AlCl diethylaluminum chloride. or monoethylaluminum dichloride, (C₂H₅)AlCl₂, or most commonly a mixture of the two, i.e. ethylaluminum sesquichloride,  $(C_2H_5)_3Al_2Cl_3$ .⁶ The aluminum alkyls need at least one halogen to be an effective co-catalyst. Vanadium-aluminum alkyl halide combinations produce complexes soluble in nonpolar hydrocarbon medium. The diethylaluminum chloride produces multiple active species whereas the ethylaluminum sesquichloride tends to produce single species. The composition of the catalyst system selected dictates the catalyst efficiency, molecular weight distribution and compositional distribution of the polymer produced.

A more recent technology uses a new class of catalyst known under the name metallocene catalysts. Over the last decade rapid developments have occured in the area of metallocene catalyst primairily for the production of polyethylene and polypropylene. These metallocene catalyst have also been found suitable for the production of ethylene-propylene copolymers.²³⁻²⁷ Metallocene catalysts are homogenous single-site systems, implying that there is a single, uniform type of catalyst present in the system. This is in contrast to the Ziegler-Natta catalysts that are heterogeneous catalysts and contain a range of catalytic sites.

A metallocene catalyst consists of a transition-metal atom sandwiched between ring structures through a bridge system that prevents ligand rotation, locked into a single geometry. They have well-defined single catalytic sites, the molecular structure and mechanisms of polymerization are well-understood. The nature of the metal center, ligands and polymerization conditions dictate the microstructures and physical properties of the polymer prepared. The simplest metallocene catalyst has the formula Cp₂MX₂, where M is one of the group 4 metals (i.e. Zr, Ti) and X is halogen atoms (mainly chlorine, Cl). Similar to Ziegler-Natta catalysts, a co-catalyst (i.e. methylaluminoxane (MAO)) activator is necessary to achieve high catalyst efficiency.²⁸ The catalytic properties of the single-site catalysts can be controlled by modification of the structure of the catalyst.

Metallocenes offer significant advantages and routes to new products. Different manufacturers use proprietary metallocene catalysts to produce ethylenepropylene elastomers with unique properties. The metallocene catalysts show very high activity, more importantly higher reactivity to propylene, narrow molecualr weight distribution, and offer broader composition range relative to the traditional Ziegler-Natta catalysts. They keep their activity at higher polymerization temperatures for longer time than the commonly employed Ziegler-Natta catalysts. A catalyst site can undergo many chain transfer events producing multiple polymer chains before the catalyst site loses its activity. Metallocene catalysts usually give a different comonomer distribution than traditional Ziegler-Natta catalysts. Due to their high catalyst activity the products are cleaner, the amount of catalyst residues in the polymer is significantly lower than Ziegler-Natta catalysts and thus deashing steps can be eliminated. Metallocene chemistry provides routes to prepare tailor-made polymer architectures and manufacture them at better process economics than the conventional Ziegler-Natta process.

Although this technology has many advantages, some of these advantages are offset by various counter effects such as the need for higher pressure operations in the increased temperature regime, the need for highly purified monomers and solvents due to the sensitivity of metallocene catalysts to poisoning by adverse compounds like moisture, and the high cost of the metallocene catalyst itself. Metallocene technology has progressed to industrial production of EPDM and currently ExxonMobil Chemical, Dow Chemical and Mitsui Companies use this technology to produce these polymers. Further developments in this field are needed to fully exploit the possibilities to produce the wide variety of EPDM molecular structures, suitable for the diverse application of these elastomers which are dictated by the market and end-use requirements. A brief comparison of the product attributes of conventional Ziegler-Natta (ZN) and metallocene EPDM is given in Table 5.

	Conventional ZN	Metallocene	Consequences
MW / Mooney Viscosity	Low (ML=20) to very high (200+) with oil extension	Very low (ML=5) to max ML~ 100* at 125°C	Limited low hardness compounds and high resiliency compound
MWD MLRA	Medium to broad and bimodal, long chain branching	Narrow Mid range, no branching	Limited extrusion processing, requires blend with broad MWD
Ethylene content	From 50 to 80%, random with limited propylene incorporation	From low (10%) to very high (>80%), non blocky sequences	Improved low temp. compression set / flexibility
ENB content	Up to 11% + (Beyond efficiency decrease). Other diene possible	Limited to 7% (ENB imcorporation), efficient cure.	Good high temp. CS, fast cure rate / high cure state at low diene content

Table 5: Product Attributes of Ziegler–Natta vs. Metallocene EPDM

* Upper end of ML limited by the finishing process

EPDM elastomers are manufactured by solution, slurry or gas-phase polymerization processes. The most widely used is the solution process, in which the polymerization is carried out in a hydrocarbon diluent (e.g., hexane). The polymer formed dissolves in the diluent to form a polymer solution. In the solution process catalyst, co-catalyst, dry solvent, ethylene, propylene, and optional diene are continuously and proportionately fed to one or a series of polymerization vessels.^{29,30} The polymerization reaction is highly exothermic and the heat of reaction is removed by means of cooling systems, either external cooling of the reactor wall or deep cooling of the reactor feed, or combinations. Most commonly, hydrogen is used as the chain-transfer agent to regulate the average molecular weight. At a predetermined elastomer solution concentration, the polymerization is terminated by killing the catalyst by vigorously stirring the solution with water. The monomers and solvent are removed by passing the polymer solution continuously through a flash tank under reduced pressure. The monomers and the solvent are recycled into the feed stream. Catalyst residues of (i.e. vanadium and aluminum) are removed as soluble salts by a deashing step, by washing with water. Excessive residues of catalyst and co-catalyst can cause discoloration, can affect the oxidative and thermal stability of the polymers and electrical properties. Stabilizers, antioxidants and extenders (optional for oil extended grades) are added followed by a steam stripping process where most of the remaining monomers and solvents are removed resulting in a slurry of polymer crumbs, which then passes through a few additional down stream finishing processes to obtain the dry polymer. The rubber crumb is pressed into bales, wrapped in plastic films and packaged for storage and shipment. Figure 7 shows a general schematic flow chart of the solutions process for ethylene-propylene rubber manufacturing.²⁹



Figure 7: Solution Process for EP(D)M Polymer Manufacturing²⁹

A second method for producing EPDM is similar to "bulk polymerization" known as Slurry Process,³¹ in which a non-solvent for the EPDM is used as the diluent. Commonly, liquid propylene monomer is used as the diluent. Ethylene and catalysts are pumped into a reactor filled with propylene. Rapid polymerization occurs forming crumbs of polymer in the propylene diluent. The advantages of the Slurry process is that it is easy to control temperature as the precipitated crumby EPDM particles in the slurry have low viscosity. The finishing step only involves the removal of propylene, eliminating the need for solvent handling equipment. Other advantages include higher production rates due to higher slurry concentrations compared to the solution process, the ability to achieve higher molecular weight EPDMs (because the viscosity rise of the solution does not apply), and the lower catalyst level needed in comparison with the solution process (because of the great abundance of propylene as the monomer). The great disadvantage of the slurry process is that the catalyst residues tend to become occluded in the precipitated EPDM leading to intermolecular branching reactions (see the next paragraph) and probability of premature crosslinking reactions during storage. Another disadvantage is, as described earlier excessive catalyst residues negatively affect the long term aging properties of vulcanized rubber.

A more recent technical development in the field of EPDM manufacture is the gas-phase process,³² an extension of the well known gas-phase processes for polyethylene and polypropylene. Gaseous monomers ethylene, propylene and third monomer ENB are fed in to a fluid-bed reaction vessel, the heat of the reaction is removed through circulation of the gas, which serves to fluidize the polymer bed as well as to act as the raw material for the polymerization. A steady stream of fluidization aid (carbon black powder) is used to prevent sticking together of the granules.³³ The gas-phase technology is solvent and diluent free, so no stripping is required. The unused monomers are recovered by purging and are recycled. The main advantage of gas-phase technology is that drying and finishing steps are completely eliminated and no water is involved in the process. The final product is in a granular form, directly recovered from the reactor. Similar to the slurry process, in gas-phase process there is no deashing step, and the residual catalyst stays in the polymer. The amount of catalyst residue could be relatively high if conventional Ziegler-Natta catalysts are used. It may be possible to lower catalyst residue if metallocene catalysts are used for this process (see earlier section). Another difficult step in this process is the removal of unreacted third monomer such as ENB from the product. An extra purging step is used to remove the third monomer.³⁴ Dow Chemical had one plant using this technology, which was initially developed by Union Carbide. This plant was recently closed, most likely because of less attractive economics compared to a solution plant.

One of the important parameters that affect the rheological properties of EPDM compounds is the extent of long chain branching present in the polymer independently from molecular weight and molecular weight distribution. The processing characteristics and cured physical properties of the compounds can be tuned by the level of branching in the polymer.^{35,36} For EPDM, longchain branching can be introduced in a controlled fashion during polymerization. Uncontrolled chain branching can lead to unwanted gel formation in the product. This can happen by at least two mechanisms; the dominant mechanism in Ziegler-Natta polymerization is through cationic coupling of pendant double bonds in the diene moiety.^{37,38} Use of a diene, such as vinyl-norbornene and to a lesser extent dicyclopentadiene, can result in substantial amounts of branching due to steric factors and closer reactivity of the two double bonds.³⁷ The extent of this reaction strongly depends on the Lewis acidity of the catalyst components and can be controlled by the selection of co-catalyst and a suitable Lewis base. Long-chain branching in metallocene catalysis is believed to occur through a copolymerization path, in which a vinyl terminated polymer chains formed by the chain transfer events are incorporated into a growing polymer chain.³⁹⁻⁴¹

### Compounding and Vulcanization of EPDM elastomers

EPDM ethylene-propylene rubber is very elastic material, even at low Mooney viscosity. The EPDM polymer has amorphous structure, except for grades with greater than 65 weight percent ethylene content. In general, the rubber does not crystallize on stretching and, therefore, must be reinforced to achieve useful properties. Except for applications where ethylene-propylene elastomers are blended with plastics or utilized as an additive in motor oil, the polymer is usually modified with fillers, plasticizers and a cure system to bring out the desired performance attributes for specific end-use applications. EPDM rubber compounds contain many ingredients with the base EPDM polymer ranging up to more than 35% of the total formulation. The major factors in designing EPDM rubber compounds are based primarily on the physical properties (hardness) and elastic (compression set) performance of the final rubber article. However, the processing behavior of the compound is also equally important because the material must be amenable to mixing, forming or shaping, and vulcanization.

Finally, the third key element of compound design is its production cost. Thus, a formulation must be optimized to yield the best balance of these factors. Furnace-type carbon black fillers are chiefly employed to impart the requisite reinforcement for strength and mechanical properties. Semi-reinforcing furnace blacks from the N500, N600 and N700 series, as classified according to ASTM D 2516, are the major carbon black fillers for EPDM. However, other grades of carbon black are also used for special applications or requirements. Carbon black, inorganic fillers and process oils can be incorporated from 30 to 500 parts per hundred of rubber (phr). This approach, coupled with the inherent and comparatively low specific gravity of EPDM ethylene-propylene elastomers, allows for cost-effective compounds.

In most cases, property requirements of the application and preference for sulfur-cure will lead the grade choice toward EPDM terpolymers instead of EPM copolymers. However, certain performance requirements, such as extreme heat resistance or in uncured applications, may direct the choice toward EPM copolymers. Especially with terpolymers, there are also situations where a blend of EPDM grades will be best for a particular application. The grade or blend of grades finally selected will influence, to a great extent, the processing characteristics of the compound, the level of physical properties achieved and, to a lesser extent, the compound cost. Refer to Table 4 for property, processing benefits and limitations on EPDM molecular parameters such as molecular weight, ethylene content, diene content and MWD. Some rubber compounders generally blend broad and narrow MWD grades to achieve the right combination of compound processing and cured performance such as cure rate, green-strength and compression set.

### **Compounding Ingredients**

### Carbon Black Reinforcement

The most widely used and best reinforcing fillers are carbon blacks. The important properties are particle size and structure. The medium particle size, higher structure types, such as N539, N659 and N762, favor reinforcement and increase both hardness and stiffness. The finer particle size blacks (i.e. N330) are difficult to mix and disperse in EPDM. They also produce compounds with much higher viscosities than the medium particle types. Coarser or low structure blacks are suggested for increased elongation and/or scorch time when high loadings are required. The effect of carbon black structure and particle size is illustrated in Figure 8. New structures of carbon black, such as Spheron types from Cabot, have been recently developed to offer a better balance between processing (particle size) and reinforcement properties (structure).

		PARTICLE SIZE FINE COARSE	STRUCTURE LOW <del></del> HIGH
Processing	Improves		
Reinforcement	Increases	-	
Optimum loading (for tensile and tear) at increased oil loadings	Increases		
Mooney Viscosity, modulus and hardness	Increases	-	
Mooney Scorch, elongation and resilience	Increases		-
Compound cost	Increases		
Best overall performance: N550, N683, N650 Best for cost compounding: N550, N650, N762 bl	ends		

## Figure 8: Effect of Carbon Black Particle Size and Structure on Compound Properties⁵

The impact of carbon black type on EPDM compound and vulcanizate properties is illustrated in Table 6. Carbon black fillers, varying from fine to coarse particle size, are compared in an intermediate Mooney viscosity, high ethylene content EPDM terpolymer. The base formulation contains 200 parts of carbon black and 120 phr of process oil. Two sulfur cure systems are used – a general purpose (low cost) and a fast cure. In general, at this level of filler and plasticizer, which is typical for EPDM polymers, there is no benefit to using carbon blacks smaller in particle size, higher in surface area than N550, because of poor dispersion.

Carbon Black Grade	N330	N358	N550	N660	N683	N762	N990
Low cost cure: TMTD (1.5), MBT (0.5), Sulfur (1.5) (Press Cured 20 min. @ 160°C)							
Surface area, CTAB, (inversely related to particle size), m ² /g	83	75	42	35	39	24	9
Structure, DBP absorption, m ² /100g	100	160	120	90	130	65	43
Hardness, Shore A	84	90	81	80	80	70	58
100% Modulus, MPa	4.1	6.1	5.0	4.1	5.0	2.4	1.0
Tensile strength, MPa	8.9	8.3	9.2	9.9	9.9	9.3	7.9
Elongation at break, %	240	160	220	300	240	500	800
Fast cure: TMTD (0.8), TeDEC-8 Cured 20 min. @ 160°C)	30% (0.8	3), DPT1	Γ (0.8), Λ	ЛВТ (1.5	5), Sulfui	r (2.0) (F	Press
Surface area, CTAB, (inversely related to particle size), m ² /g	83	75	42	35	39	24	9
Structure, DBP absorption, m ² /100g	100	160	120	90	130	65	43
Hardness, Shore A	85	90	81	80	82	75	58
100% modulus, MPa	4.7	7.1	5.5	5.2	5.7	3.3	0.9
Tensile strength, MPa	11.2	10.5	10.9	11.2	11.4	10.9	9.7
Elongation at break, %	210	140	190	240	210	380	700
Comp. Set, 22 hrs. @ 70°C, %	24	29	23	22	23	24	28
Mooney Viscosity, ML (1+8) @ 100°C, MU	76	100+	58	48	47	33	17

Table 6: Comparison of Carbon Blacks in Typical EPDM Compounds⁵

## Mineral Filler Reinforcement

Inorganic fillers are used in white or colored compounds or as extenders in carbon black stocks to reduce cost. Silicas, clays, talcs and whiting are examples of the classes of mineral fillers most commonly used. Frequently, a combination of fillers is used to obtain the required balance of reinforcing properties, processability and economics for the particular application. Fine particle size silicas are the most reinforcing of the mineral fillers. However, they are difficult to disperse in EPDM, retard cure, and produce boardy, hard stocks. Hard clays are easier to mix and extrude, provide some reinforcement, and retard cure to a lesser extent than silicas. To overcome the retarding effect, small amounts of diethylene glycol or polyethylene glycols are commonly added. Whiting, soft clays and most talcs impart little reinforcement, but aid processing by reducing compound viscosity. Figure 9 summarizes the effects of different mineral fillers. Specific properties and processing characteristics obtained with several different types of mineral fillers in an intermediate Mooney viscosity, high ethylene content EPDM compound are shown in Table 7. A low phr of diethylene glycol was used in the formulation to negate the retarding effect of the mineral filler.

COMPOUND		
Good reinforcement	Silica, hard clay, platy talc	
Good mixing	Silicate, calcined clay, platy talc	
Good extrusion	Silica, platy talc, calcined clay	
Good internal mixing	All except ground whiting	
Lowest viscosity	Platy talc, whiting	
VULCANIZATE		
Highest hardness	Silica, silicate	
Highest modulus	Silica, platy talc	
Highest tear	Silica, silicate	
Good compression set	Whiting, soft clay	
Good water resistance	Calcined clay, platy talc, soft clay	

## Figure 9: Effect of Mineral Fillers on EPDM Compound Properties

Coupling agents in mineral-filled EPDM compounds are an important requirement for balancing processability and physical properties. Diethylene glycol or polyethylene glycols are commonly used for minimizing the retarding effect of acidic mineral fillers. Silane coupling agents are also strongly recommended in mineral-filled EPDM formulations to improve polymer-filler interaction. In general, the silane contains dual functionality. For EPDM compounds, the organo-functional group is usually an amino, mercapto or vinyl substituted unit. The other functionality is a hydrolyzable alkoxy group attached to the silicon. In practice, the alkoxy group hydrolyzes in the presence of moisture found on the surface of the mineral filler. The resulting silanol product then couples or attaches to the surface of the silica, clay or talc. During vulcanization, the organic group reacts with the polymer and cure system and links into the network. To be effective in the compound, the silane coupling agent must be reactive to some degree with both the polymer network and filler system.

Filler Type	Platy Talc	Hard Clay	Calcined Clay	Silica
Loading, phr	248	234	236	120
Hardness, Shore A	67	61	60	76
300% Modulus, MPa	3.5	2.1	2.0	2.1
Tensile, MPa	9.3	9.8	6.3	11.6
Elongation, %	630	810	640	850
Mooney Viscosity ML (1+8) @ 100°C	28	51	32	106
Mooney Scorch @ 130°C				
Minutes to 3 pt. rise	14	16	14	11
Garvey Die Extrusion Rate, cm/min.	195	190	150	175
Whiteness	Grayish	Yellowish	Good	Good

Table 7: Comparison of Mineral Fillers in a Typical EPDM Compound⁵

## Plasticizers

Ethylene-propylene rubber is compatible with either paraffinic or naphthenic process oils. Hydrocarbon oils having a high aromatic content should be avoided because they have a detrimental effect on cure; aromatic oils significantly affect the cure efficiency of peroxides and reduce the cure state of sulfur-cured compounds. Paraffinic oil has the potential for exudation/bleeding when used at very high amount in high ethylene crystalline EPDM compounds. Viscosity is also an important consideration when selecting an oil plasticizer. In general, the high viscosity oils are less volatile, enhance physical properties development, improve heat resistance, and minimize shrinkage. Lower viscosity oils improve both resilience and low temperature flexibility, and tend to reduce compound plasticity. Because of the very high filler loadings often employed in EPDM compounds, the process oil performs several important functions:

- · Improves wetting and incorporation of fillers
- · Reduces power consumption of the mixing equipment
- Lowers batch temperature
- Reduces the risk of compound scorch
- Improves extrusion and all other shaping operations

As an extender, oil almost always lowers compound cost. Table 8 is a guide to the selection of process oil type for EPDM products. Instead of petroleum oils, synthetic plasticizers such as polyalkylbenzene or Elevast[™] polymer modifier may be used, especially for peroxide cures and high heat resistance. Elevast polymer modifier is reported to enable formulators to elevate product performance. Key benefits include improved processing, higher crosslink density for peroxide cure, lower compression set, enhanced extreme-temperature performance, and increased permanence of the plasticizer in the compound.⁴² Examples of EPDM compounds containing Elevast[™] modifier are given in Tables 26 and 27.

For	Use
Best physical properties	High viscosity oils
Maximum heat resistance	High viscosity paraffinic oils
Highest resilience and best low temperature flexibility	Low viscosity oils
Lowest compound viscosity	Low viscosity oils
Peroxide cures	Paraffinic oils, synthetic plasticizers

Table 8: Process oil Selection Guide for EPDM Compounds 5

## Other Ingredients

Zinc oxide and stearic acid are included in all sulfur-vulcanized EPDM compounds as part of the cure system. Stearic acid helps to solubilize the zinc oxide to form a complex with the sulfur curatives. It also provides some extra mill release in highly loaded, soft compounds, but this function is usually better handled by adjusting mill conditions or polymer type. Stearic acid should be avoided in peroxide cured compounds. Acidic components promote ionic breakdown of peroxide resulting in reduced radical generation for cure.43 Calcium stearate is a suitable replacement if mill release is needed. Calcium oxide is added in compounds that are extruded to capture the volatiles present in the fillers, and prevent the development of a micro-porosity. This is even more important when high content of mineral fillers are present in the formulation. Antioxidants or antiozonants are not generally needed in most of the sulfurcured EPDM compounds, when service temperature is below 100°C. For high service temperature, i.e. 125°C, a combination of guinoline and amine-based antioxidants are recommended to scavenge free-radicals and prevent early degradation of the EPDM network structure (see section on Vulcanization for more details).

## Mixing of EPDM Compounds

The prime objective in mixing the formulation ingredients is to obtain a homogeneous incorporation of carbon black and oil in the polymer, i.e. a compound. The mixing conditions should be designed in such a way as to avoid undispersed polymer, black or oil. The mixing of EPDM compounds is preferably done in an internal mixer, but can also be accomplished, at reduced production efficiency on an open mill.

## Internal Mixing

The mixing of EPDM stocks in an internal mixer is preferred for all polymer grades. The low to intermediate molecular weight grades (those with a Mooney viscosity in the range of 20-50) begin incorporating fillers immediately. Higher Mooney (high-ethylene grades) are usually available in friable bales. This easy-mixing form facilitates rapid ingestion of compounding ingredients in an internal mixer. Oil extended grades are designed to simplify rapid dispersion of fillers and process oil, mainly in recipes where the plasticizer is very high, as in low hardness compounds. The optimum batch size or loading in an internal

mixer is dependent on both machine considerations and compound viscosity. Mixer conditions include rotor design and speed, ram pressure, and rotor-wall clearance. Depending on these parameters and a compound hardness in the range of 60-70 Shore A, a fill factor of 0.75 is typically used. The size of the batch is then computed from the mixer volume and the compound density as follows:

#### Batch Size = density x mixer volume (cm³) x fill factor

For a compound hardness above 70 Shore A, the fill factor ranges from 0.60-0.70 in order to reduce the shear heat build-up. Whereas for soft compounds below 60 Shore A, the fill factor is increased to the range of 0.80-0.87 to generate enough shear for improved filler dispersion.

EPDM compounding and mixing differs from the other technical rubbers in the sense its polymer content is minor vs. fillers and oil. Therefore to improve the productivity and the dispersion quality, it is recommended to use an "upsidedown mixing method" with the EPDM. By adding first carbon black, mineral filler, additives and oil, the apparent volume occupied by the powders is reduced quickly due to wetting by the oil, allowing the introduction of the polymer at the optimum mixer volume loading for best mixing efficiency. The mixing power then reaches a peak at about 80 to 90°C, indicating that the filler incorporation completed. After a ram-up for cleaning and for air elimination, the power decreases, signaling an effective filler dispersion work. Generally the masterbatch dump occurs at 120 to 150°C, depending on the compound viscosity. The curatives are introduced into the master batch during a second pass process in the internal mixer, at a lower temperature, generally 70 to 90°C. The second pass can also be carried out on a mill or in a kneader. It is possible to produce the full EPDM batch in one pass when intermeshing rotors, good temperature control and PLC monitoring are available. The cycle differs from above by a reduction of the rotor speed after an earlier "ram-up" to control the temperature rise. The curatives are then introduced at about 80-90°C with a dump temperature not exceeding 100°C to prevent a pre-scorching effect. For certain applications, the batch from the internal mixer is dumped on a series of open mills having a stock blender to cool down and finalize the dispersion of the fillers and curatives. This is particularly important in the one-pass mix procedure, where the residence time in the internal mixer is short. For applications requiring the best surface aspect, like automotive weatherseals, it is recommended to filter the stock in a strainer and gear pump to eliminate all undispersed particles, typically carbon black grits and mineral fillers agglomerates.

Compounds having low filler content are mixed according to a "conventional" procedure. The ingredients are added in the following order: polymer, zinc oxide and stearic acid first after masticating the rubber bale. Then one-half filler is introduced during oil injection, and then the remaining fillers, dumping the mix at similar temperatures as described above. It is also possible to run a one-pass mix procedure, respecting the tight temperature control with the rotor speed variation. Soft sponge stocks, compounds with very high oil levels, low filler content and low-viscosity stocks should be mixed according to conventional

procedure with oil introduction in two shots to maximize the shear for best filler dispersion. Generally, the mixing time in a large internal mixer does not exceed three to four minutes.

The milling of properly compounded EPDM stocks can be easily accomplished on cool two-roll mills, but with a lower productivity than in internal mixer. Typically, compound will stay longer on a follower (dump) open-mill to cool down and complete the filler and curatives dispersion. Generally in modern plant layout, open mills are used to increase the productivity by cooling the batch and finalizing the filler dispersion during the time a new batch runs in the internal mixing. Even the most temperature sensitive accelerator can be added at that time on open mill.

### Mill Mixing

Polymers having a Mooney viscosity of 20-50, as well as oil extended grades, are especially recommended for mill mixing. The EPDM is first plasticized on the mill, banding on the fastest and coldest roll. The polymer has an initial tendency to resist banding, which is overcome after a few passes through a tight nip. Once a band is formed, the stearic acid, zinc oxide and filler should be added as rapidly as the polymer will incorporate these ingredients, without concern about large amounts of unmixed filler on top of the mill. Process oil should be added with the carbon black to avoid mill surface lubrication and loss of banding. To save time, a manually prepared pre-mix of black and oil may be used. Such a pre-mix consists of all the oil plus sufficient carbon black to make a somewhat dry paste – usually about equal weights of carbon black and oil. Leaving a small amount of stock on the mill, for "seeding" the next batch to be mixed, can save mixing time. During mixing, the batch may flip to the faster roll. If a temperature differential is maintained between the rolls, the batch should return to the cooler, slower roll when the addition of compounding ingredients is complete.

## Vulcanization of EPDM Polymers

Vulcanization (also called curing) is primarily a crosslinking process in which chemical bonds or bridges are formed between adjacent polymer chains. The nature of the resulting three-dimensional network crosslink is characteristic of the cure system employed. This irreversible process enhances the strength and elastic properties of the rubber compound and imparts greater dimensional stability and reduced set or creep over a wide temperature range. The elastomeric material becomes less plastic and more resistant to swelling in organic fluids. However, once the vulcanization process is complete, the rubber compound (usually called a rubber vulcanizate) cannot be recycled in the usual sense, unlike a thermoplastic material. Ethylene and propylene are the basic monomeric units of EPDM elastomers, and the generalized structures are presented in Figure 10. These chemical formulas are oversimplified. Of particular interest here is the location of the tertiary and allylic hydrogen in the EPDM chain.



Figure 10: Chemical Structure of Ethylene-propylene Rubber

### Peroxide Crosslinking

EPM copolymer is crosslinked exclusively via a free-radical mechanism. This is usually accomplished via the decomposition of organic peroxides. EPM curing using electron beam irradiation is also possible. Diacyl (VAROX® A-75) and dialkyl (VAROX VC-R, and VAROX DBPH) peroxides such as t-butyl perbenzoate (VAROX TBPB) are commonly used. Dicumyl peroxide (VAROX DCP) is widely used although there is a concern about odor from its acetophenone by-product. The mechanism of peroxide crosslinking involves the decomposition of the peroxide to form peroxy radicals that abstract the tertiary hydrogen on the copolymer main chain to form polymer radical.⁴³⁻⁴⁵ A polymeric radical subsequently combines with an adjacent polymer radical to complete the crosslink. This reaction is explained in detail in the "Peroxide Crosslinking of Elastomers" chapter of this handbook.

In general, free-radical vulcanization is enhanced by utilizing polyfunctional coagents such as ethylene dimethacrylate, triallyl cyanurate, trimethylolpropane trimethacrylate, and maleimides in appropriate levels. Coagents increase the crosslinking efficiency of the peroxide, overcome steric-hindrance effects, and minimize undesirable side reactions which may inhibit obtaining a good state of cure.⁴⁵ However, the decomposition rate of the peroxide, which is a function of temperature, is not altered.

Acidic compounding ingredients such as fatty acids (stearic acid), low pH carbon blacks (lower than 6) and low pH silica, promote ionic breakdown of peroxides and should be avoided.⁴³ Calcium stearate can be employed in place of stearic acid with peroxide cures. Aluminum silicate-based clays, which are widely used in mineral-filled compounds, are also acidic in nature. Antidegradants like AGERITE® RESIN D® may be added to the compound to insure that the peroxide decomposes radically rather than ionically. Antidegradants can reduce peroxide crosslinking efficiency by interfering with free radicals before they can react with

the polymer chain. One undesirable side reaction with free-radical vulcanization is the competing chain breakdown at the tertiary hydrogen site. For this reason, higher ethylene grades of EPM, which have fewer sites, are preferred for peroxide vulcanization, whenever rheological or end-use considerations permit. The nature and quantity of peroxide agents for EPM should be adjusted to meet individual needs for scorch safety, cure development and compound properties.

Peroxide-cure systems can also be used with EPDM. The principal sites for crosslinking are at or near the side chain double bond on the diene.⁴⁶ Reactivity rates are significantly greater for EPDM terpolymers due to the presence of allylic hydrogen on the diene. Peroxides are used with EPM and EPDM when elastic property retention and lowest compression set are required at high service temperatures, >150°C. Generally, these are high-quality compounds in which the process oil level is minimized to avoid interference of the active freeradical with the polymer network. An example of a low Mooney EPDM polymer molding compound cured using peroxide is given in Table 23. Higher modulus vulcanizates can be achieved with increasing peroxide concentration, but it will be detrimental to elongation at break. Curing EPDM with peroxide requires an environment free of oxygen to minimize chain scission and depolymerization of the EPDM, noticeable by a tacky surface and carbon black staining. This is particularly sensitive in extrusion, where microwave / hot air oven cannot be used, in steam cure where a deep purging of the vessel is necessary before proceeding to the cure (i.e. coolant hoses) and in molding to prevent excessive mold fouling.

### Sulfur Vulcanization

Sulfur vulcanization⁴⁷⁻⁵¹ through the diene is used in the majority of EPDM applications. The type of crosslink is related to the specific cure system used. High sulfur systems favor the formation of a polysulfidic bond. These vulcanizates offer high stress-strain properties and good flexibility, but thermal stability is lower compared to sulfur donor systems generating monosulfide bonds. Vulcanization rate is related to the amount and type of diene present in the polymer, as well as to the cure system. When properly boosted with ultra accelerators, a nominal 5 weight percent ENB grade can be vulcanized in fast cure cycles. However, the amount of diene is not the only controlling factor. Narrow MWD polymers attain a higher cure rate and state than do broad MWD polymers as illustrated by the cure meter traces in Figure 11.



Figure 11: Effect of Molecular Weight Distribution on Cure State⁶

A basic sulfur cure system for EPDM consists of sulfur or sulfur-donors, primary accelerators (thiazoles, sulfenamides) and ultra accelerators (thiurams, dithiocarbamates). Usually, combinations of benzothiazole derivatives or sulfenamides with so-called ultra-accelerators like thiuram compounds or dithiocarbamates are used.⁵² Organic accelerators critical to the use of sulfur as a vulcanizing agent tend to be based on one of five structures: a thiazole, thiocarbamyl, alkoxythio carbonyl, dialkylthio phosphoryl or a diamino-2,4,6-triazinyl (see Figure 12).⁵³ The presence of fatty acid (stearic acid) and zinc oxide forms a complex with the sulfur-based chemical species that is soluble in the rubber compound to allow reaction with the double bonds of the EPDM (see Figure 13).⁵⁶ The cure rate is affected by the content of zinc oxide and its form. Finely divided ZnO (called "active") is effective to reduce the cure time, and in particular the scorch time that is used to improve productivity of continuous vulcanization processes.



Figure 12: Fundamental Structures of Organic Accelerators 53



Figure 13: Probable Mechanism of Thiuram Accelerated Vulcanization⁵⁴

Compared to more highly unsaturated rubbers, very large amounts of thiuram and dithiocarbamates are used in EPDM; up to 2 to 3 phr of each can be used in some applications. The solubility of these accelerators is limited in EPDM, and hence mixtures of accelerator are used to keep the individual amount of accelerators below the solubility threshold for each one and to obtain EPDM vulcanizates with high state of cure. Bloom resistance is also a factor in choice of a sulfur system. Bloom is a gradual migration to the surface of a slightly soluble by-product of sulfur vulcanization, usually a zinc dialkyl dithiocarbamate. Bloom is especially sensitive to press cures. Limited amounts of mixed accelerators give less bloom than equivalent amounts of a single accelerator due to solubility reasons. Polyethylene glycol (i.e. PEG 3350) inhibits the formation of bloom by increasing the solubility of the accelerators. Some sulfur-cure systems which bloom in press cures do not give bloom in steam cures. The use of polyethylene glycols may result in reduced Mooney scorch values and faster cure development in the compound. See Table 6 for low cost cure and fast cure sulfur compound formulations. Sulfur vulcanization is very robust and most of the curing processes, pressured and pressureless (molding or steam, microwave, hot air, Rotocure, etc.) can be used without restriction. It is also the lowest cost curing system.

Accelerators containing secondary amine groups embedded in their chemical structure such as thiurams, dithiocarbamates and some sulfenamides when used with sulfur results in the formation of carcinogenic secondary N-nitrosamines (Figure 14) as by-products. During the vulcanization process accelerators such as tetramethylthiuram disulfide (TMTD) are partly decomposed to their parent

secondary amines. Reaction with atmospheric nitrogen oxide can lead to N-nitrosamine generation. Such accelerators are restricted in some countries. New ultra-accelerator systems like BENZYL ZIMATE® (zinc dibenzyldithiocarbamate) or BENZYL TUADS® (tetrabenzyl thiuramdisulfide) may be used in such cases. This exception is due to the thermal stability of the secondary amine formed (Figure 15) and it not volatizing to react with atmospheric nitrogen oxides due to its decomposition temperature of 300°C.⁵⁵



Secondary Amine Nitrogen Oxides Nitrosamine

Figure 14: Nitrosamine Formation⁵³



dibenzyl amine

Figure 15: Degradation Product of TBzTD⁵⁵

### Resin Vulcanization

Alkyl phenol-formaldehyde resins or polyhalomethylol resins can be used to cure EPDM for extreme heat and compression set resistance, and for high temperature curing stability.⁵⁶ A Lewis acid, like SnCl₂ or chlorosulfonated polyethylene (Hypalon[®] 40), and zinc oxide are used as activators. The initiating process is the formation of a benzyl carbonium ion from a methylol group of the resin. Zinc oxide reacts with halogen to catalyze the carbonium ion's attack on the olefin residue of the polymer, producing a carbon-carbon crosslink.^{57,58} Resin vulcanization is less commonly used for thermoset EPDM application. Resin vulcanization is the choice cure system for thermoplastic vulcanizates (TPVs).

# Properties of EPDM Rubber Compounds

Materials chemists and engineers design EPDM compounds with a target vulcanizate and processing performance for a given application. Each compounding ingredient is carefully selected to aid in plant processing, and/or enhance the properties of the base polymer in the compound, and effect vulcanization. Ethylene-propylene rubber compounds do not require the use of expensive antiozonants which can bloom and/or stain. This is an important contribution of the saturated nature of the molecular backbone.

Properly formulated ethylene-propylene rubber vulcanizates display many important properties such as:

- Outstanding resistance to ozone attack
- Excellent weathering ability
- Excellent heat resistance
- Wide range of tensile strength and hardness
- Excellent electrical resistance
- Flexibility at low temperatures
- · Good chemical resistance, especially to polar media
- Resistance to moisture and steam

The ethylene-propylene rubber compounds impart these significant features by virtue of the outstanding properties of the EPDM molecule. EPDM compounds cannot be used in service with aliphatic solvents, gasoline and oil. There is a rapid swell leading to the destruction of the compound. Only compounds adequately formulated with high molecular weight EPDM can resist occasional exposure to these fluids. See the oil resistance section below for a more detailed discussion. Typical ethylene-propylene rubber compound and vulcanizate properties are further described in Table 9.

The compounding versatility of EPDM elastomers is very broad and the wide range of properties obtained with EPDM elastomer compounds spans a large area of heat and oil resistance attributes for elastomers as depicted by D 2000 Matrix in Figure 16. EPDM compounds meet BA, CA, DA, BC and BE material classifications, as noted by the shaded area of the chart.

Property	Typical Value Range
ASTM D 2000 Classification	BA, CA, DA, BC, BE
Mechanical Properties	
Hardness, Shore A	35 to 95
Tensile, MPa	4 to 22
Elongation, %	150 to 1000
Tear Strength, kN/m	15 to 50
Compression Set, 70 hrs. @ 150°C, 25% Deflection %	15 to 35
Electrical Properties	
Dielectric Constant	2.8
Power Factor, %	0.25
Dielectric Strength, kV/mm	26
Volume Resistivity, ohm-cm	1 x 10 ¹⁶
Thermal Properties	
Brittleness Point, °C	-55 to -65
Minimum Temperature for Continuous Service, °C	-50
Maximum Temperature for Continuous Service, °C	150
Maximum Temperature for Intermittent Service, °C	175
Maximum Theoretical Temperature to Break Hydrocarbon Bonds, °C	204
Heat Capacity	
N650 (40), GPF Oil (40), J/(kg·K)	1950
N650 (160), GPF Oil (100), J/(kg•K)	1790
Dynamic Properties	
Resilience (Yerzley), %	75
Elastic Spring Rate (15Hz), kN/m	550
Loss Tangent (15Hz), %	14
Chemical Resistance	
Weather	Excellent
Ozone	Excellent
Radiation	Excellent
Water	Excellent
Acids and Alkalis	Excellent to Good
Aliphatic Hydrocarbons	Fair to Poor
Aromatic Hydrocarbons	Fair to Poor
ASTM Oils	Fair to Poor
Oxygenated Solvents	Good
Animal and Vegetable Oils	Fair
Brake Fluid (non-petroleum)	Excellent
Glycol-Water	Excellent
Flame Resistance, Limiting O ₂ Index	Poor (can be improved by reformulating)

Table 9: Typical Properties of EPDM Compounds and Vulcanizates⁵



As noted before, much of the environmental stability of EPDM results from the fact that side-chain double bonds, although reactive, do not act as sites for polymer chain breakdown. Table 10 and Table 11 compare EPDM properties to those of other commonly used rubbers containing main-chain double bonds. EPDM elastomers compounds show excellent ozone resistance and weathering performance compared to other rubber compounds.

Rubber Type	EPDM	NR*	SBR*	IIR*	CR*
Specific Gravity (Polymer), g/cm ³	0.86	0.92	0.94	0.92	1.23
Tensile, MPa (max.)	22	28	24	21	28
Elongation, %	500	700	500	700	500
Operating Temperature, °C (max.)	150-175	75-120	75-120	35-180	90-150
Brittle Point, °C	-65	-55	-60	-60	-45
Compression Set, 22 hrs. @ 100°C, %	10-30	10-15	15-30	15-30	15-30
Resilience (Yerzley), %	75	80	65	30	75
Tear Strength, kN/m	15-50	35-45	25-35	25-35	35-45
Dielectric Constant	2.8	2.9	2.9	2.5	6.7
Volume Resistivity, ohm•cm	10 ¹⁶	10 ¹⁵	10 ¹⁵	10 ¹⁵	10 ¹²

Table 10: Physical Properties of EPDM vs. Other Diene Rubbers⁵

(NR) Natural Rubber, (SBR) Styrene-Butadiene Rubber, (IIR) Isobutylene-Isoprene Rubber (Butyl Rubber), (CR) Chloroprene Rubber (Neoprene)

Rubber Type	EPDM	NR	SBR	lir	CR
Weathering	E	F to G	F to G	Е	G
Ozone Resistance	E	Р	F	G	G
Acid and Alkali Resistance	G to E	G	G	G	Е
Oil and Solvent Resistance	P to F	Р	P to F	Р	G
Abrasion Resistance	F	G to E	G	P to F	G to E
Compression Set	G to E	E	G	G	G
Tear Resistance	F to G	E	F to G	F	G to E
Low Temperature Flexibility	G to E	G to E	F to G	G to E	F
Steam Aging	G to E	Р	Р	E	G
Air Permeation	F	F	F	E	F

 Table 11: Resistance of EPDM vs. Other Diene Rubber Vulcanizates

E= Excellent, G= Good, F= Fair, P= Poor

Heat aging studies indicate that properly compounded EPM/EPDM vulcanizates provide excellent heat resistance properties and are suitable for continuous service up to 150°C, with excursions up to 175°C. This excellent performance by a hydrocarbon rubber is attributed to the completely saturated polymer backbone and the isolation of the pendant olefinic sites from the main polymer chain. Thus, EPM/EPDM offers the best heat resistance of the general purpose rubbers and is more cost-effective than special purpose rubbers. In EPDM, free radical vulcanization resulting in carbon-carbon crosslinks gives better heat aging than the best mono-sulfidic sulfur crosslinks.

Ethylene-propylene rubber vulcanizates demonstrate excellent resistance to acids, alkalis and hot detergent solutions. EPM/EPDM is also resistant to salt solutions, oxygenated solvents, synthetic hydraulic fluids and, to some extent, animal fats. Table 12 gives the results of immersing a typical EPDM compound in different solvents and chemical solutions. This compound is based on a high Mooney EPDM, medium level of ENB grade with 200 phr of N550 carbon black, 100 phr of process oil, and a sulfur cure system. It was not optimized for maximum resistance to any particular chemical or class of chemical reagents. Although ethylene-propylene rubber compounds have only limited resistance when immersed in hydrocarbon solvents, such as toluene and gasoline, they can be useful in a hydrocarbon atmosphere when exposure is intermittent or mild. This is evident by their successful use in automotive underhood applications.
	Volume Change, %	Retained Tensile, %	Retained Elongation, %	Hardness Change, Pts.
Hydrocarbon Oils and Solven	ts (Immersec	1 72 hrs. @ 10	0°C or 72 hours	@ Solvent B.P.)
IRM 901 Oil (paraffinic)	+57	108	89	-31
IRM 903 Oil (aromatic)	+103	65	68	-39
Hexane	+60	59	48	-28
Methyl Ethyl Ketone	-9	77	64	+4
Perchloroethylene	+69	61	61	-38
Toluene	+97	42	48	-38
Ester Plasticizer				
Dioctyl Phthalate	+3	112	84	-2
Aqueous Solutions				
Distilled Water	+1	117	87	0
Detergent (1%)	+2	120	86	+1
Hydrochloric Acid (10%)	+9	121	87	-4
Sodium Chloride (25%)	0	123	89	-3
Sodium Hydroxide (10%)	+1	126	89	+2

Table 12: Chemical Resistance of a Typical EPDM Rubber Vulcanizate⁵

The resilience of a very high MW EPDM vulcanizate at room temperature is less than that of natural rubber, and generally equivalent to styrene-butadiene and polychloroprene elastomers. Although the low temperature brittle point of ethylene-propylene rubber is about the same as that of styrene-butadiene rubber, it retains a greater percentage of its resilience at low temperatures. Figure 17 shows this in terms of stiffness. Recovery from compressive load deflection at low temperature is highly dependent upon the composition of the monomers in an EPDM elastomer. Low ethylene-to-propylene ratio of monomers results in rapid recovery following load deformation. This is due to the level of crystallinity in certain grades. Low ethylene polymers have essentially amorphous morphology and recover from low temperature compression faster than their higher ethylene counterparts. A comparison of the low temperature recovery following compression-deflection at -40°C is shown in Figure 18.



Figure 17: Stiffness in Torsion (Logarithmic Scale) vs. Temperature⁵



Figure 18: Effect of Ethylene on Recovery From Compression @ -40°C5

The dynamic response of ethylene-propylene rubber compounds is close to that of natural rubber compounds as indicated in the Yerzley Resilience test comparison shown in Figure 19. Ethylene-propylene rubber, however, can be a good choice for dynamic parts because its age resistance better preserves initial design characteristics with time and environmental extremes. EPDM is a good first choice when high resiliency is desired. Where high damping is called for, butyl rubber is the proper choice as shown in the Yerzley Resilience test.



Figure 19: Yerzley Resilience Test Results⁵

# **EPDM Compound Selection for Specific Properties**

## **Oil Resistance**

The molecular structure of EPDM elastomers is similar to that of other nonpolar hydrocarbons, so that they are usually rated "poor" in their resistance to such oils and solvents. However, proper polymer selection and compounding enable EPDM polymers to be used in moderate oil resistant applications. High molecular weight, high ethylene content grades which are highly loaded with fillers and process oil yield a less degree of swelling in ASTM No. 3 oil. EPDM grades with a very high ENB content give low volume swell in oil and are recommended as long as physical properties are not compromised. The combination of high molecular weight and high ethylene permits the maximum filler loading to be utilized. This, in turn, limits the amount of polymer, which swells as it absorbs the hydrocarbon fluid. A high level of process oil, in effect, pre-swells the polymer so that it retains its dimensions and properties to a greater extent after immersion in oil. Very high ethylene grades (above 77-78%) cannot accept high levels of process oil without significant bleeding shortly after incorporation. The influence of filler and oil loading, EPDM ethylene content and molecular weight on oil swell of the vulcanizates is illustrated in Figure 20. In this example, the test fluid is ASTM No. 3 oil. This oil has since been replaced with IRM 903, and similar performance is expected in this test fluid.





## Heat Resistance

EPDM polymers can be compounded to achieve good heat aging performance at a temperature of 175°C. Selection of the appropriate grade of ethylene-propylene rubber and cure system primarily dictates the level of heat resistance. However, the type of plasticizer in the compound, and the inclusion of antioxidants or heat stabilizer additives further extend the service life while exposed to heat. All EPDM terpolymers are suitable for heat aging service up to 100°C. From 100 to 150°C, high molecular weight, high ethylene and low ENB content grades are preferred. Sulfur-donor cure systems are also recommended for heat aging requirements at 125°C and 150°C. Above 150°C, EPM copolymers and peroxide cure systems are required. When exposed to prolonged heat, ethylene-propylene rubbers exhibit an increase in hardness and a loss in elongation. The mechanism involves the absorption of oxygen within the network, causing cyclization or continuous crosslinking. Antioxidants such as the mercaptobenzimidazole derivatives (VANOX® MTI and VANOX ZMTI) are especially useful to inhibit oxygen uptake in EPDM. Adding 5 to 15 phr of metal (Zn or Mg) oxide, in combination with the antioxidant, is very effective in extending the service life.

# Processing Performance

Collapse resistance is important in continuous vulcanization because of the high temperatures and the buoyancy pressures of the solid and liquid media. High molecular weight and very high diene EPDM grades are preferred for maximum collapse resistance. Both types of polymers also resist the development of porosity at the high cure temperatures, preventing deterioration of quality and giving higher output.

The processing characteristics of rubber compounds are primarily governed in order of importance by polymer type (ENB content, MW), carbon black content, oil content, and carbon black and oil type. Refer to Table 4 to review the effects of Mooney viscosity, ethylene content and MWD on processing characteristic of a compound. Medium and large particle size carbon blacks with high structure are usually used for the many extrusion applications for EPDM grades. Among these are N550, N650, N762 and N683. N990 carbon black is also used in specialty stocks. These carbon blacks may be interchanged according to a simple rule of thumb based on oil absorption:

- 100 parts N550 absorb about 110 parts oil
- 100 parts N650 absorb about 110 parts oil
- 100 parts N762 absorb about 70 parts oil
- 100 parts N990 absorb about 30 parts oil

N330 and other fine particle carbon blacks are seldom recommended in EPDM. Special circumstances may call for them, but good dispersion is difficult in the presence of the large amounts (25 to 100 phr) of oil necessary to reduce compound viscosity. High-viscosity paraffinic process oils are best for physical property development. Medium-viscosity naphthenic oils also perform well.

The contour curve is a very useful method of presenting rubber compounding data. It is similar to a line of constant elevation on a topographical map, representing a single value over the range of the grid coordinates. In rubber technology, the coordinates are usually expressed in loading levels of fillers and plasticizers in the compound. A blend of EPDM grades or concentration of curing agent may also represent one axis on a chart. The family of curves so generated is called a contour plot and can be used in two different ways: to determine the general effect of the compounding variables, i.e. filler, oil, EPDM blend, curing agent, etc., on a property of interest; or to select a combination of filler and plasticizer, polymer blend system, or curative concentration to produce a desired property value. Generating a library of contour charts helps the application technologists for faster compound development and troubleshooting.

#### **Vulcanization and Processing Methods**

EPDM rubber compounds can be vulcanized on all common rubber curing factory equipment such those used in the compression molding, transfer molding, injection molding, steam curing, hot-air curing, and salt bath curing processes. The various types of molding are covered in detail in the *Molded Goods* chapter of this book.

All EPDM grades may be used in these molding operations, but each of these molding methods requires a different compounding approach to achieve efficient mold fill. The low Mooney, fast curing (high and very high diene) EPDM grades are preferred in the more sophisticated transfer and injection processes. Because of their excellent flow characteristics and fast cure rates, compounds using low MW EPDM grades have found wide application in highquality or intricately designed molded parts. Also, many molded sponge articles take advantage of the fast-cure and low-density possible with these grades. Higher Mooney grades are also applicable for molding operations as long as the compounds have adequate scorch safety and low viscosity for mold fill. The specific techniques for molding EPDM compounds are similar to those used for other elastomers.

Similar to other rubber compounds, EPDM compounds can be fabricated by the extrusion process, where cold-feed equipment is preferred. Compounds with high cold green strength process better on cold-feed extruders. In general, crystalline EPDM, having high molecular weight, provides high green strength, good extruder feed and fast extrusion rates. The high ethylene content helps to provide some thermoplasticity to the compounds. Green strength tends to decrease with increased temperature, and cool stocks (<40°C) feed best on cold-feed extruders. Maintaining relatively low feed temperature will avoid slippage between the stock and the screw and provide consistent extrusion. Only very high hardness compounds (90 Shore A+) require hot feeding. Typical processing conditions for a 80 Shore A compound are: feed zone (40°C); metering (70°C); screw (50°C); Die (60-90°C), depending of the compound viscosity. Extrudate temperature is generally kept between 70 and 100°C to prevent pre-scorch in extruder head.

Calendering is the fabrication method of choice for producing EPDM membranes that are used in pond or ditch liners, moisture barriers and single ply roofing membranes. EPDM compound rheology has to be carefully designed for viscosity control, dimensional stability and gauge uniformity. Low to medium crystallinity, medium molecular weight and broad molecular weight distribution EPDMs are suitable for good calenderability. Use of high-structure fillers and compatible, high-viscosity plasticizers will insure optimum performance. Two-, three-, and four-roll calenders are all used to form suitably compounded EPDM grades into sheet materials. Processing temperatures are selected to effect stock release from the hotter rolls. Forming roll temperatures are maintained at 80 to 110°C, and release rolls from 90 to 120°C. A minimum temperature differential of 10°C is recommended with the final range selection, depending upon compound design, desired dimensional tolerances and operating speed. Optimum gauge control and minimum shrinkage are consistent with high roll temperatures and good down-stream cooling via stacked drums. In the case of three-roll calenders, it is possible to use the third roll for cooling purposes. However, its temperature will be determined by the process: a warmer roll is necessary for ply-up and skimming operations.

Open steam in an autoclave has long been used to cure extruded or calendered products. With this method, articles are fabricated or formed in a continuous operation (i.e. sheets, profiles, hoses, etc) and accumulated for later batch vulcanization in a steam autoclave. The article may be in direct contact with the steam or wrapped with fabric tape during vulcanization. Preferably EPDM with low ENB (~3%) content is used for slow cure rate and to obtain a uniform crosslink density between the core and the outside layers of rubber compounds, example roof sheeting. Low ENB EPDM is also used for peroxide cured

automotive and industrial hoses that are preformed on a mandrel. The autoclave must be purged from air before curing to prevent EPDM depolymerization and sticky part surface.

Continuous vulcanization (CV) has the advantage of combined processing and curing steps into one continuous operation. Basically, there are four stages to the continuous vulcanization process:

- 1. Formation of the profile through the die
- 2. Heating to curing temperature
- 3. Curing
- 4. Cooling

Heat may be generated inside the extrudate by dielectric heating (Ultra High Frequency (UHF)), by friction (Shear Head), or by heat transfer from the outside (Infra-red, Hot Air, Fluid Bed, and Liquid Curing Media (LCM)). Curing is achieved by maintaining the temperature for the time needed to fully crosslink the rubber. Ethylene-propylene rubber itself is non-polar and does not respond to UHF heating, but common compounding ingredients like carbon black increase microwave receptivity. Extrusion grade carbon blacks, GPF N660 and FEF N550, work well, as does polar materials such as polyethylene glycol. More recently, Electron Beam Radiation has attracted some attention. A high molecular weight, high ethylene content, and narrow MWD ENB grade shows particularly good cure response to this method.

# Applications

The use of ethylene-propylene elastomers spans a broad range of technologies within the rubber industry, as listed in Table 13. Each market segment takes advantage of the many key benefits of EPDM-based rubber: excellent ozone and weather resistance, excellent heat resistance, low compression set, and low temperature flexibility, all combined with economy of manufacture. In the selected examples that follow, at least one compound in each industrial application is illustrated. In this section, a short description of the different EPDM applications, a typical compound formulation, and properties for the respective application are given.

	Market Segment			
Product	Automotive	Industrial Goods	Building and Construction	Electrical
Belting		Х		
Dense seals	Х		Х	
LV, MV, Wire and Cable				Х
Extruded Sponge	Х		Х	
Hose and Tube	Х	Х		Х
Molded Goods	Х	Х	Х	Х
Molded Sponge	Х	Х		
Sheeting			Х	
Thermo Plastic Olefins (TPO)	Х		Х	Х
Thermoplastic Vulcanizate (TPV)	Х	Х	Х	Х

 Table 13: Product and Markets Using Ethylene-propylene Rubbers

## Automotive

EPDM compounds are used for window channels, weatherstrips (sponge and dense), mounts, vent strips, car body sponge seals, brake parts, hose, tubing, protective strips and hydraulic seals. EPDM compounds are used for exterior parts where resistance to weathering like weatherseals and for under the hood parts where resistance to heat are required. Body seal formulations have generally a fast curing EPDM for high extrusion speed and good compression set. This maintains a balance between the vulcanization reaction and decomposition of the blowing agent, to control the formation and the dimension of close cells. EPDM properties (molecular weight, ethylene content, ENB content) are critical for the best sealing properties: low door closing effort over a wide range of temperature, retaining the contact force over the life time of the automobile. Therefore preferred EPDM characteristics for this application are: high MW to produce soft compounds with high elasticity; low ethylene content to maintain low rigidity, even at -30°C; high ENB content for fast curing to generate a closed skin; controlled cell dimension; and high crosslink density for long term compression set. Table 14 shows a typical sponge profile formulation.

EPDM compounds are also the choice for window channel applications, replacing SBR due to the inherent ozone resistance, weatherability, and ability to be compounded for resistance to paint stain, making it ideal for this application. Additionally, requirements become more severe as automotive companies trend toward the flush-glass design which exposes more of the window channel surface to the environment. Some of the requirements for window channel compounds are:

- Low compression set
- Good heat aging property retention

- Smooth extruded appearance
- Very fast cure
- Good flock and metal adhesion
- Ability to be corner molded
- · Ability to form tight seals to minimize wind noise
- · Easy installation

Table 15 provides an example of a window channel formulation which was compounded to meet the above requirements. A cure system of low sulfur with sulfur donors is used to favor the formation of monosulfidic crosslinks for optimum heat aging. Resilience is important for noise insulation. Therefore high molecular weight EPDM with high ENB content is generally selected. The need to achieve good flock adhesion as well as to establish a high state of cure in the short time available in continuous vulcanization requires the use of a high diene EPDM polymer base. Low hardness compounds (< 50 Shore A) are also used in sealing applications, which requires compounds with a higher amount of oil than carbon black. Therefore processing (mixing, extrusion) is critical and requires high molecular weight oil extended EPDM to accept and disperse a high amount of plasticizing oil, as well as provide sufficient collapse resistance during the extrusion of such low viscosity compounds.

#### Automotive and Industrial Hose

EPDM rubber compounds are widely used in many automotive and industrial hose products, taking advantage of their outstanding thermal and oxidative stability, and their excellent chemical resistance to polar organic and aqueous inorganic fluids. EPDM rubber can be compounded to achieve the broad range of tensile strength and durometer required in this application segment. In addition to the usual requirements for mechanical properties, heat resistance and compression set, coolant hoses are also expected to possess good low temperature (-40°C) sealing properties and electrochemical resistance. Collapse resistance is also a key property due to the method of hose fabrication. Hose is generally composed of a tube, extruded first, braided with yarn to provide pressure resistance and then the cover stock is coextruded on top. This uncured hose is then inserted on a mandrel that provides the final shape. This assembly is cured in a steam autoclave for normally 30 minutes at 180°C. If the hose is peroxide cured, the autoclave must be purged from air to prevent the depolymerization of the hose cover. Higher underhood temperatures, as a result of lower hood lines, reduced air flow within the engine area, and turbo charge, have brought about the need for greater heat-resistant compounds for items such as coolant, emission, and brake hoses and air ducts. EPDM polymers for industrial hose and tube applications are normally medium-to-high Mooney and high ethylene content to accommodate high levels of fillers and process oil and have a high collapse resistance. An industrial hose and a coolant hose formulations are shown in Tables 16 and 17, respectively.

#### Building and Construction

Applications include sheet for roofing and waterproofing, profiles for sealing,

window gaskets, bearing pads and sponge pipe insulation. One of the largest applications for ethylene-propylene rubber is single-ply roofing. This application replaces traditional built-up asphalt roofing on the basis of higher performance, life expectancy and lower cost. Today, EPDM roof membranes have gained recognition for being:

- · Architecturally sound and aesthetically pleasing
- Ozone and weather resistant
- Durable
- · Extensible in all directions, over high and low extremes of temperature

In North America, EPDM is specified more than any other single-ply system and covers more roof area than all others combined. Table 18 is an example of EPDM polymer based roof membrane compound.

Extruded building profiles for windows, doors and walls must maintain an elastic seal over a wide temperature range, must also be resistant to weathering, making EPDM an ideal material for this use. The profiles are usually vulcanized continuously with several different CV systems. An amorphous, low ethylene grade insures that low temperature flexibility requirements are met. An example of an EPDM building profile compound is shown in Tables 19.

## Electrical

Applications include power cable and medium-voltage insulation, lowvoltage insulation, cable jackets, connectors and cable filler. Several property advantages of ethylene-propylene rubber have led to its increased use in the electrical industry, where long-term service life is a key performance requirement. In addition to its outstanding ozone and corona resistance, ethylene-propylene rubber has good electrical characteristics, excellent tree resistance, excellent insulation stability in water, and long service even when exposed to extremely high and low temperatures, all essential for wire and cable applications. EPM and EPDM have been used successfully in medium-voltage cable insulation for many years due to their excellent cable flexibility and electrical performance (see Table 20).⁵⁹ Electrical loss limitations for low-voltage insulation are not so strict, and more highly-loaded terpolymer compounds can be used. Peroxide cure is needed for long-term aging stability, electrical properties, and corrosion of the conductor (see Table 21).

Jacketing or sheathing for electrical cables is another use requiring longterm weather stability. Good physical properties for abrasion resistance during installation and maintenance are also required. In the electrical industry, the major applications for molded goods are connectors and accessory components. A large percentage of rubber electrical accessory parts, e.g., push-on connectors, are injection-molded. The three major requirements for an underground residential distribution (URD) connector are to establish and maintain satisfactory electrical connections, maintain a high level of insulation integrity, and provide a good seal against the entrance of water. Ethylene-propylene terpolymers are commonly used in these applications for their outstanding ozone, weathering resistance and good aging properties. A low Mooney, amorphous EPDM is recommended to achieve good dispersion and processibility with carbon black and inorganic fillers. Table 22 is a typical example of a compound used for injection molding URD connectors.

#### Molded Industrial Goods

Applications include pipe and appliance gaskets, o-rings, machine mounts, belting and mechanical goods. Appliances, such as washing machines, require rubbery gaskets and seals with good sealing ability, long life, resistance to aqueous solutions, and good heat resistance. These molded parts can be made from various EPDM polymers as shown by the formulation in Tables 23, 24, 25 and 26. Seals for concrete or plastic underground pipes must offer excellent sealing over long service time. A bimodal EPDM has replaced SBR in this application for its unique weathering resistance combined with a high stress relaxation under compression.

#### Industrial Belts and Power Transmission Belts

EPDM copolymers are increasingly being used as the base material for industrial belts and power transmission belts, specifically automotive V-ribbed belts. Since this type of elastomer is more cost effective and offers broader operating temperature ranges than polychloroprene or its other alternatives. Both sulfur and peroxide cured EPDM compounds have been developed for belt applications. Even though the saturated backbone of EPDM provides good heat resistance, certain antioxidant packages will further enhance it. For example, the combination alpha-methylstyrenated diphenylamine (alpha-MSDPA) with zinc 2-mercaptotoluimidazole (VANOX[®] ZMTI) is suggested for peroxide cured EPDM belt compounds.⁶⁰ Peroxide-coagent cure systems provide improved heat aging over sulfur systems and can also be formulated to have the required balance of properties for automotive V-ribbed belts. Dynamic properties and fatigue resistance of peroxide cured EPDM compounds were found to be significantly enhanced by using zinc diacrylate (ZDA) or zinc dimethacrylate (ZDMA). On peroxide curing, the ZDA becomes incorporated into the crosslink network. When subjected to stress, bonds to the zinc in the network will undergo cleavage and will reform. In another benefit to belt applications, ZDA addition is claimed to enhance rubber/textile adhesion and improved pilling resistance for peroxide cured EPDM.⁶¹ Selection of the right EPDM grade is based on the type of production process being used and the physical properties required for the rubber article. A peroxide cured belt formulation is shown in Table 27.

## Plastic Modification

Elastomers have been used to modify the properties of plastics and extend their performance capabilities, such as stress-crack resistance and low temperature flexibility, since the 1940s. EPDM polymers have proven to be very effective for the modification of polyolefin thermoplastics such as polypropylene, polyethylene, polybutylene, ethylene vinyl acetate (EVA) and ethylene methyl acrylate (EMA). By using various combinations of these polymers, often with the addition of fillers, process oils and other additives, a broad range of thermoplastic olefins (TPOs) of varying modulus can be developed for specific end use applications. In general, TPOs based on polypropylene usually contain 15 to 40% of amorphous and/or semi-crystalline EPDM polymers.⁶²⁻⁶⁴ Blends are tailored through compounding to match specific end-use requirements including flexural modulus, impact strength, paintability and surface appearance. These TPOs were used extensively in the automotive industry for both internal and external applications. The EPDM polymer enhances the rubbery quality of the ethylene copolymer resins, such as ethylene vinyl acetate (EVA) or ethylene methyl acrylate (EMA), and increases their ability to accept fillers. Such blends are used for film applications and in highly filled versions for sound deadening sheeting and thermoformable automotive carpet backing. Although the trend nowadays is to use plastomers (ethylene-octene, ethylene-butene types) for plastic modification due to processing and cost benefits, the EP polymers made using the metallocene technology could be equally valuable.

Another class of elastomers that are used in polar plastic modification is the maleic anhydride (MA) grafted (about 1%) EPDM polymers. Addition of 10 to 15% of these MA-grafted EPDM into Nylon compounds improves the cold impact resistance. These products are also used as coupling agents for polar materials dispersed in polyolefin matrix. An example is the polypropylene reinforced with glass fibers. They also are used in halogen free flame retardant thermoplastic cable as coupling agents between the filler (aluminum trihydrate) and the thermoplastic matrix (blend of EVA and EPDM) in order to provide the desired tensile strength. ExxonMobil Chemical sells these grafted EPDM under the trademark of Exxelor[™].

## **EPDM for Thermoplastic Vulcanizates**

Thermoplastic vulcanizates (TPVs) are an emerging class of engineering thermoplastic elastomers (TPEs) which possess the elasticity of conventional elastomers and processability of thermoplastics. TPVs are normally produced by a process of "dynamic vulcanization", which is a process of vulcanizing or cross-linking the elastomeric component during intimate melt mixing with the thermoplastic resin, together with plasticizers (i.e. process oils), fillers, stabilizers, and a cross-linking system, under high shear and above the melting point of the thermoplastic component which is usually polypropylene.^{65,66} EPDM based TPV compositions have found several commercial applications as these materials have high use temperature, solvent resistance and elastic properties to meet the application requirements, in addition they offer low system cost, design flexibility, recyclability, and improved aesthetics. They are particularly useful for making articles by blow molding, extrusion, injection molding, thermo-forming, elasto-welding and compression molding techniques. In addition, thermoplastic elastomers are often used for making vehicle parts, such as weatherseals, brake parts including, but not limited to cups, coupling disks, diaphragm cups, boots such as constant velocity joints and rack and pinion joints, and tubing, sealing gaskets, parts of hydraulically or pneumatically operated apparatus, O-rings, pistons, valves, valve seats, and valve guides.

Ingredients	phr	
Vistalon [™] EPDM 8800	115.0	
Spheron [®] 5000 Carbon Black	90.0	
CaCO₃ Omya BSH	30.0	
Flexon [®] 815 Oil	95.0	
Stearic Acid	1.5	
Zinc Oxide (Active)	4.0	
Carbowax [®] 3350	1.0	
Calcium Oxide	2.0	
	1.5	
ALIAX [®] (MBIS) (80%) Accelerator	1.0	
VANAY® DBC Accolorator	0.0	
RENZYL ZIMATE® (70%) Accelerator	1.8	
Rhenocure® ZAT (70%)	1.0	
Rhenocure TP/G (50%)	1.5	
Celogen® OT	2.0	
Porofor ADC	1.5	
Total	350.1	
Specific Gravity	1.12	
Mooney Viscosity, ML 1+4 (100°C)	28	
Mooney Scorch @ 125°C		
Minutes to 5 pt. rise	3.7	
MDR, arc ± 0.5°, 180°C		
M₋ (dN•m)	0.7	
M _H (dN•m)	10.4	
t _s 2 (min)	0.4	
ť 90 (min)	2.6	
Omega Shape Profile, Extrusion UHF / Hot Air Cured		
Density	0.64	
Surface Roughness		
Ra, µm	3.0	
Compression Load Deflection Force @ 40% Deflection		
Room Temperature N/210 cm	71	
-30°C. N/20 cm	149	
	140	
Extrusion Spood m/min	1	
	4	
Mass Prossure Bar	2.0	
Extruder Outlet Temperature °C	27	
LIFE Outlet Temperature, °C	170	
Wall Thickness, mm	2.8	
	2.0	
Load Deflection Force @ 50% Deflection	- 4	
Room remperature, N/20 cm	/1	
-30 C, N/20 CM	149	
Compression Set on Profile,		
22 hrs. @ 70°C, 40% Deflection, %	16	
1000 hrs. @ 70°C, 40% Deflection, %	46	

 Table 14: Automotive Sponge Door Seal Compound (UHF- Hot Air Process)

Ingredients	phr	
Vistalon EPDM 7500	100.0	
N550 FEF Carbon Black	110.0	
N660 GPF Carbon Black	60.0	
Omyacarb [®] BL Calcium Carbonate	30.0	
Flexon 876 Oil	85.0	
	3.0	
AFLUX [®] 42M	3.0	
	1.5	
	5.0	
Sulfur	1.0	
CAPTAX (MBT) Accelerator	1.0	
METHYL TLIADS [®] Accelerator	0.8	
SLIL FADS® Accelerator	1.0	
ETHYL ZIMATE Accelerator	0.8	
Total	409.6	
Specific Gravity	1.23	
Moonev Viscositv. ML 1+4 (100°C)	63	
$ODR + 3^{\circ} arc + 180^{\circ}C$		
$M_{\rm L}$ (dN·m)	8	
$M_{\mu}$ (dN•m)	55	
$t_{a} 2 (min)$	0.7	
t' 90 (min)	27	
Criticizal Divisional Director Current 4 min @ 1900	2.1	
Unginal Physicals, Press Cured 4 min. @ 180 C	07	
Hardness, Shore A	67	
Tuusiin MD	3.8	
Tensue, MPa	8.7	
Elongation, %	285	
Physical Properties After Heat Aging inAir, 168 hrs. @ 70°C		
Hardness, Shore A	70	
100% Modulus, MPa	3.8	
Tensile, MPa	9	
Elongation, %	225	
Tear Resistance, DIN 53507A		
kN/m	8.1	
Compression Set, ASTM Method B, Press Cured 8 min. @ 180°C		
22 hrs. @ 70°C, %	15	

Table 15: Automotive Dense Weatherstrip Compound (UHF – Hot Air Process)

Ingredients	phr
Vistalon EPDM 5601 N650 GPF-HS Carbon Black N762 SRF-LM Carbon Black Calcium Carbonate	100.00 100.00 90.00 50.00
Sunpar® 2280 Zinc Oxide Stearic Acid	110.00 10.00 1.00
Sulfur METHYL TUADS METHYL ZIMATE BUTYL ZIMATE	0.75 2.50 2.50 2.50
Sulfasan® R (DTDM)	1.70
Total	470.95
Specific Gravity	1.26
Mooney Viscosity, ML 1+4 (100°C)	57
Mooney Scorch @ 125°C Minutes to 5 pt. rise	14.2
ODR, ± 3° arc, 180°C M _L (dN•m)	6.4
$M_{\rm H}$ (dN-m)	61.8
t' 90 (min)	5.2
Original Physicals, Press Cured 4 min. @ 180°C	
Hardness, Shore A	71
100% Modulus, MPa	3.4
Elongation. %	370
Physical Properties After Heat Aging in Air, 70 hrs. @ 125°C	
Hardness, Shore A	76
Tensile, MPa	10.5
Elongation, %	224
Iear Resistance	12.0
DIN 53507A. kN/m	15.7
Compression Set, ASTM Method B, 22 hrs. @ 70°C	
%	7

Table 16: Industrial Hose Compound (Press Cured)

Ingredients	phr	
Vistalon EPDM 7001	100.0	
N650 GPF-HS Carbon Black	70.0	
N762 SRF-LM Carbon Black	100.0	
Sunpar 2280	80.0	
Zinc Oxide	5.0	
Stearic Acid	1.0	
	0.5	
INADS® Accolorator	1.2	
BLITYL ZIMATE	2.0	
Sulfasan R (DTDM)	2.0	
Total	356.9	
Mooney Viscosity, ML 1+4 (100°C)	59	
Mooney Scorch @ 125°C		
Minutes to 5 pt. rise	23.7	
MDR. ± 3° arc. 180°C		
$M_{\rm L}$ (dN•m)	1.6	
M _H (dN•m)	14.5	
t _s 2 (min)	1.7	
ť 90 (min)	3.9	
Original Physicals, Press Cured 4 min. @ 180°C		
Hardness, Shore A	74	
100% Modulus, MPa	4.0	
Tensile, MPa	11.9	
Elongation, %	440	
Physical Properties After Heat Aging in Air, 168 hrs. @ 100°C		
Hardness, Shore A	78	
100% Modulus, MPa	6.7	
Tensile, MPa	14.8	
Elongation, %	270	
Physical Properties After Aging in 50:50 Water/Glycol, 168 hrs. @ 100°	С	
Hardness, Shore A	74	
100% Modulus, MPa	4.7	
Tensile, MPa	13.4	
Elongation, %	366	
Tear Resistance, Press Cured t 90 + 4 min.		
ASTM Die C, kN/m	37	
DIN 53507A, kN/m	16	
Compression Set, ASTM Method B, Press Cured & 90 + 6 min.		
70 hrs. @ 125°C, %	45	

Table 17: Automotive Coolant Hose Compound

Ingredients	phr
Vistalon EPDM 3702	100.0
N650 Carbon Black	80.0
N326 Carbon Black	15.0
	75.0
	4.0
Stearic Acid	2.0
Sulfur	1.0
VANAX NS Accelerator	2.9
BUTYL ZIMATE	0.2
Total	340.1
Mooney Viscosity, ML 1+4 (100°C)	66
Mooney Scorch @ 125°C	
Minutes to 5 pt. rise	37
MDR, ± 3° arc, 160°C	
M₋ (dN•m)	1.7
M _H (dN•m)	20.4
t _s 2 (min)	10.3
ť 90 (min)	24.9
Original Physicals, Press cured ť 90 + 5 min. @ 160°C	
Hardness, Shore A	71
100% Modulus, MPa	2.8
Tensile, MPa	10.2
Elongation, %	460
Physical Properties After Heat Aging in Air, 28 days @ 116°C	
Hardness, Shore A	79
100% Modulus, MPa	5.9
Tensile, MPa	10.7
Elongation, %	260
Tear Resistance, ASTM Die C	
kN/m	36.5
Peel Strength	
Exxon Peel Test, kN/m	15.9
Ozone Resistance @ 40°C	
50% Extension @ 166 hrs.	No cracks

 Table 18: EPDM Roof Sheeting Membrane Compound (Autoclave Cure)

Ingredients	phr	
Vistalon EPDM 3666	175.0	
N774 SRF Carbon Black	110.0	
Sillitin Z	100.0	
Flexon 876 Oil	35.0	
Zinc Oxide	10.0	
Stearic Acid	1.5	
Carbowax 3350	5.0	
Calcium Oxide	10.0	
Silane Polyvest 25	3.0	
Sulfur	1.5	
CAPTAX (MBT) Accelerator	1.5	
METHYL TUADS [®] Accelerator	0.6	
SULFADS Accelerator	1.0	
BUTYL ZIMATE Accelerator	1.0	
	0.8	
Total	455.9	
Specific Gravity	1.23	
Mooney Viscosity, ML 1+4 (100°C)	46	
Mooney Scorch @ 125°C		
Minutes to 5 pt. rise	6	
ODR @ 180°C, ± 3° arc		
M₋ (dN•m)	8	
M _H (dN•m)	35	
t _s 2 (min)	0.6	
ť 90 (min)	1.8	
Original Physicals, Press Cured 4 min. @ 180°C		
Hardness, Shore A	54	
100% Modulus, MPa	2.0	
Tensile, MPa	9.8	
Elongation, %	480	
Physical Properties After Heat Aging in Air, 168 hrs. @ 70°C		
Hardness, Shore A	60.5	
100% Modulus. MPa	3.0	
Tensile, MPa	9.6	
Flongation %	350	
Tear Resistance		
ASTM Die C. kN/m	34	
DIN 53507A	11.3	
Compression Set. ASTM Method B. Press Cured 8 min @ 180°C		
22 hrs. @ 70°C, %	22	

 Table 19: Low-hardness Dense Building Profile Compound

Ingredients	phr	
Vistalon EPDM 1703P	100.0	
Translink [®] 37 Calcined Clay	60.0	
AGERITE MA Antioxidant	1.5	
Drimix [®] A-172 Silane	1.0	
Zinc Oxide	5.0	
Lead Red ERD-90	5.0	
LDPE Escorene ^{TT} LD-400	5.0	
Paraffin Wax (133°F M.P.)	5.0	
	6.5	
Total	189.0	
Specific Gravity	1.2	
ODR, ± 3° arc, 200°C, 30 min. chart		
M _L (dN•m)	8	
M _H (dN•m)	115	
t _s 2 (min)	0.6	
ť 90 (min)	1.7	
Original Physicals, Press Cured 20 min. @ 165°C		
Hardness, Shore A	90	
100% Modulus, MPa	6.8	
Tensile. MPa	11.8	
Elongation, %	250	
Physical Properties After Heat Aging, 336 hrs. @ 150 C		
Hardness, Pts. Change	1	
Tensile. % Change	4	
Elongation, % Change	-4	
Dielectric Strength, V/mil	944	
Dielectric Constant @ 60HZ		
Dry @ Room Temperature	2 64	
14 Days in Water @ 90°C	2 39	
Dissination Factor @ 60 Hz	2.00	
Dry @ Room Temperature	0.25	
14 Days in Water $@ 90^{\circ}$	0.23	
H Days III Water @ 30 C	0.40	

# Table 20: Medium Voltage Cable Insulation

Ingredients	phr
Vistalon EPDM 7001	100.0
Burgess KE Clay	260.0
AGERITE RESIN D [®] Antioxidant	1.5
Drimix A-172 Silane	1.0
Sunpar 2280 OII	70.0
VARUX 602-40KE PEIOXIDE	10.0
Total	442.5
Specific Gravity	1.45
Mooney Viscosity, ML 1+8 (100°C)	59
ODR, ± 3° arc, 165°C, 30 min. chart	
M₋ (dN•m)	7.5
M _H (dN•m)	42.2
ts 2 (min)	2.4
ť 90 (min)	24.7
Original Physicals, Press Cured 20 min. @ 165°C	
Hardness, Shore A	73
100% Modulus, MPa	5.6
Tensile Strength, MPa	8.7
Elongation, %	194
Volume Resistivity,	
Ohm-cm	2.13E+15
Dielectric Constant	
Dry @ Room Temperature	3.0
28 Days @ 90°C	3.2
Dissipation Factor, Original	
Dry @ Room Temperature	0.0047
28 Days @ 90°C	0.0527

Table 21: Low Voltage Welding Cable Insulation Compound

Ingredients	phr
Vistalon EPDM 2504	100.0
Burgess KE	110.0
FEF N550 Carbon Black	2.0
ASTM Type 104B Process Oil	40.0
AGERITE MA Antioxidant	1.0
Drimix A-172 Silane	1.0
Zinc Oxide	5.0
Stearic Acid	1.0
VANFRE® AP-2 Process Aid	3.0
Sulfur	0.2
VAROX 802-40KE Peroxide	6.5
Chemlink [®] 30 Dispersion	1.5
Total	271.2
Mooney Viscosity, ML 1+8 (100°C)	27
Original Physicals, Press Cured 10 min. @ 177°C	
Hardness, Shore A	62
100% Modulus, MPa	3
Tensile, MPa	8.9
Elongation, %	300

 Table 22: Injection Molding Compound for URD Connectors

Ingredients	phr	
Vistalon EPDM 2504	100.0	
N550 FEF Carbon Black	55.0	
PE WAX MANMAY® HISPECIAL	2.0	
Flectol® H	1.0	
VAROX DCP-40C	5.0	
Total	164.0	
Specific Gravity	1.06	
Mooney Viscosity, ML 1+4 (100°C)	75	
ODR, ± 3° arc, 180°C		
M∟ (dN•m)	12	
M _H (dN•m)	120	
t _s 2 (min)	0.9	
ť 90 (min)	6.9	
Original Physicals, Press Cured 4 min. @ 180°C		
Hardness, IRHD	73	
Tensile, MPa	18.5	
Elongation, %	250	
Physical Properties After Heat Aging, 168 hrs. @ 70°C		
Hardness, IRHD, Pts. Change	1	
Tensile, % Change	-10	
Elongation, % Change	-4	
weight, alter 96 hrs., % Change	-1	
Physical Properties After Aging in DOT #4 Brake Fluid, 168 hrs. @ 150°	С	
Hardness, IRHD, Pts. Change	-2	
Tensile, % Change	4	
Volume after 70 brs % Change	16	
	1.0	
Compression Set, ASTM Method B, Press Cured 8 min. @ 180°C	0	
22 1115. @ 70 0, /0	9	

Table 23: Peroxide Cured Molded Brake Part

Ingredients	phr	
Vistalon EPDM 5601 Flexon 876 Oil Stearic Acid	100.0 80.0 1.0	
AGERITE RESIN D	0.5	
Carbowax 3350	3.0	
Zinc Oxide	2.0	
Ultrasil® VN3 Silica	30.0	
Sillikolloid [®] P 87	100.0	
Sultur ALTAX (MBTS) (80%)	0.5	
Rhenocure ZAT (70%)	2.0	
BENZYL ZIMATE (70%)	0.5	
Rhenocure S/G (80%)	1.0	
	327.5	
Specific Gravity	1.1	
Mooney Viscosity, ML 1+4 (100°C)	32	
Mooney Scorch @ 125°C Minutes to 5 pt. rise	19	
MDR, 0.5 arc, 180°C		
M _L (dN•m)	0.9	
$t_{\rm e} 2 ({\rm min})$	0.2 1.3	
ť 90 (min)	3.4	
Compression Set, ASTM Method B, Press Cured 8 min. @ 180°C		
24 hrs. @ 70°C, 30% Deflection, %	25	
24 hrs. @ 100°C, 30% Deflection, %	61	
Original Physicals	10	
Hardness, Shore A	43	
300% Modulus, MPa	26	
Tensile, MPa	10.3	
Elongation, %	825	
Tear Resistance, DIN 53507A		
@ 23°C, kN/m	16.2	
@ 40°C, kN/m	10.7	
Physical Properties After Aging in Air, 72 hrs. @ 125°C	. 0	
naruness, Pts. Unange Weight % Change	+8 -1.9	
Physical Properties After Aging in Detergent (Ariel) 72 hrs. $\bigcirc ORC$	1.0	
Hardness, Pts. Change	-4	
Weight, % Change	6.5	

Table 24: Non-black Injection Molding Compound (Washing Machine Gasket)

Ingredients	phr	
Vistalon EPDM 7500 N550 FEF Carbon Black Flexon 680 Oil	100.0 75.0 75.0	
Carbowax 3350	2.0	
Flectol H	1.0	
Zinc Oxide	5.0	
Sulfur	0.5	
CAPTAX (MBT)	1.0	
METHYL TUADS (TMTD)	0.5	
Sunasan R (DTDM)	1.0	
lotal	262.0	
Specific Gravity	1.05	
Mooney Viscosity, ML 1+4 (100°C)	35	
ODR, ± 3 arc, 180°C		
M _L (dN•m)	6	
$M_{H}$ (dN•m)	41	
t _s 2 (min)	1.4	
	3.0	
Original Physicals, Press Cured 4 min. @ 180°C	10	
Hardness, IRHD 100% Modulus, MPa	48	
Tensile MPa	14.2	
Elongation, %	685	
Compression Set ASTM Method B Press Cured 8 min @ 180°C		
24 hrs. @ 70°C, 40% Deflection (+2 hrs. relax), %	12	
Tear Resistance		
DIN 53507A, kN/m	7	
Hardness, Shore A. Increase @ I ow Temperature		
168 hrs. @ -10°C	+6	
Compression Relaxation. Room Temperature @ 40% Deflection		
Initial Force, %	1.76	
Force Retention After 100 hrs., %	93	
Force Retention After 1,000 hrs., %	85	
Force Retention After 100,000 hrs., %	78	

Table 25: Injection Molded Pipe Seal Compound

Ingredients	phr	
Vistalon EPDM 8800	100.0	
Vistalon EPDM 785	50.0	
N550 FEF Carbon Black	70.0	
Sillitin Z 86 Mineral Filler	60.0	
Elevast Modifier 170	27.5	
Elevast Modifier 120	20.0	
Silane A-172	1.0	
TAC Sulfur	3.0	
Sullur Bhanagran CaO 80	0.1	
	10.0	
VAROA 802-40RL	10.0	
Total	346.6	
Specific Gravity	1.16	
Mooney Viscosity, ML 1+4 (100°C)	40.3	
MDR, 0.5° arc, 180°C		
M₋ (dN•m)	1	
M _H (dN•m)	19.4	
t _s 2 (min)	0.51	
ť 90 (min)	5.4	
Compression Set, ASTM Method B, Press Cured 12 min. @ 180°C		
22 hrs. @ 85°C, 25% Deflection, %	4	
Compression Set, ASTM Method B, Press Cured 8 min. @ 180°C		
22 hrs. @ -20°C, 25% Deflection, %	13.5	
Original Physicals		
Hardness, Shore A	64	
100% Modulus MPa	6.0	
Tensile, MPa	12.2	
Elongation, %	160	
Physical Properties After Aging in Air, 168 hrs. @ 85°C		
Hardness, Shore A	65	
100% Modulus, MPa	6.0	
Tensile, MPa	12.6	
Elongation, %	160	

Table 26: Injection Molding Wiper Blade Compound with Elevast[™] Modifier

Ingredients	phr	
Vistalon™ EPDM 706 N330 HAF Carbon Black	100.0 50.0	
Elevast Modifier C30	10.0	
AGERITE D TMQ	1.0	
VAROX 802-40KE	5.0	
Saret SR-634	15.0	
Total	181.0	
Mooney Viscosity, ML 1+8 (100°C)	92	
Mooney Scorch @ 125°C Minutes to 5 pt. rise	9	
MDR, 180°C		
M _H (dN•m)	101	
ť 90 (min)	11	
Original Physicals, Press Cured 20 min. @ 185°C		
Hardness, Shore A	74	
Tensile, MPa	20	
Elongation, %	360	
Physical Properties After Aging in Air, 168 hrs. @ 125°C		
Tensile, % Change	+2	
Elongation, % Change	-10	
Green Adhesion, T-peel Peak Load		
kN/m	5.2	
Tear Resistance, ASTM Die C @ 125°C		
kN/m	20	

Table 27: Transmission Belt Compound with Elevast Modifier⁶¹

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#### THE NEOPRENES

#### by Jonathan Karas

DuPont Performance Elastomers LLC Stow, OH

Neoprene is the generic name for polymers of chloroprene (2-chloro-1,3butadiene). Neoprene was commercialized in 1931 by E.I. du Pont de Nemours and Company and is currently manufactured in the United States by DuPont Performance Elastomers, in La Place, LA.

#### Neoprene Types

DuPont Performance Elastomers offers 12 types of solid Neoprene polymers and 4 types of Neoprene liquid dispersions.

Neoprenes are classified as general purpose, adhesive and liquid dispersion types. General-purpose types are used in a variety of elastomeric applications, particularly molded and extruded goods, hoses, belts, wires and cables, heels and soles of shoes, coated fabrics, and gaskets. The adhesive type of Neoprene is adaptable to the manufacture of solvent-based adhesives that are characterized by quick set and high bond strength. The liquid dispersion types involve unique application processes and end uses. Neoprene liquid dispersions are generally used in adhesives, binders, coatings, dipped goods, waterborne adhesives, elasticizers, and foams.

#### **General Purpose Neoprene**

For general-purpose applications, the selection of type and grade of Neoprene is usually based upon a combination of four factors. The first factor is product performance. This is defined by the most important physical properties for optimum service life, such as tear and flex resistance (belts), compression set and stress relaxation resistance (seals, bearing pads), and high temperature resistance.

The second selection factor is crystallization resistance as dictated by product operating temperatures and/or processing needs. Neoprene is a strain-crystallizing polymer much like natural rubber. Unstrained Neoprene will also crystallize at rest, most rapidly at -10°C, causing an increase in stiffness of uncured stocks and an increase in hardness and modulus of vulcanizates. The incorporation of comonomers in the polymer decreases this rate of crystallization.

The third and fourth factors are polymer viscosity, as defined by processing operations, and building tack, when ease of lamination in processing is required.

The general-purpose types of Neoprene can be processed using standard rubber machinery. The G types are light cream to light amber in color. Neoprene W types are white to silvery grey, and Neoprene T types are white to light cream. The densities of Neoprene G, W, and T types range from between 1.23 and 1.25 g/cm³ at 23°C.

Neoprene vulcanizates meet the requirements of ASTM D 2000 (SAE J200) BC or BE materials. Neoprene can be compounded to produce vulcanizates having characteristic properties over the following ranges:

- Tensile strength up to 25.6 MPa (4000 psi)
- Elongation at break up to 900%
- Hardness, Shore A, 20 to 90
- Compression set as low as 10% (Method B, 22 hrs. @ 70°C)
- Yerzley Resilience up to 85%

While no single compound will reflect the extremes of the ranges shown above, the distinguishing characteristics of general purpose Neoprene are described below.

# Neoprene G Types

Neoprene G types are copolymers of chloroprene with sulfur. After polymerization is stopped, combinations of thiuram disulfides and dithiocarbamates are added to the emulsion prior to isolation of the polymer to reduce molecular weight and provide the desired polymer viscosity. Compared to Neoprene W types, the Neoprene G types have the following characteristics:

- More limited raw polymer storage stability: When fully compounded, greater susceptibility to total heat history in processing and storage time (i.e. more prone to viscosity increase and reduction of scorch time).
- Peptizable to varying degrees: Therefore, G types can provide workable, more highly loaded stocks with minimum plasticizer levels.
- Tackier and less nervy (with the exception of Neoprene WB): These properties lend themselves to extrusion, frictioning, calendering and building operations as in hose and belt manufacture, and minimized knitting and backrinding problems in molding.
- Compounds based on G types: Require no additional organic accelerator, though some may be added as required for processing and property requirements.
- Vulcanizates based on G types: Higher tear strength, flex fatigue resistance, elongation at break, resilience, and a 'snappier' feel.

Neoprene GNA provides highly resilient vulcanizates with good tear resistance and moderate crystallization resistance. This type should not be used in applications where resistance to discoloration or staining of finishes is required, because, unlike other Neoprene types produced by DuPont Performance Elastomers, Neoprene GNA contains a stabilizer that is a staining antioxidant.

Neoprene GRT is more resistant to crystallization than either Neoprene GNA or GW because of the inclusion of an additional comonomer, 2,3-dichloro-1,3-butadiene. It is especially suited for friction and skim stocks, sheet goods, and other products that require good tack retention.

*Neoprene GW* is a unique G type that features good uncompounded stability and a lower degree of peptizability. Tear strength, resilience, and flex crack resistance are similar to those of other Neoprene G types. Vulcanizates of Neoprene GW retain physical properties after heat aging better than those based on other Neoprene G types, but have slightly less building tack. Compression set resistance lies between that of traditional Neoprene G and W types.

# Neoprene W Types

Compared to Neoprene G types, Neoprene W types have the following characteristics:

- · Greater polymer stability.
- · Faster mixing capability.
- · Cannot be mechanically or chemically peptized.
- Compounds less prone to mill sticking and collapse on extrusion.
- Compounds require organic accelerators. By selection of type and level, greater latitude in processing safety and cure rate is possible.
- Can accept higher levels of filler for a given level of compression set or tensile strength, yielding compounds that are more economical.
- Offer superior vulcanizate heat and compression set resistance.

Neoprene W, WM 1, WHV and WHV 100 are nonstaining, general purpose polychloroprenes. The four grades differ only in Mooney viscosity. Compounds and vulcanizates based on these polymers crystallize quickly. The wide range of viscosities available with these polymers makes it possible to accommodate virtually any desired loading of fillers and plasticizers while still maintaining workable compound viscosity. Neoprene WHV and WHV 100 grades are frequently blended with lower viscosity Neoprene grades to increase viscosity and green strength of compounds.

Neoprene WRT and WD are nonstaining, crystallization-resistant copolymers of chloroprene and 2,3-dichloro-1,3-butadiene. The two types differ only in Mooney viscosity. Slightly greater amounts of accelerators are required with Neoprene WRT and WD to achieve cure rates comparable to those of Neoprene W and WHV. Neoprene WD is particularly well suited for compounds that contain large amounts of ester plasticizers for flexibility at extremely low temperatures when maximum crystallization resistance is also required. The high viscosity of Neoprene WD allows such compounds to be processed without excessive sticking.

Neoprene WB is manufactured in the same viscosity range as Neoprene W. Compounds of Neoprene WB have outstanding extrusion characteristics and have firmer more collapse-resistant profiles that extrude faster and at lower temperatures than compounds made with other Neoprene grades. The surfaces of extrudates based on Neoprene WB are also smoother than those based on other Neoprene types. The resistance of Neoprene WB vulcanizates to heat, oil, ozone, and compression set is comparable to that of vulcanizates based on other Neoprene W types, but Neoprene WB vulcanizates are lower in tensile strength, tear strength, and resistance to flex cut growth and abrasion. Because of its physical properties, Neoprene WB is often used in blends (10-30% of the total polymer weight) with other Neoprene types to improve processing.

# Neoprene T Types

Neoprene T types are very similar to Neoprene W types, but they also contain a highly crosslinked microscopic "gel" form of polychloroprene, similar to that contained in Neoprene WB, which acts as an internal processing aid. As a result, Neoprene T types generally process better than Neoprene G types and most Neoprene W types. They offer very smooth, fast extruding and calendering compounds with little or no sacrifice of physical properties. The raw polymer storage stability of Neoprene T types is similar to that of Neoprene W types. Other properties are also similar to the Neoprene W types.

Neoprene TW and TW 100 are structurally similar polymers of different Mooney viscosity.

# Adhesive Type Neoprenes

Neoprene AD 20 is a rapidly crystallizing polymer used in the manufacture of adhesives. It is cream to pale amber in color, and contains no gel component. The viscosities of Neoprene AD 20 and products produced from Neoprene AD 20 are very stable during storage. The density of Neoprene AD 20 is 1.23 g/cm³ at 23°C.

Although toluene and other aromatic solvents are generally used as the primary solvents in many products containing Neoprene AD 20, many other solvent systems, including aliphatic and oxygenated solvents, will dissolve Neoprene AD 20, whether in chip or milled form.

## **Neoprene Liquid Dispersion**

Neoprene liquid dispersions are aqueous anionic colloidal dispersions of chloroprene homopolymers or of copolymers of chloroprene and other monomers, such as sulfur or 2,3-dichloro-1,3-butadiene. The products have a unique combination of characteristics including excellent film formation, high cohesive strength without curing, elastomeric properties over a wide temperature range, and considerable resistance to the degrading effects of weather, ozone, heat, water, and many oils and chemicals.

Neoprene liquid dispersions contain varying levels of microscopic gel that impart different properties (gel is defined as polymer insoluble in tetrahydrofuran). Four types of Neoprene liquid dispersions are currently produced, Neoprene 571, Neoprene 671A, Neoprene 750, and Neoprene 842A. Neoprene liquid dispersions have pH values of 12 or higher.

*Neoprene* 571 contains a high modulus copolymer of chloroprene and sulfur. Cured films based on Neoprene 571 have high strength in addition to good oil resistance and low permanent set. Neoprene 571 is used to produce adhesives, coatings, dipped goods, and elasticized concrete. Neoprene 671A contains a high modulus polychloroprene homopolymer with good wet gel elongation and wet gel tensile strength resulting in good resistance to gel cracking, either alone or when blended with other Neoprene liquid dispersions. Neoprene 671A is used to produce dipped goods, construction mastics, laminating adhesives, impregnated paper, bonded batts, water-based contact bond adhesives, coatings, and foam products.

Neoprene 750 contains a medium modulus, crystallization-resistant copolymer of chloroprene and 2,3-dichloro-1,3-butadiene. It forms strong, highly extensible films, and these film properties develop rapidly after coagulation. Neoprene 750 provides films that have characteristics similar to those of natural rubber with respect to softness and pliability, while retaining the superior properties of Neoprene. Due to its excellent crystallization resistance, products made with Neoprene 750 do not stiffen or lose their desirable 'snappiness' with time. Films of very low modulus can be made with Neoprene 750, and the wet gel strength of freshly prepared films is excellent. Because of these properties, Neoprene 750 is an outstanding choice for dipped goods, adhesives, and for many other applications.

*Neoprene 842A* contains a medium modulus polychloroprene homopolymer. It forms films of medium strength that exhibit a medium crystallization rate. Suggested end uses include bonded batts, laminating adhesives, impregnated paper, industrial coatings, dipped goods, and elasticized concrete.

#### Solid Neoprene Applications

The wide range of physical property values exhibited by Neoprene vulcanizates permits use of these products in a host of elastomeric applications.

*Wire and Cable* – Neoprene provides oil, abrasion, and weather resistance for power cable, service entrance, drop wire, ship wiring, portable cables, and cords.

*Covers and Tubes for Hose* – Neoprene provides resistance to heat, chemicals, abrasion, oil and weather, as well as physical toughness. Products include industrial and automotive hose, hydraulic hose, welding hose, oil suction and discharge hose, oil delivery hose, and air hose.

*Belts* – The heat and flex resistance of Neoprene vulcanizates is useful in V-belts and other power transmission belts used in automotive, agricultural, and industrial applications. Neoprene is also widely used to produce conveyor belts for industrial and mining service where flame resistance is important.

*Molded and Extruded Parts* – The versatile properties of Neoprene make it suitable for numerous applications in the automotive and industrial fields. Other important uses include appliance parts, pipe gaskets, airsprings, bridge bearings, building bearings, building seals, O-rings, and cellular products.

Adhesives – The use of Neoprene in elastomeric adhesives is widespread because of its combination of polarity (allowing use with a wide range of substrates), crystallinity (leading to development of early and improved bond strength), and high auto-adhesion. Principal uses include industrial, shoe, furniture, automotive, and construction industries.

Other Outstanding Uses – Solid Neoprene polymers are used to make wetsuit sponge, coated fabrics, and soles and heels of shoes.

## Liquid Dispersion Neoprene Applications

Neoprene liquid dispersions are used to make supported and unsupported films, resilient foam for low smoke and flame-retardant cushioning, modifiers for asphalt and cement, binders as saturants and wet-end additives for fibrous products and aggregates, mastics, and adhesives that are pressure sensitive, heat, or solvent activated for laminating and contact bonding.

#### **Compounding of Solid Neoprene Polymers**

Compounds based upon Neoprene will normally contain most of the classes of ingredients listed below.

Class	Typical Material
Metal Oxides	Magnesium oxide and zinc oxide
Vulcanization accelerator	Thioureas or sulfur based systems
Stabilizers	Octylated diphenylamine
Fillers	Carbon black, clay, silica, talc
Plasticizers	Aromatic oils, esters
Processing aids	Stearic acid, waxes, polyethylene

## Metal Oxides

The use of four parts of magnesium oxide (magnesia) and five parts of zinc oxide generally results in a good balance of processing safety and cure rate and this ratio is typically used in Neoprene compounds. The omission of magnesium oxide results in compounds with little scorch safety. Higher levels of magnesia may be desirable for high temperature molding, especially injection molding, to increase scorch safety. Lower levels of magnesia may be used in some continuous vulcanization cure systems. Suitable grades of magnesium oxide are fine particle precipitated calcined types with surface activities measured by iodine number preferably above 130. Scorch times are directly related to the activity of the magnesium oxide incorporated in the compound with higher activity grades providing increased scorch safety. The particular grade of zinc oxide used has a smaller impact on cure properties, although very coarse grades may result in slower cure rates.

Equations 1 to 3 illustrate the vulcanization mechanism of polychloroprene. It is believed that the principal curing site is at the location of the allylic chloride formed by 1,2 addition of the monomer unit in the polymer chain. This crosslinking site occurs relatively infrequently in the linear chain. The chlorine in the 1,2 addition configuration is allylic and, accordingly, labile. The equilibrium of Equation 1 probably shifts to the right-hand side in the presence of ZnO during the vulcanization of Neoprene:



Equation 2:



The ZnCl₂ formed is an active catalyst of vulcanization. Unless it can be scavenged, its presence during processing operations can cause scorching problems. Equation 3 shows how magnesium oxide acts as a stabilizer during processing:

Equation 3:

$$\begin{array}{ccc} H_2O & OH \\ / \\ 2 \text{ ZnCl}_2 + \text{MgO} & \rightarrow & 2 \text{ Zn} - \text{Cl} + \text{MgCl}_2 \end{array}$$

#### Vulcanization Accelerators

The levels of zinc oxide and magnesium oxide recommended above are sufficient to cure G types in the absence of any organic accelerators. An accelerator such as ethylene thiourea (ETU) accelerates the vulcanization process when rapid cures are required. The cure rate of Neoprene W types with metallic oxides alone is slow; accordingly, an organic accelerator is always included in W type formulations. ETU is most frequently used, either alone or in combination with DURAX[®] or METHYL TUADS[®] to improve scorch safety in black stocks, or in combination with ALTAX[®] to improve scorch safety in mineral filled stocks.

The curing mechanism of Neoprene with sulfur-bearing accelerators is illustrated below with ETU. This leads to the development of sulfur bridges or crosslinks in addition to the oxygen bridges in Equation 2. This series of reactions is described in Equations 4 and 5 on the following page:

Equation 4:

Equation 5:

 $\begin{array}{cccc} | & & | & | \\ C=CH-CH_2 & + & CI-C-CH=CH_2 & \rightarrow & [ & C=CH-CH_2-]_2-S + & ZnCI_2 \\ | & \backslash & S-ZnCI & | & | & | \end{array}$ 

Table 1 lists the common curing systems for Neoprene W and T types, in order of increasing cure rate and decreasing processing safety.

	phr	
Ingredients	(Neoprene)	Primary Use
UNADS® DOTG Sulfur	0.5-1.0 0.5-1.0	Maximum processing safety
ETU ALTAX	0.55-0.75 0.5-1.0	Mineral filler loading
ETU METHYL TUADS or DURAX	0.4-0.75 0.5-1.0	Carbon black loading
UNADS DOTG Sulfur ETU	0.5 0.5 1.0 0.2-0.4	Medium to fast cure with moderate processing safety
ETU	0.4-0.75	Maximum economy Optimum heat/compression set resistance
Methylthiazolidinethione	0.4-1.5	Substitute for ETU Sometimes inconsistent cure, use higher level for high carbon black loading
ETU VANAX [®] PML	1.0-2.0 0.5-1.0	Fast curing stocks, usually used in LCM cure
TBTU	3.0	Excellent set and ozone resistance, non- staining
THIATE [®] EF-2 Epoxy Resin	0.75-1.5 1.0-2.0	Excellent compression set resistance
Salicylic Acid	1.0-2.0	High elongation/tear strength

Table 1: Acceleration Systems for Neoprene W and T types*

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Ingredients	phr (Neoprene)	Primary Use
THIATE H	1.0-2.0	Fast high temperature cures (LCM) Practical cures at lower temperatures
THIATE U	1.0-2.0	Same as THIATE H with slightly slower set-up and better scorch
DPTU (Thiocarbanilide)	1.0-2.0	Same as DETU
* All systems include 4 parts MgO and 5 parts ZnO		

Table 1: Acceleration Systems for Neoprene W and T types* (continued)

In summary, when curing Neoprene with organic acceleration systems other than ETU, use:

- VANAX CPA to provide similar physical properties.
- UNADS, sulfur, and DOTG or DPG for compounds requiring a slow cure rate, good dynamic properties, and when maximum resistance to heat or compression set above 70°C is not required.
- THIATE H, THIATE EF-2 with an epoxy resin, or ETU with VANAX PML when low-temperature or continuous vulcanization cure is required. These stocks will have little scorch safety; heat history must be kept to a minimum.
- Salicylic acid for lightly loaded compositions requiring high modulus.

Although they provide very low compression set and good processing safety, peroxide cures promote poor heat aging in Neoprene, even when high levels of efficient antioxidants are incorporated.

## Antioxidants

An antioxidant must be included in compounding formulations because Neoprene vulcanizates contain some degree of unsaturation. A minimum of 2 parts per hundred (phr) of antioxidant should be present in a compound, although greater quantities can be employed to improve resistance to heat and ozone. AGERITE[®] STALITE[®] S is the most commonly used antioxidant in Neoprene. Quinolines seriously affect scorch and bin storage and should be avoided.

Effective antiozonants tend to adversely affect processing safety and promote staining. Among para-phenylene diamine (PPD) derivatives, mixed diaryl-PPD has only a slight effect upon scorch and bin storage while providing the best balance of long-term protection, being non-extractable in water, and of low volatility. However, all PPD derivatives may cause migratory and contact staining of painted surfaces. There are commercially available non-staining antiozonants, but they are not as efficient.

## Fillers

Although the most highly reinforcing carbon blacks can, under optimized mixing conditions, give the best tensile and tear strength values, highly reinforcing carbon blacks are difficult to disperse. The N300 series of carbon

blacks are the finest particle size carbon blacks generally employed. For most applications, N500, N600, and N700 series of carbon blacks, and N990 carbon black, or blends of these types, enable specification and service requirements to be met. The N500 or N600 series of carbon blacks, alone or blended with N700 series of carbon blacks, are preferred for extrusion or calendering stocks. Where requirements permit, economical compounds may be prepared using high loadings of N600 or N700 series of carbon blacks with significant levels of plasticizer. Alternatively, blends of N700 series of carbon blacks with mineral fillers such as clay or whiting can be considered where compression set and physical property requirements are modest.

The most common mineral fillers used in Neoprene formulations are precipitated silica, calcium silicate, china clay, and whiting. Hydrated alumina may be incorporated to raise ignition temperatures and limit oxygen index values.

Precipitated silica, preferably with triethanolamine or other dispersing aid at levels up to 3 phr, gives the highest tensile strength, elongation at break, and tear resistance in cured compounds. Hard or soft china clays may be utilized depending on the degree of reinforcement and loading required. Calcined clays are often helpful to optimize compression set and electrical properties.

Whiting is an inexpensive non-reinforcing filler, but it adversely affects compression set and weather resistance. If used, a stearate coated precipitated grade is preferable. Platy talc may be incorporated for good extrusion and electrical properties.

## Plasticizers

Softeners, plasticizers, and extenders are frequently added to Neoprene to facilitate processing, enhance specific properties, or reduce cost. Care must be taken both in selection of type and quantity to ensure that the attractive property balance characteristic of Neoprene vulcanizates is maintained.

Aromatic process oils are the most commonly used plasticizers in compounds of Neoprene, as they are nearly completely compatible. Aromatic oils will increase uncured tack, but may cause staining. Naphthenic oils can be used at levels of up to 20 phr, and are preferred to aromatic oils in light colored, nonstaining products. They also provide better long-term heat resistance. Paraffinic oils should be avoided because they will often bloom at levels as low as 5 phr.

Ester plasticizers are required to maintain and increase flexibility of Neoprene vulcanizates at low temperatures but tend to increase the crystallization rate of the polymer. Most commercial types are suitable, depending upon the desired balance of low temperature flexibility, volatility, and cost. Dioctyl sebacate (DOS) is often selected because it provides a favorable combination of these factors. Butyl oleate is effective at low temperatures, but it is relatively volatile at 100°C. Because of their low volatility, polymeric esters should be used where a broad service temperature is required. Phthalates may be an economical choice where low temperature requirements permit their use.

Polymeric, hydrocarbon, or coumarone-indene resins can retard crystallization and improve building tack and frictioning. They do not improve low temperature flexibility. Phosphates tend to be used where self-extinguishing characteristics are important but low temperature flexibility is not critical.

Chlorinated hydrocarbon and chlorinated wax plasticizers are available both in solid and liquid forms with chlorine content between 40 and 70%. Liquid forms tend to cause mold sticking; therefore, solid grades or blends are generally preferred. Use of these plasticizers is confined to Neoprene compounds with optimum ignition resistance or self-extinguishing characteristics.

Vegetable oils can also be used as plasticizers in Neoprene compounds. Rapeseed oil provides exceptional heat resistance, while linseed oil can improve the ozone resistance of vulcanizates and safflower oil can improve the weather resistance of vulcanizates. Certain other vegetable oils are less compatible and can even reduce the heat and/or ozone resistance of vulcanizates. The use of vegetable oils may promote the growth of fungus on the surface of the materials.

Vulcanized vegetable oils can be used to extend Neoprene stocks or to add body and dryness to highly extended compounds. These plasticizers also improve processing of compounds that contain large amounts of plasticizer for the purpose of providing low durometer values.

#### Processing Aids

General purpose processing aids include stearic acid, petrolatum, paraffin or microcrystalline waxes, and low molecular weight polyethylene. Stearic acid is particularly effective in minimizing mill and calender roll sticking. To prevent significant retardation of cure rate, levels of processing aids should be limited to 1 phr in compounds of W types and 2 phr in compounds of G types. Typically, 1 phr of petrolatum, 1 to 3 phr of wax or up to 5 phr of low molecular weight polyethylene may be incorporated. Note, however, that enhanced roll release with the latter requires temperatures above the softening point of the polyethylene. Polyethylene is effective as an internal mold release agent, as are waxes.

*Cis*-1,4-polybutadiene incorporated at a level of 3 to 5 phr provides maximum roll release properties in very sticky stocks. Slight activation of cure will be observed.

For ease of mixing, reduction of structure and nerve, and optimum physical properties in silica loaded Neoprene compounds, triethanolamine or calcium stearate should be included at levels up 3 phr. Both should be added with a small amount of filler early in the mixing cycle.

#### Peptizing Agents

Peptization occurs either by chemical reaction (addition of peptizers) or by physical softening (milling). Peptizers (particularly VANAX 552 or DPG) are used with Neoprene G types to adjust compound viscosity. They have no effect on vulcanizate hardness. As previously mentioned, there are no practical peptizers for Neoprene W or T types.

# **Compounding Solid Neoprene Types**

## Abrasion Resistance

Incorporation of fine particle size carbon blacks, for example N326 carbon black, is particularly useful where abrasion resistance is required with high resistance to tear and chipping. Naphthenic plasticizers are recommended, but their level should be kept to a minimum. Neoprene G type polymers are preferable for abrasion resistant compounds, with Neoprene GW being the best.

# Adhesion to Metal

Wherever property balance permits, combinations of reinforcing blacks with 10 phr of precipitated silica will enhance bond strength. Plasticizer levels, preferably aromatic oil or DOS for low temperature flexibility, should be kept to a minimum. An excess of any plasticizer or process aid may impair bond strength.

All major suppliers of bonding agents offer one- or two-part primer systems for bonding Neoprene to ferrous or other metals. General guidelines include:

- Ensure the metal surface is degreased and chemically clean. Preparation for primer application may be completed by grit or alumina blasting (ferrous and nonferrous metals) or phosphate etching/coating processes (ferrous metals).
- Where indicated, use any proprietary metal treatment recommended by the primer supplier.
- Apply primer(s) as recommended by the supplier to the preferred film thicknesses where this is known to be critical.
- Store prepared or primed metals under non-humid conditions and use promptly.
- After introducing primed metals to the mold, quickly load the compound blanks and close the press.
- With standard (non-positive) compression molds, ensure compound viscosity is sufficiently high to maintain adequate cavity pressure for optimum bonding (this is not necessarily the same as ram pressure).
- · Avoid unnecessarily high molding temperatures.

## Adhesion to Textile Fibers

Adhesion of Neoprene compounds to fibers depends upon the nature of the fiber. For example, fabric treatment is normally not required for cotton. A low viscosity grade of Neoprene GRT will provide maximum penetration and wetting of a fabric or fiber.

When nylon or polyester is used, a primer coat of 30% Neoprene compound solution in toluene containing 4-6% organic isocyanate is applied as a dip or spread coat. The isocyanate treated fabric must be protected from atmospheric moisture between dipping or spreading and final coating to ensure maximum bond strength.

For polyester tension members, as used in raw-edge V-belts, the cord supplier will normally pretreat the polyester with an isocyanate primer followed by a resorcinol-formaldehyde/vinyl pyridine/polychloroprene latex dip.

#### Blending Neoprene with Other Elastomers

Blends of Neoprene and natural rubber (NR) provide good hot tear strength and building tack. Blends of Neoprene and styrene-butadiene rubber (SBR) are often desirable for compound cost reduction, and blends of nitrile-butadiene rubber (NBR) exhibit enhanced oil and fuel resistance. Careful compounding is necessary to minimize modification of the unique combination of properties offered by Neoprene. When preparing blends with diene rubber, Neoprene W types are preferred to G types since residual thiuram in the latter causes poor processing safety.

The viscosities of the polymers to be blended should be as close as possible. If flex fatigue or outdoor weathering resistance are important factors, the split masterbatch mixing technique should be specified in order to optimize dispersion of fillers and plasticizers. This involves preparation of separate masterbatches based on each blend polymer, with filler and plasticizer levels adjusted to obtain a similar viscosity in each polymer masterbatch. The masterbatches are then blended together thoroughly at the time curatives are added.

It is important to remember that Neoprene is a relatively slow curing elastomer that requires acceleration systems that react extremely rapidly when used in other diene-based elastomers. When selecting curing systems for the co-vulcanization of blends based upon Neoprene, the need for adequate processing safety and storage stability of the final compound should be fully considered. For blends with NR and SBR, a sulfur-based cure system should be used. In blends with NBR, Neoprene G types are recommended at a minimum of 75% of the total polymer weight. In these blends with NBR, 0.25-0.5 phr of ETHYL TUADS[®] can be included as a curative.

For polarity reasons, EPDM is normally limited to 15-20% of the total polymer weight in blends with Neoprene. The inclusion of EPDM improves nonstaining static ozone resistance. Because of the incompatible nature of the polymers, the split masterbatch mixing technique is considered essential. A sulfur based cure system should be used.

The presence of NR, SBR, and NBR in polymer blends with Neoprene will adversely affect the ozone resistance of the compound. It is essential to include at least 2 phr of antiozonant, preferably one of the mixed diaryl PPD types in such blend compositions.

The addition of Neoprene W to resin cured heat resistant butyl rubber (IIR) at up to 10% of the total polymer weight, e.g., for tire curing bags, greatly reduces the tendency of the compounds to soften and lose mechanical strength during use.

#### Building Tack

The use of low viscosity Neoprene GRT provides the highest levels of building tack. In applications in which a Neoprene W type is used and high tack is desired, WRT is preferred. When a Neoprene compound requires a plasticizer, the inclusion of aromatic plasticizers will provide more tack than naphthenic or ester plasticizers. Other tack promoters include coumarone-indene resins, especially liquid types, wood rosin derivatives, and phenolic resins such as Koresin[®], available from BASF. Aromatic oils are more prone to cause troublesome sticking than other types. To maintain building tack, dusting agents should not be applied to sheeted stocks. Batch-off liners should be of a nonstick type.

## Compression Set Resistance, Stress Relaxation, Compression Recovery

Tight cure of a crystallization resistant Neoprene grade is fundamental to optimization of these properties. Neoprene WRT or blends with Neoprene WD are recommended when optimizing compounds for molding applications, and Neoprene WB is a good choice if extrusion is involved. For the most demanding specifications, use of 1.5 phr of THIATE EF-2 with 0.5-1.0 phr of an epoxy resin extends shelf life. Most requirements can be met by using 1 phr of ETU in combination with THIATE EF-2 for very fast cures.

Selection of the correct grade of magnesium oxide is important. With respect to carbon blacks, N990 carbon black usually provides the lowest set/stress relaxation values for a given level of addition, but reinforcing carbon blacks, previously listed, or blends, may be required to meet tensile or tear property requirements. Mineral fillers should be avoided except where necessary and then used at low levels.

Recovery from compression at low temperatures (0 to -40°C) is improved by minimizing the level of ester plasticizer, such as DOS, in the formulation, and any additional plasticizer should be an aromatic oil type. This minimizes the crystallization accelerating effect of the ester plasticizer.

## Creep Resistance

For optimum creep resistance, normal compounding considerations apply except that minimum levels of ester plasticizers should be utilized. Extended cures at moderate temperatures, for example, 30 minutes at 150°C, will ensure maximum crosslink density is attained.

## Chemical Resistance

The use of acidic fillers should be avoided. Best acid resistance is usually achieved when 100 phr of barytes or blanc fixe is employed. High plasticizer levels should be avoided when contact between the compound and oxidizing agents is expected.

## Crystallization Resistance

For the best possible crystallization resistance, compounds based upon Neoprene WRT or WD are recommended. Should a G type be necessary, Neoprene GRT is preferred, but it is not quite as resistant to crystallization as Neoprene WRT or WD. Blends of Neoprene with *cis*-1,4-polybutadiene at levels up to 30% of the total polymer weight also show improved crystallization resistance, with predictable decreases in tensile strength, and oil and ozone resistance.

Preferred plasticizers include aromatic oils or hydrocarbon resins, such as Kenflex[®] A-1. The hydrocarbon resins are more effective as crystallization inhibitors in the uncured state. Ester plasticizers should be avoided, but, if necessary for low temperature flexibility, the minimum amount possible should be used.

Inclusion of sulfur in the cure system will also retard vulcanizate crystallization, but this will be at the expense of heat aging and compression set resistance.

#### Electrical Properties

Because it is more polar than non-halogenated hydrocarbon based elastomers, Neoprene is not normally considered a primary insulating material. To optimize its capabilities, mineral fillers should be specified due to their higher insulation resistance and dielectric properties as compared with carbon blacks. Platy talcs such as Mistron Vapor[®] are recommended for dielectric strength. Ester plasticizers should be avoided. Up to 15 phr of naphthenic oil may be incorporated as a plasticizer, but a hydrocarbon resin plasticizer will further optimize insulation resistance.

Where antistatic properties are essential, incorporation of conductive furnace blacks such as N472 is recommended. Care must be taken to select a safe processing cure system, and a Neoprene grade of sufficiently low viscosity to minimize heat generation during processing should be selected.

#### Flex Cracking Resistance

Neoprene G types, especially Neoprene GW or GRT, have the best inherent flex-fatigue resistance properties. Neoprene GW may be preferred where cut growth resistance is a primary requirement.

When possible, compounds should contain N772 or N774 carbon blacks, or blends of these carbon blacks with N990 carbon black, to promote low modulus and high elongation. Use of up to 20 phr of precipitated silica in combination with a dispersing aid will also improve flex-cracking resistance.

Aromatic oil plasticizers should be present at the minimum level. The use of thiourea accelerators should be avoided.

It is preferable that compounds contain a good antioxidant/antiozonant system such as 2 phr of AGERITE STALITE S and 1 phr of mixed diaryl-PPD. All grades benefit from the inclusion of up to 2 phr of VANOX[®] ZMTI. This acts as a heat stabilizer but may decrease compound bin storage stability.

Excellent dispersion is also essential if optimum flex fatigue properties are to be achieved.

#### Flame Resistance

Solid or liquid chlorinated paraffins having combined chlorine contents between 40 and 70% may be used both to plasticize Neoprene compounds and to increase the available chlorine level. To minimize the mill stickiness that use of these additives induces, it is recommended that higher viscosity Neoprene W types such as Neoprene WHV or WD be used. Blends of solid and liquid chlorinated paraffins also reduce the tendency of Neoprene compounds to stick to mills.

Hydrated alumina enhances the self-extinguishing characteristics of Neoprene and raises auto-ignition temperatures of Neoprene compounds. It may be used in combination with carbon black to achieve tensile strength requirements. China clays and calcium silicate are also useful but do not provide the specific effects of hydrated alumina.

Other additives that enhance self-extinguishing properties include antimony trioxide, preferably as a synergistic combination with halogenated flame retardants. Unacceptable afterglow promoted by antimony trioxide can be prevented by inclusion of an intumescent crust forming agent such as zinc borate to exclude oxygen. Magnesium hydroxide can be added to enhance smoke suppressant properties. Hydrocarbon based plasticizers and process aids should be avoided or severely limited since they support combustion.

#### Food Contact

A list of Neoprene types suitable for use in compounds that meet the regulatory requirements of FDA 21.CFR.177.2600 (rubber articles intended for repeated use) is available.

Attention is drawn to the limitations on compound ingredients imposed in FDA regulations, and to permissible extraction limits. ETU is not an acceptable accelerator. Information on alternatives to ETU is available on request.

#### Heat Resistance

Neoprene W or T type polymers are the best choices for heat resistance compounds because they do not contain free or combined sulfur. Use of minimal levels of high activity magnesium oxide is essential to achieve the highest level of heat resistance, except in applications in which the Neoprene vulcanizate will be in contact with natural or synthetic fibers.

A preferred antioxidant is 2-4 phr of AGERITE STALITE S, in combination with 1.5 phr mixed diaryl-PPD if high-ozone resistance is also required. The addition of 2 phr of VANOX MTI will also improve heat resistance. Alternatively, 1 phr of N-phenyl-N'-(p-toluenesulfonyl)-PPD will also improve heat resistance. A tight cure is often essential to meet end-user specifications and can be achieved by addition of thiourea accelerators to the cure system.

Carbon blacks such as N550, N772, or similar carbon blacks, alone or as blends with precipitated silica or reinforcing clays are suitable fillers in heat resistant Neoprene compounds. Fine particle size calcium carbonate confers

good heat resistance but impairs physical properties, weathering, and water resistance. Some studies have shown that the inclusion of 5 phr of zinc borate improves the heat resistance of Neoprene compounds.

Selection of plasticizer type is important. Rapeseed oil or polyesters are recommended for permanence. Among ester plasticizers, DOS is a preferred type for its balance of high and low temperature performance. Plasticizers to be avoided include butyl oleate and naphthenic oils due to their volatility, and aromatic oils. Inclusion of IIR rubber in a Neoprene compound at levels up to 5% of the total rubber has been found to help counter the natural hardening of the polymer on long-term exposure to high temperatures, as does 5.4 phr calcium stearate substituted for the standard 4 phr of high activity magnesium oxide, but neither approach has been commonly adopted.

#### High Resilience

A tightly cured Neoprene G type polymer is generally recommended for high resilience applications. Neoprene GW is a good candidate and may meet requirements without additional acceleration. N990 carbon black is a preferred filler for highest resilience. Where reinforcing types are essential, low structure variants should be specified. Use of the lowest amount of filler possible is recommended.

Naphthenic oils or ester plasticizers in amounts up to 15 phr are preferred. Polyesters, resins of all types, and factices should be avoided.

If the overall required property balance permits its inclusion, up to 20% of the total polymer weight may be *cis*-1,4-polybutadiene. This will enhance resilience. The split masterbatch mixing technique is likely to be necessary when using *cis*-1,4-polybutadiene, and the possibility of problems due to scorch should be considered.

#### See also Vibration Damping

## High Strength at Elevated Temperatures

Use of precipitated silica in amounts up to 40 phr, preferably including triethanolamine or other surface-active dispersing aids at levels up to 3 phr, is particularly effective in retaining physical properties at temperatures up to 200°C short term. Where extended exposure to elevated temperatures is also likely, the recommendations for optimum heat resistance should be followed.

#### Low Gas Permeability

Permeability constants for atmospheric gases such as nitrogen, oxygen, carbon dioxide, methane, and hydrogen are lower for Neoprene than NR or SBR at both 25°C and 50°C. In practice, the rate of permeation of a given gas can be significantly affected by compounding. Tight cure is a prerequisite. Therefore, a Neoprene W type compound that contains thiourea accelerator is preferred. Platy fillers such as mica or Mistron Vapor talc reduce permeability anisotropically. When significant loadings of mica are present in the compound, a lower viscosity polymer grade is likely to be required. Plasticizer levels should

be kept low and preferably, plasticizers should be avoided altogether.

#### Low Temperature Resistance

Both immediate stiffening as temperature is reduced and the slower effects of crystallization should be considered. The optimum temperature for crystallization in an unmodified compound of Neoprene is -10°C.

During processing, crystallization may impair building tack after cool storage and result in ply adhesion problems. An example of an in-service deficiency caused by crystallization might be a conveyor belt that fails to track adequately due to the resulting stiffening, thereby reducing its load carrying capacity. A certain degree of crystallization can be beneficial for wire-braided hoses since the stiffer unvulcanized extrudate better resists cutting in by the wire.

The principle factor in controlling the crystallization rate of Neoprene is polymer selection. The Neoprene W type copolymers described previously are recommended for the best crystallization resistance. Aromatic oils and polymeric or resinous plasticizers help retard crystallization. Ester plasticizers, essential for lowering glass transition temperature, accelerate crystallization. Therefore, use of such plasticizers should be restricted to the minimum level necessary.

#### Ozone Resistance

The inherent ozone resistance of Neoprene may be optimized by incorporation of antiozonants in combination with selected waxes. Antiozonants should be nonvolatile and non-extractable by water and have minimum effect upon compound bin storage stability.

For moderate ozone test requirements, 2 phr of AGERITE STALITE S in combination with three to 5 phr of a VANWAX[®] product is usually adequate. For more demanding tests, a mixed diaryl-PPD antiozonant should be specified, with the same level of wax to promote maintenance of a protective surface film. Both types of chemical antiozonant confer slight paint staining.

Suppliers of specialized waxes for use as antiozonants usually offer various grades depending upon test and service temperatures. It is advisable to ensure that the most suitable grade has been selected.

Most ester plasticizers adversely affect the ozone resistance of Neoprene vulcanizates, with the exception of butyl oleate. The use of this plasticizer can be beneficial, as is the use of raw linseed oil as a nonstaining antiozonant. Linseed oil may, however, promote fungus growth. As previously noted, 15-20% of the total polymer weight of EPDM may be included to promote nonstaining static ozone resistance where other considerations allow.

#### Minimum Staining and Discoloration

All colored Neoprene vulcanizates, especially light pastel shades, discolor rapidly, particularly when exposed to direct sunlight. This may be acceptable when solid colors are used that contain 10-15 or more phr of inorganic pigments such as red or yellow iron oxides or chromium oxide green. Rutile titanium

dioxide is the most effective UV screening pigment, used at levels up to 50 phr to mask discoloration in pastels. Eventually, some discoloration will occur.

For minimum discoloration, the use of Neoprene W types in combination with a phenolic nonstaining antioxidant is recommended. The G types of Neoprene should be avoided.

## Tear Resistance

Tear resistance of Neoprene G types is inherently better than that of Neoprene W types. Neoprene GW exhibits outstanding resistance to tear. Neoprene G types possess excellent flex fatigue resistance usually accompanied by adequate compression set resistance. Precipitated silica is a recommended filler, generally in combination with a dispersing aid, but other minerals such as silicates and hard clays may also give better tear values than most carbon blacks, at the expense of poorer compression set resistance.

Use of N326 carbon black can provide a good balance of tear and set properties when good dispersion is achieved. To promote dispersion, oil addition should be avoided during incorporation of the carbon black. Resinous plasticizers, such as coumarones or alkyl-aromatic resins at 5 phr, also help achieve optimum tear strength. Natural rubber, used at levels between 10 and 20 percent of the total rubber weight, may also assist tear strength, but will diminish oil, heat, and ozone resistance.

#### Vibration Damping

High-mechanical damping is diametrically opposite to the requirements for high resilience. A typical damping application is machinery mountings in a hot and/or oily environment. Appropriate compounds are usually highly filled with soft carbon blacks, china clays, and aromatic oil. Hence, high viscosity Neoprene WHV or WHV-100 are recommended. ETU acceleration is required for practical cure times and minimum creep in service.

#### Water Resistance

Acid acceptor systems based on 4 phr active magnesium oxide and 5 phr of zinc oxide are often satisfactory for long-term performance at or near ambient temperatures, especially in seawater or other aqueous systems containing simple salts.

Precipitated silica at levels of up to 25 phr is useful for long-term water resistance. Water absorption of Neoprene compounds containing silica is fairly high for periods up to 20 days at 70°C, followed by desorption to equilibrium. The use of silica is not recommended in composites such as cable jackets due to blister formation.

#### Weather Resistance

The main atmospheric factors that affect Neoprene are UV light and ozone. Temperature and humidity also contribute. UV light promotes surface crazing, but a minimum of 15 phr of carbon blacks such as N772 or N774 can improve protection. For colored Neoprene vulcanizates, the most effective screening pigments are rutile titanium dioxide and red or yellow iron oxide, but they are far less efficient than carbon black. It is better to avoid long term direct sunlight exposure of colored Neoprene. One solution is to use a veneer based upon Hypalon[®] chlorosulfonated polyethylene.

Provision against ozone attack should follow recommendations.

# **Processing Neoprene**

Processing techniques for Neoprene are similar to those used for other general purpose rubbers. The most important consideration is to avoid precure or scorching. This can be accomplished by keeping heat history at a minimum through the use of short mixing cycles and by mixing at the lowest possible temperatures. Mixing temperatures for fully compounded stocks should not exceed 110°C. Thorough cooling of sheeted stocks to the center is important.

# Mixing

A conventional internal mixing cycle calls for the addition of processing aids such as lubricants or peptizers after the polymer is broken down or masses. Next, stabilizers such as antioxidants and magnesium oxide are added. Fillers and plasticizers are incorporated next. Finally, zinc oxide, curing agents, and accelerators are added. This general mixing technique is applicable to both internal (Banbury[®]) and external (mill) procedures. If scorch safety is a concern, the zinc oxide and any accelerators should be added in a second pass or on the finishing mill. A dump temperature above 105°C for clay-loaded compounds helps minimize the content of cure-retarding moisture.

## Calendering

For preparation of calendered sheet or skim coating fabric, compounds based on Neoprene T types or blends containing Neoprene WB are preferred since the presence of gel reduces nerve and gives smoother sheets. Using relatively high filler loading levels will also help provide smooth processing stocks.

Typical conditions on a three roll calender for stocks of Neoprene G types require the following roll temperatures:

Top Roll	70°C to 90°C (158°F to 194°F)
Middle Roll	50°C to 60°C (122°F to 140°F)
Bottom Roll	32°C to 38°C (90°F to 100°F)

Neoprene W types are best calendered at temperatures on both the top and middle rolls ranging from 7°C to  $12^{\circ}$ C ( $10^{\circ}$ F to  $20^{\circ}$ F) higher than those used for Neoprene G types. Internal lubricants may be added to the compound as needed.

# Frictioning

A compound designed for frictioning will typically be based on a Neoprene G type polymer. Moderate carbon black and oil loadings are acceptable.

Typical roll temperatures are as follows:

Top Roll	80°C to 90°C (176°F to 194°F)
Middle Roll	$60^\circ C$ to $70^\circ C$ (140°F to 158°F)
Bottom Roll	80°C to 90°C (176°F to 194°F)

Unlike NR, Neoprene usually adheres to the cooler roll. Where necessary, a mill coating can be used to ensure adhesion to the center roll. Picking usually indicates the center roll is too hot. If the top roll tends to pluck stock from the center roll, the top roll may be too cool. In second pass frictioning, plucking of the first side by the bottom roll suggests that this roll is too cold.

## Extrusion

Neoprene T types have outstanding extrusion characteristics because they are essentially free of both nerve and shrinkage. Blends with Neoprene WB will also possess these characteristics, but there will be some loss in physical properties. Neoprene WHV and WD types both impart stiffness in blends with other types of Neoprene, or in highly extended compounds, and thereby maintain collapse resistance.

Although popular in non-black stocks of Neoprene, the use of clay can promote die drag necessitating use of internal release agents and/or a higher green strength base polymer. When precipitated silica is used for high vulcanizate tear strength, rough extrusion may be prevented by incorporation of up to 3 phr of triethanolamine, calcium stearate, or other surface-active dispersing aids, added to the mixer with some oil before addition of the silica.

Neoprene compounds extrude best when a cooled barrel (graduated from  $20^{\circ}$ C to  $60^{\circ}$ C) and screw (40-60°C), warm head (70-80°C), and hot die (90-100°C) are used.

Cold feed vacuum extrusion is suggested with fast curing stocks for continuous vulcanization of profiles. Also, the addition of 4-10 phr of dispersed calcium oxide to the compound as a desiccant is recommended. Because this processing method usually requires short cure times at high temperatures, the use of active thiourea-based accelerators such as THIATE EF-2, THIATE H, or ETU in combination with VANAX PML are commonly used. In addition, the magnesium oxide level may be reduced to enhance cure rate. These changes necessitate careful control of storage times, temperatures, and all processing steps to minimize heat history.

## Molding

Most Neoprene compounds present little or no difficulties in compression, transfer, or injection molding operations. Any problems tend to be those commonly encountered in elastomer molding operations and are amenable to the same solutions.

Mold fouling in Neoprene compounds can be complex, but it may be minimized by observing these guidelines:

- Specify nickel-chrome tool steels.
- Include at least four 4 phr of high activity magnesium oxide, and up to 8-10 phr if fouling is present.
- Include an effective non-reactive internal mold release agent such as low molecular weight polyethylene.
- · Ensure plasticizers do not contain free acids.
- Set the highest barrel temperature consistent with safe processing and freedom from precure in the barrel so that the compound injects into the cavity at as high a temperature as possible.
- Do not specify higher mold temperatures than are necessary for efficient production. Temperatures of 180-185°C are usually adequate, with a recommended upper limit of 200°C.

# Bonding during Molding - see Adhesion to Metals

# Open Steam Curing

As with all elastomers, profiles based upon Neoprene may exhibit water spotting in open steam cure due to poorly located steam entry points, ineffective traps, or a cold autoclave. Faster curing compounds are least affected. Curing in a dry preheated talc bed is beneficial. Calendered sheet may be cured on drums wrapped in nylon or cotton fabric in the conventional way. High pressure CV cure of cable sheathing presents no unusual problems.

Distortion or collapse of extruded profiles, especially thin-walled sections, is minimized by use of gel-containing polymers such as Neoprene WB or T types, or blends, preferably compounded with carbon blacks such as N550.

Porosity may be caused by moisture or entrained air in the compound, or too slow a modulus rise. Inclusion of calcium oxide desiccant will scavenge the water. Air may be eliminated by increasing polymer viscosity, use of a screen pack behind the die to increase back-pressure, or by vacuum extrusion.

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#### CHLORINATED POLYETHYLENE

## by Srdjan Kisin* and Gary Marchand**

*Dow Europe GmbH, Horgen, Switzerland **The Dow Chemical Company, Freeport, TX

Chlorinated polyethylene¹, or CM as it is designated in ASTM D 1418, is manufactured by free radical substitution of the hydrogens of polyethylene by chlorine atoms. Hydrochloric acid, a by-product of the substitution reaction, is removed in the manufacturing process either by extensive water washing or neutralization with sodium hydroxide.

Since the chlorination reaction is a free radical substitution, its mechanism is not appreciably affected by the medium, hence the reaction can be conducted either in solution, in gaseous suspension, or in aqueous slurry suspension. A variety of polyethylenes can be used to produce chlorinated polyethylene. By far the most important of these are the linear high density polyethylenes produced by Ziegler-Natta catalysis in a slurry process.² The structure of chlorinated polyethylene may be schematically represented as:

# [-CH₂-CHCI-CH₂-CH₂-]_n

The Dow Chemical Company produces chlorinated polyethylene under the trade name TYRINTM and is the sole European-based manufacturer of these polymers, producing them at Stade, Germany. TYRIN is available as a powder, having an average particle size of 250–300  $\mu$ m, depending on the grade. To avoid the powder particles from agglomerating, antiblock agent is routinely added to the material. Usually, calcium stearate, talc or calcium carbonate are used as antiblock agents.

TYRIN chlorinated polyethylene resins are available in various grades depending on chlorine content, molecular weight and residual polyethylene crystallinity, as shown in Table 1.

Product Grade	Chlorine (%)	Melt Viscosity (Pa·s)	<b>Mooney</b> (ML 1+4 @ 125°C)	Heat of Fusion (J/g)
TYRIN 6000	35	2400		<2
TYRIN 7100	36	2400		<2
TYRIN 7000	35	2900		<2
TYRIN 2500E	25	2400		<2
TYRIN 3611E	36	800		<2
TYRIN 4211E	42	1000		<2
TYRIN CM 3630E	36		80	<2
TYRIN CM 3551E	35		90	<2

**Table 1: Typical Chlorinated Polyethylenes** 

## **Physical Properties**

The physical properties of chlorinated polyethylene change significantly

according to the chlorine level, and can be grouped in to three types of physical property behavior:

- Crystalline thermoplastic behavior, similar to polyethylene, occurs at chlorine levels of less than 25% by weight.
- Elastomeric behavior occurs at chlorine levels between 25% and 45% by weight.
- Rigid plastic behavior occurs at chlorine levels above 45% by weight.

As the chlorine content increases, the tensile strength and 100% modulus or hardness decrease until chlorine levels reach about 36%. With the increasing chlorine levels, tensile strength and hardness or 100% modulus begin to increase again while the glass transition temperature of the chlorinated polyethylene approaches room temperature. The optimal level of chlorine for elastomeric grades is between 30% and 40% by weight, because this gives the best combination of low Tg (-20°C), low hardness, improved hydrocarbon resistance, and fire retardancy. Flame retardancy and oil resistance generally increase with the increasing chlorine levels.

There are several other material characteristics that may be important to the application of chlorinated polyethylenes:

- Changes in molecular weight affect the usual balance of processability and mechanical properties of the resins.
- The type and amount of antiblock affect the potential for the resin particles to adhere together during storage.
- Variations in residual Na⁺ levels, dependent on the method used eliminate hydrochloric acid from the material (low Na⁺ residuals are required for some wire and cable elastomeric applications).

Chlorinated polyethylene undergoes a loss of hydrochloric acid when exposed to temperatures over 150°C for significant periods of time.^{3,4} The stability of chlorinated polyethylene can be significantly improved by compounding with a variety of acid acceptors such as magnesium oxide or epoxidized soybean oils. For chlorine contents of over 30% by weight, chlorinated polyethylene generally has better oxidation resistance than the parent polyethylene. The addition of hindered phenols or amines increases the oxidation resistance further.

# Compounding

Properties of the chlorinated polyethylenes can be tailored for specific applications by compounding. For example, these polymers can be compounded for very good low temperature performance. In this case, proper selection of ester plasticizers is essential for the optimum flexibility of end products. For specific applications, chlorinated polyethylene elastomers can be compounded to perform at temperatures as low as -50°C.

Chlorinated polyethylene polymers are resistant to a broad spectrum of chemicals, which is an important attribute for many of the commercial applications of these materials.⁶ In general, their resistance to inorganic salt solutions, acids,

and most bases is good, while their resistance to hydrocarbons varies widely. Their resistance to most paraffin-type hydrocarbons is excellent, while exposure to hydrocarbons with more aromatic content can cause swelling and reduced service life. Exposure to ketones, ethers, and chlorinated hydrocarbons may cause substantial swelling and dissolution of the polymer.

Material selection for compounding of chlorinated polyethylene for elastomeric applications is dependent on the type of cure system used. Three main types of cure system are widely used with chlorinated polyethylenes: peroxide cures, anionic sulfur cures (e.g., mercaptothiadiazole)⁵, or irradiation.

The formulations for peroxide and irradiation cure systems are similar. Both are dependent on carbon-carbon bond formation between polymer chains. Acidic fillers, acidic plasticizers, and zinc compounds should be avoided, regardless of the cure system selected. Aromatic oils should be avoided in peroxide and irradiation cure systems.

The anionic sulfur cure systems should be used without chlorinated paraffins, lead compounds, epoxy compounds, or adhesion promoters based on isocyanates or resorcinal-formaldehyde. Magnesium oxide has been used as a heat stabilizer in both peroxide and anionic sulfur cure systems. Alkyl-substituted trimellitates are excellent plasticizers, which provide high efficiency of plasticization and excellent high and low temperature performance in all types of cure systems. Carbon blacks provide excellent reinforcement of chlorinated polyethylene-based compounds. For colored compounds, clays, calcium carbonates and silicas are suitable for use.

## Processing

Processing chlorinated polyethylenes into thermoset elastomers can be accomplished on conventional rubber compounding equipment such as internal mixers of the Banbury type, or two-roll mills. Internal mixers allow shorter mix cycles, which are made possible by using an "upside-down" mixing procedure. The dry components are added first, followed by the liquid components, then the chlorinated polyethylene. Typical drop temperatures are 100 to 105°C.

# Applications

Applications of chlorinated polyethylene that require flexible elastomeric properties usually include chlorinated polyethylene as the main polymeric component. Specific applications include automotive hose covers, industrial hose, molded goods, and wire and cable jacketing. Typical starting point formulations, and expected physical properties for hydraulic hose tube and covers, are listed in Table 2. Examples of starting point formulations for general flexible cord and heavy-duty flexible cord jackets are listed in Tables 3 and 4. Please note that all the properties of theses formulations are listed as indications and will depend on the specific ingredients used and on the compounding procedure followed.

The largest application for chlorinated polyethylenes is in the modification of PVC, olefinics, and styrenic polymers. Chlorinated polyethylenes are used to impact-modify rigid PVC compositions for applications such as window profiles, rigid sheets and siding. Chlorinated polyethylenes can be added to ABS resins to improve both impact strength and ignition resistance. Blends of chlorinated polyethylene and olefinics have been used to make ignition resistant thermoplastic wire and cable jackets.

Ingredients (phr)	Α	В
TYRIN CM 3630E	100.0	100.0
N762 Carbon Black		100.0
N550 Carbon Black	50.0	
Calcined Clay*	50.0	
TOTM (Trioctyl Trimellitate)		20.0
Phthalate Ester Plasticizer	35.0	
MgOH (nigh activity)	7.0	
MgO (calcined, high surface area) Echo® Δ		10.0
Butvraldehvde-amine (e.g. VANAX [®] 808)	1.0	1.5
Polyethylene (Brookfield viscosity @ 140°C 0 18 Pas)	2.0	2.0
Polyethylene Glycol	1.0	1.0
Totals	248.5	237.5
* Alkaline clay fillers should be used in elastomeric compounds be catalyze dehydrochlorination reaction	cause presence	of acids will
Mooney Viscosity, ML 1+4 @ 100°C	77	155
Mooney Scorch @ 121°C		
Minimum Viscosity	34	75
Minutes to 5 pt. Rise	8	5
ODR @ 160°C, 3° Arc, 30 min. chart		
M _L (dN·m)	13	32
M _H (dN⋅m)	67	112
t _s 2 (min)	2	2
ť 90 (min)	15	10
	4	0
Original Physicals, Press Cured 25 min. @ 160°C		
Hardness, Shore A	80	87
100% Modulus, MPa	6.2	13.7
Flongetion %	12.4	10
	374	109
Retained Properties After Aging in Air, 70 hrs. @ 150°C	1	F
Taroniess, Pts. Change	109	5 110
Flongation %	108	45
Retained Properties After Aging in Air 168 hrs @ $125^{\circ}$ C		10
Hardness Pts Change	4	4
100% Modulus. %	174	115
Tensile, %	108	111
Elongation, %	65	68

 Table 2: Hydraulic Hose Tube and Cover Formulations

# Table 2: Hydraulic Hose Tube and Cover Formulations (continued)

Retained Properties After Aging in Air, 1000 hrs. @ 125°C Hardness, Pts. Change Tensile, % Elongation, %	14 137 17	8 111 37
Retained Properties After Aging in IRM 903 Oil, 70 hrs. @ 150°C Hardness, Pts. Change 100% Modulus, % Tensile, % Elongation, % Volume, %	-27 117 89 44 51	-20  87 37 45
Retained Properties After Aging in Dextron III, 70 hrs. @ 150°C Hardness, Pts. Change 100% Modulus, % Tensile, % Elongation, % Volume, %	-12 120 69 31 25	-11  85 32 26
Retained Properties After Aging in Fuel B, 70 hrs. @ 23°C Hardness, Pts. Change 100% Modulus, % Tensile, % Elongation, % Volume, %	-24 67 79 80 34	-24 72 73 66 39
Compression Set, Method B 70 hrs. @ 25°C, % Tear, Die C, kN/m	57 250	41 241
Low Temperature Properties, DSC, °C	-40	-37

# Table 3: General Purpose Flexible Cord Jacket (90°C) Formulation

Ingredients	phr
TYRIN CM 3630E	100.0
Trimethylolpropane Trimethacrylate	5.0
VAROX [®] 802-40KE Peroxide	5.0
N550 Carbon Black	35.0
Calcium Carbonate	150.0
Diisonyl Phthalate	38.0
Paraffin Wax	2.0
MgO (calcined, high surface area)	5.0
Total	340.0
Specific Gravity	1.067
Mooney Scorch at 121°C	
Minimum Viscosity	25
Minutes to 5 pt. Rise	>25
ODR at 204°C, 3° Arc, 6 min. chart	
M _L (dN⋅m)	8
M _H (dN⋅m)	65
ť 90 (min)	1.73

	UL 62, 1.10	T)/ 4
	Specification	I Y-4
Vulcanizate Properties 1.16 mm. (0.046 in.) Inst Cured 2 min. in 1.72 MP	ulation on No. 14 AWG Aluminum Wire a (245 psi) gauge steam	
Original Physicals		
100% Modulus, MPa		4.3
200% Modulus, MPa		5.9
Tensile, MPa	8.2	9.7
Elongation, %	200 min	457
Retained Properties After	Aging in Air, 240 hrs. @ 110°C	
Tensile, %	50 min	111
Elongation, %	50 min	86
Retained Properties After Aging in IRM 902 Oil, 18 hrs. @ 121°C		
Tensile, %	60 min	95
Elongation, %	60 min	68

# Table 3: General Purpose Flexible Cord Jacket (90°C) Formulation (continued)

# Table 4: Heavy Duty Flexible Cord Jacket (90°C) Formulation

Ingredients	phr
TYRIN CM 3630E	100.0
Trimethylolpropane Trimethacrylate	5.0
VAROX [®] 802-40KE	5.0
Calcium Carbonate	30.0
Hydrated Aluminum Silicate	20.0
Precipitated Hydrated Amorphous Silica	20.0
TOTM (Trioctyl Trimellitate)	30.0
MgO (calcined, high surface area)	4.0
Antioxidant (e.g., AGERITE [®] RESIN D [®] )	0.2
Total	214.2
Specific Gravity	1.384
Mooney Scorch at 121°C	
Minimum Viscosity	23.5
Minutes to 5 pt. rise	>25
ODR at 204°C, 3° Arc, 6 min. chart	
M _L (dN·m)	10
M _H (dN·m)	75
ť 90 (min)	2.0

ic IC	CEA S-68-516 4.4.11, EA S-19-81 7.6.19.1.7	TV 7
Vulcanizate Properties	Specification	11-7
1.16 mm. (0.046 in.) Insula Cured 2 min. in 1.72 MPa	ation on No. 14 AWG Aluminum Wire (245 psi) gauge steam	
Original Physicals		
100% Modulus, MPa		3.2
200% Modulus, MPa	3.45 min	4.8
Tensile, MPa	12.3 min	15.8
Elongation, %	300 min	572
Retained Properties After A	ging in Air, 168 hrs. @ 100°C	
Tensile, %	85 min	115
Elongation, %	85 min	95
Retained Properties After Aging in IRM 902 Oil, 18 hrs. @ 121°C		
Tensile, %	60 min	99
Elongation, %	60 min	82

## Table 4: Heavy Duty Flexible Cord Jacket (90°C) Formulation (continued)

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# CROSSLINKED POLYETHYLENE

# by E. P. Marsden*

Borealis Compounds Inc. Port Murray, NJ *Retired

Commercially available polyethylene resins have traditionally been grouped into two basic families according to the processes by which they are manufactured. Over the last few years the development of single site metallocene catalysts, and the use of multiple reactors, have created sub-sets of the basic families:

- Polymers produced by a Low Pressure Process
- Polymers produced by a High Pressure Process
- Polymers produced by Single Site (Metallocene) Catalysts
- Multiple Reactor Systems

Polymers Produced by a Low Pressure Process–These polymers are generally produced using transition metal catalysts at low pressure, in the gas phase, in solution or in slurry. Such polymers are essentially linear, or contain short chain branches and are, in reality, copolymers of ethylene with one or more higher  $\alpha$ -olefins. High Density Polyethylene (HDPE), Linear Low Density Polyethylene (LLDPE) and Very Low Density Polyethylene (VLDPE) are members of this family.

Polymers Produced by a High Pressure Process – These polymers of ethylene, with or without polar comonomers, are produced by a high pressure free radical process. Such polymers are not only highly branched, but also contain a significant number of long chain branches. Low Density Polyethylene (LDPE) and the polar copolymers of ethylene with ethyl acrylate (EEA), butyl acrylate (EBA), methyl acrylate (EMA), vinyl acetate (EVA), acrylic acid (EAA) and vinyl trimethoxy silane (EVTMS) are typical members of this family.

Polymers Produced by Single Site (Metallocene) Catalysts – Conventional catalysts contain reaction sites that have different reactivity, both in terms of the rate of polymerization and, if a comonomer is used, in terms of the rate of incorporation of the comonomer. This leads to a product that is relatively heterogeneous, and the final product properties are the weighted average of the properties of the various structures present in the polymer.

In contrast, polymers made by using single site catalysts are homogeneous, both in terms of molecular weight and the amount of comonomer incorporated, and its distribution along the individual polymer chains.

Materials produced using single site catalysts have better strength and clarity than do materials produced by using conventional catalysts. However, the narrow molecular weight distribution can make for difficult processing. *Multiple Reactor Systems* – Multiple reactors allow blends to be made at the molecular level rather than by physical mixing. Reactor blending enhances all the properties that a blend is intended to promote, e.g., toughness, optical properties and processability.

Multiple reactors can be used to produce the same polymer but with different molecular weight distributions, totally different polymers or combinations of the two. Reactors of different types can be linked together to provide unique properties not obtainable with a single reactor system.

# **General Properties of Polyethylene**

Polyethylene and its copolymers are all semi-crystalline, regardless of the method by which they are made. The higher the degree of crystallinity, the higher the density. Crystallinity is a function of molecular weight, the molecular weight distribution, the nature and quantity of the comonomer and the distribution of the comonomer across the various molecular weight fractions. Low-pressure polyethylenes are commercially available in the density range of 880 to 963 kg/m³, with melt indices of 0.01 to several hundred. These polymers may contain comonomers such as propene, butene, hexene, octene or 4-methyl pent-1-ene. High-pressure polyethylenes have densities between 917 and 930 kg/m³ and melt indices of 0.1 to 50. The densities of polar copolymers vary according to the comonomer. The stiffness of these polymers is also a function of crystallinity, which is mainly governed by the amount of higher olefin or polar comonomer that is incorporated. As the temperature of the polymer approaches its melting point, crystallinity is reduced, and it loses all its mechanical strength. The majority of polyethylenes therefore cannot be used above 70 to 80° C, and polar copolymers are limited to still lower maximum temperatures.

# Effects of Crosslinking Polyethylene

Crosslinking (curing) increases the molecular weight of the polymer by tying the polymer chains together. (In theory any article which is made of crosslinked material is a single molecule.) As a result of this process, the resistance to thermal deformation is greatly increased, allowing damage free use at temperatures close to and even above the polymers melting point. To illustrate this point, uncrosslinked thermoplastic power cables have a rated temperature of 75° C, while crosslinked thermoset cables can operate at 90° C. Similarly, crosslinked pipes can be used for hot water service, while thermoplastic pipes are restricted to cold water service.

Uncrosslinked thermoplastic materials can be melted and formed any number of times. Once crosslinked, a thermoset material cannot be recycled. Nevertheless, it can be heated and deformed and the deformed shape maintained by rapid cooling. Reheating the deformed shape causes it to revert to the original shape. The shrink tubing industry uses this "memory effect".

Other important effects of crosslinking are an increase in resistance to solvents, physical toughness and environmental stress crack resistance (ESCR). Both of these advantages are used, for instance, by the rotomolder. A low molecular

weight, low viscosity material is required to evenly fill the rotating mold used to form the part. However, this uncrosslinked material would have poor impact strength and poor stress cracking resistance when exposed to detergents and oils, which may be found in the operating environment. Crosslinking imparts toughness and stress crack resistance to the material.

Some of the more common properties of polyethylenes that depend on density and modification by crosslinking are shown in Table 1.

Property	Effect of Increasing Density on Property	Change in Property on Crosslinking
Stiffness	+	=
Hardness	++	=
Tensile strength	+	+
Abrasion resistance	+	+
Resistance to creep	+	+
Solvent resistance	+	+
Thermal Conductivity	+	=
Thermal Expansion	+	-
Melting point	+	-
Shrinkage	-	-
Crosslinkability	-	N/R
Elongation at break		-
Stress crack resistance		++
Impact strength		++
Permeability	-	-
Transparency	-	-
Filler acceptance		=

Table 1: Effect of Density and Crosslinking on Properties of Polyethylene

## **Crosslinking Processes**

## Peroxide Cure (Vulcanization)

Peroxide crosslinking of polyethylene requires a thermoforming step. The polymer is heated above its melting point, but below the decomposition temperature of the peroxide. A crosslinking step follows in which the temperature of the polymer/peroxide mixture is raised sufficiently so as to decompose the peroxide to peroxy radicals. These radicals then abstract hydrogen from the polyethylene chain to form carbon radicals. These radicals can then react with other carbon radicals to form a crosslink.

Peroxides of different decomposition temperatures are available for crosslinking polyethylene. For LDPE, which has a melting point of 110° C, VAROX[®] DCP (dicumyl peroxide) is used. For HDPE, with a melting point of 130° C, high temperature peroxides such as VAROX DBPH (2,5-dimethyl-2,5-di-[t-butylperoxy]hexane), or VAROX 130 (2,5-dimethyl-2,5-di(tert-butylperoxy) Hexyne-3) are used.

Care must be taken that premature crosslinking (scorch or pre-cure) does not occur in the extruder during the thermoforming step since it adversely affects both the aesthetics and properties of the finished article. Excessive scorch formation during extrusion will ultimately limit the fabrication rate of peroxide cured polyethylene products.

Peroxides usually have limited solubility in polyethylenes, and are prone to "sweatout", particularly if stored for long periods and if exposed to temperatures much below room temperature. Multifunctional cure boosters, such as triallyl isocyanurate (TAIC or DIAK[®] No.7), are often added to the formulation to reduce the peroxide level and/or to improve crosslinking efficiency. In some cases it is also possible to similarly reduce peroxide content by increasing the degree of unsaturation in the polymer chain to boost reactivity.

#### Moisture Cure

The moisture cure process, which was first discovered in the 1960's by Midland Silicones, Ltd. (later Dow Corning), requires the presence of alkoxy silane functionality in the polymer backbone. There are several variations of the method, but all depend on thermoplastic extrusion, followed by an off-line exposure to moisture to facilitate hydrolysis of the silane alkoxy groups to silanols, which condense, in the presence of a condensation catalyst, to form siloxane. The great advantage of the moisture cure process is that high extrusion rates are possible, since there is no danger of peroxide scorch, although all materials must be thoroughly dry to avoid moisture scorch. Most modern compounds contain a scorch inhibitor that scavenges free moisture, which reduces or even eliminates physical drying of the compounds before use. Major end uses for silane crosslinking are low and medium voltage cables and crosslinked pipe.

#### Sioplas R Process (Two Step Process)

An initial extrusion grafting step is performed which requires the addition of 1 to 2% of a vinyl alkoxy silane (normally vinyl trimethoxy of triethoxy silane) and 0.05 to 0.25% of an organic peroxide such as VAROX DCP (dicumyl peroxide), t-butyl cumyl peroxide or VAROX 231 (1,1 bis-[t-butylperoxy]-3,3,5-trimethyl-cyclohexyl). The extrusion must provide adequate mixing of the three components, and occur at a sufficiently high temperature to decompose the peroxide and create sufficient polymer radicals to enable grafting of the vinyl silane. The grafted polymer, which is still thermoplastic, is pelletized for subsequent use. It is, of course, reactive to moisture, and care must be taken to prevent exposure to moisture during storage. Shelf lives of 3 to 6 months are typically achieved in practice.

The second step of the process is the thermoforming of the desired product: cable, pipe, or film. A catalyst masterbatch, including fillers or other additives such as flame retardants, if required, is mixed with the grafted resin, and the compound is then extruded, usually on a conventional extruder.

#### Monosil R (One Step Process)

Mixing, grafting and extrusion are carried out in a proprietary single screw extruder with an L/D ratio of 30/1. The polyethylene is fed into the extruder simultaneously with a liquid mixture of silane, peroxide and crosslinking catalyst. The liquids are typically absorbed onto an inert carrier. The long screw permits dispersion, grafting and homogenization, and the grafted melt is immediately thermoformed. The complexity of the proprietary extrusion and liquid pumping system of this process is formidable; highly skilled personnel, constant process supervision and consistent raw materials are required for trouble-free operation. The introduction of "dry" processes which use carriers for the silane and other liquid additives have helped to simplify this complex process.

#### Ethylene-Silane Copolymer

Copolymerization of ethylene and vinyl silanes (typically vinyl trimethoxy silane) produces polyethylene copolymers of well-defined structure, cleanliness and reactivity. The formulator mixes a catalyst masterbatch with the copolymer and extrudes or thermoforms it in a manner similar to the Sioplas process. The superior shelf life, cleanliness and product consistency of this copolymer have enabled the replacement of Sioplas in a large number of product areas.

As noted, all moisture cure processes require a separate off-line curing step. The extrudate is crosslinked by immersion in hot water, by exposure to steam in a "sauna", or by storage in humid air; the rate of crosslinking is roughly proportional to the square of the thickness of the polyethylene, and increases according to the decreasing density or crystallinity of the polymers. Typically, a reel of 14 AWG wire insulated with 30 mil LDPE will fully crosslink in 4 to 5 hours in 80 to 90° C water. Medium voltage cable, e.g., 220 mil wall, requires 16 to 24 hours to fully cure.

The recent introduction of cure systems using highly active crosslinking catalysts has allowed curing times to be drastically reduced. Curing times that could only be obtained at elevated temperatures are now realizable at room temperature, thus avoiding investment in saunas or immersion baths. These products are commonly known as "Ambient Cure" systems.

#### Radiation Cure

High energy radiation, such as electron beam or X-rays, is an efficient, if somewhat costly, method of crosslinking polyethylene.

Radiation, like peroxides, induces the formation of radicals and carbon-carbon crosslinking. Crosslinking during irradiation normally occurs at low temperature (below the melt point of the polymer), and thus produces crosslinked structures different than peroxide-cured systems, which are crosslinked in the molten state. The structure of a crosslinked polymer depends to a large extent on its crystalline morphology, since the major crosslinking sites are found in the amorphous part of the polymer.

The advantage of a radiation cure is that the process is applicable to natural or filled medium and high-density polyethylenes, which pose serious scorch related problems for peroxide curing. Unlike peroxide curing the only by-products of radiation curing in an inert atmosphere are hydrogen and low molecular weight hydrocarbons. Whereas these may cause voids or even bubbles in thick-walled parts, they are nontoxic and nonodiferous by-products. For example, irradiated film has been used for more than thirty years in direct food contact applications for which peroxide and moisture cure systems are not allowed.

The disadvantages of irradiation are: a maximum thickness of only several mm, generally poor aging characteristics due to antioxidant deactivation, and the difficulty of homogeneous irradiation.

#### Applications

#### Wire and Cable

For cable manufacture, XLPE typically requires that the polymer be extruded, using a low shear screw and a streamlined die head, onto a conductor at a temperature no higher than 135° C, to avoid scorch. The cable feeds into a vulcanization tube at a temperature of 200 to 450° C. The high temperature causes the peroxide to decompose, and crosslinking occurs. The rate is generally limited by the time required to transfer sufficient heat to the polymer/peroxide mixture in order to cause peroxide decomposition. Subsequently the crosslinked cable is cooled to below the melting point of the polymer so as to permit deformation-free wind-up. The length of the vulcanization tube and the temperatures in the tube are therefore major factors affecting the rate of extrusion. The choice of peroxide is also a critical factor, as each peroxide has a maximum safe processing temperature and a characteristic cure temperature and rate. VAROX DCP, VAROX 802, di-tert-butyl peroxide or VAROX DBPH are most frequently used.

The vulcanization tube may be vertical, catenary or horizontal. Heat for curing may be supplied by steam, nitrogen under pressure, silicone oil or molten salts. Water or cold nitrogen is used for cooling. This explains the descriptive terms: steam cure, dry cure/wet cool and dry cure/dry cool. The high pressure in the vulcanization process minimizes the occurrence of voids in the polymer caused by the peroxide decomposition products. The pressure also reduces sagging of the polymer in the thermoplastic state as it is heated above its melting point. The melt strength of the polymer is an important factor in preventing sagging. Vertical extrusion virtually eliminates all sagging.

Dry cure is almost always used for higher voltage cables (>15 kV) due to the great reduction in micro voids (which are caused by the condensation of steam). It has been suggested that microvoids are a major factor in the initial electrical breakdown strength of the cable. Indeed, it is claimed that dry cure/dry cool cables typically show 10 to 20% higher breakdown strengths than do steam cured cables. Increases in output rate of 10 to 15% are possible, since higher temperatures can be attained in the curing tube than with steam.

A typical peroxide cured medium voltage power cable insulation compound is shown in Table 2.

Ingredients	V	Veight, %
Low Density Polyethylene (LDPE)		97 - 98
VAROX DCP Peroxide		1.5 - 2.0
Antioxidant		0.2 - 0-5
	Typical	Values
Original Tensile Properties	Crosslinked	Thermoplastic
Hardness, Shore D	50	40
Tensile, MPa	19.31	15.17
Elongation, %	400	500
Retained Properties After Aging 168 hrs.	@ 136° C	
Tensile, MPa	100%	Melts
Elongation, %	95%	Melts
Brittleness Temperature	-75° C	-35° C

Table 2: Medium Voltage Power Cable Insulation Compound

#### Pipe

Pipe is crosslinked by peroxide in a long die ("Engel" Process), since a vulcanization tube would deform the pipe before crosslinking could take place.

Crosslinking of polyethylene pipe provides increased long-term strength, in that the characteristic "knee", exhibited by the thermoplastic pipe under pressure testing, is shifted up two or three orders of magnitude. Further, environmental stress crack resistance is no longer a concern and the pipe can be rated for use at higher temperatures in more aggressive media. In Europe, XLPE pipe, rated up to 95° C, is manufactured by moisture cure, irradiation and peroxide processes.

Due to massive failures of domestic hot water pipes made of poly (butene-1), pipes made from XLPE, and in particular moisture-crosslinkable silane copolymer materials, now dominate this market.

## Rotomolding

Grades of powdered polyethylene that contain peroxide, antioxidants and colorants can be successfully crosslinked by the rotomolding process.

Generally, high temperature peroxides such as VAROX DBPH or VAROX 130 are employed with additional cure boosters such as VANAX[®] MBM. The polyethylenes can also be specifically designed to contain high carbon-carbon unsaturation, which will reduce the required amount of peroxide that leads to lower void content in the molded polymer.

As shown in the Table 3 below, crosslinking a linear high density resin improves several properties that are of particular importance in applications such as chemical storage tanks for which toughness and safety are key requirements:

- Resistance to chemical attack (ESCR)
- Impact Strength
- · Resistance to crack propagation from gouges (Notch test )
- Resistance to deformation under load (LTHS creep Test)

Table 3:	Comparison	of Crosslinked R	Resins vs. Linear Resins
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Test Procedure	Units	Crosslink Resin	Linear Resin
Density, ASTM D 1505	g/cc	.943	.941
ESCR Cond. A, F50, ASTM D 1693, 10% Igepal	hrs.	> 1000	< 100
Heat Distortion Temp. ASTM D 648 @ 66 psi	degrees Celsius	67°	65°
Low Temperature Impact ARM- Low Impact for 1/8" specimen	ft. Ibs	75	70
Polyethylene Notch Test (PENT) ASTM F 1473,(176° F, 350 psi)	hrs.	> 1000	< 10
Long Term Hydrostatic (LTHS) (Creep) @ 140° F	psi	900	< 500

# Shrink Tubing and Sleeves

The memory effect of crosslinked polyethylene enables the polymer to "remember" its shape when heated above its crystalline melting point. A crosslinked tube is heated above its melting point and deformed, for example, by expansion, then immediately cooled to freeze its shape. A second heating above the melting point will remove the frozen-in stresses, allowing the crosslinked network to recover its original form. Sleeves, cable joints and shrink film are manufactured by this method. Irradiation and peroxide crosslinking are the most widely used processes in this application.

# Film

Crosslinked film provides extremely high impact strength and tear resistance, and increased temperature stability. However, it can no longer be sealed by thermoforming, and applications to date have principally been in shrink film.

# Foam

Crosslinking is used in foamed polyethylene in two ways: 1) a low degree of crosslinking increases the melt strength of the polymer immediately prior to foaming, leading to regular cell formation and stability, and 2) fully crosslinking the finished foam provides dimensional stability at higher temperatures, improved solvent resistance and higher resilience.

Silane, peroxide and irradiation processes can all be used to obtain low degrees of crosslinking. Only the silane and irradiation processes are typically used to fully crosslink the foam.

# **Determining the Degree of Crosslinking**

#### Gel Content and Swelling Ratio

Extraction using boiling decalin or xylene (ASTM D 2765) allows the gel content (insoluble fraction) of the polymer to be determined. The higher the gel content, the higher the degree of crosslinking. Typical gel contents for most applications are 60 to 95% for fully crosslinked polyethylenes. However, the gel content depends on the nature of crosslinking. Peroxide and radiation crosslinking generally give higher values than does silane crosslinking.

The swelling ratio is the weight of the gel, swollen with decalin, divided by the weight of the initial sample. The lower the ratio, the more crosslinked the polymer. The swelling ratio can be used in the Flory equation to determine the average molecular weight between crosslinking sites.

The major drawback of these tests is the time required (about 24 hours) to obtain results.

## Hot Creep/Hot Set (IEC 502/540 or ICEA T-28-562)

Hot creep is a more rapid test. It measures the elongation of the polymer at  $150^{\circ}$  C or  $200^{\circ}$  C under a constant load of 0.2 or 0.6 MPa (20 or 40 N/cm²). Typically, a strip 10 mm x 100 mm is suspended in an oven and a weight is attached to provide the specified force. The elongation of the sample is measured after 15 minutes. The higher the elongation, the lower the degree of crosslinking. Typical end-use specifications require a maximum value of 175% elongation. Values of 30 to 100% elongation are usual.

On completion of the creep test, the weight is removed from the sample and the elongation is remeasured after five minutes at the test temperature. The amount of unrecovered elongation is the "Hot Set" value. Fully crosslinked samples recover completely and show zero percent hot set. Typical specifications allow a maximum of 5 to 15% hot set.

## Summary

In general, compared to their thermoplastic analogues, crosslinked polymers have increased hot deformation resistance, thus allowing higher service temperatures, increased general toughness and resilience, along with increased resistance to chemical and solvent attack.

Crosslinked polyethylene is widely used for a variety of end products, including hot water pipes, wire and cable, large rotationally - molded parts, cushion foams, and shrink tubes. Crosslinking can be affected by the thermal decomposition of peroxides, by the hydrolysis and condensation of silanes that are incorporated into the polyethylene, and by radiation.

#### NITRILE ELASTOMERS

# by Michael Gozdiff*, Mark S. Jones and Tom Hofer

Zeon Chemicals L.P. Louisville, KY *retired

The discovery of copolymerizing butadiene with acrylonitrile (ACN) to yield nitrile elastomers (NBR) is claimed by both Germany in 1930, in an account by Werner Hofmann¹, and France in a 1931 patent. Commercial nitrile rubber production began in 1935 in Germany, and in January 1939 The B.F. Goodrich Co. initiated nitrile production in the United States.² These early nitrile elastomers were polymerized at temperatures of 30°C^{3,4} or higher, and are now known as "hot" nitriles. Although by 1948 technology advances allowed polymerization to efficiently occur at temperatures as low as 0°C, because of practical considerations, polymerization reactions usually occur at 5°C to 10°C.⁵ These are referred to as "cold" nitriles.

All commercial nitrile elastomers are made by emulsion polymerization of 1,3-butadiene and acrylonitrile. The polar acrylonitrile component provides the useful contribution for product applications requiring oil and gasoline resistance, abrasion resistance, gas permeability and thermal stability.⁶ The combination of cost effectiveness and performance value is the reason demand for nitrile elastomers has steadily increased through the years. Their commercial importance is further supported by the fact that nitrile elastomers are produced at more than 20 locations in the world.

North American nitrile elastomer manufacturers are Zeon Chemicals L.P. in Louisville, KY (Nipol[®]) and ParaTec in Mexico (Paracril[®]).

# **BASIC COMPOSITION**

In their simplest form, nitrile elastomers are copolymers having acrylonitrile/ butadiene monomer ratios in the range of 18/82 to 50/50. The ACN content is one of the two primary criteria for defining every NBR. The ACN level, by reason of polarity, determines several basic properties, such as oil and solvent resistance⁷, low temperature flexibility, glass transition temperature ( $T_g$ )^{8,9}, and abrasion resistance. Higher ACN content provides improved solvent, oil and abrasion resistance, along with higher  $T_g$ , while a lower ACN content improves compression set, low temperature flexibility and resilience.¹⁰

The other primary criterion is Mooney viscosity, a measure of approximate molecular weight, or toughness. Several specific monomer ratio combinations may be available at several Mooney viscosity levels to suit different processing requirements for the manufacture of the finished rubber article.

During the nitrile manufacturing process, such additional factors as the selection of emulsifier, stabilizer and coagulation systems; tailored molecular weight distribution; and the introduction of a third monomer can further influence processing and performance properties quite significantly.

#### **Elastomer-Related Processability Considerations**

In addition to the proper selection of compounding ingredients the correct choice of nitrile elastomer can be very important to optimize compounds for extrusion, calendering, compression molding, injection molding, embossing, etc.

Factors affecting the processability characteristics of compounds include the nitrile rubber's acrylonitrile content, molecular weight, polymer architecture, and the types and amounts of non-polymer components present in the elastomer. Polymer architecture includes the extent of branching and gel, the *cis, trans,* and vinyl butadiene percentages, the molecular weight distribution and the comonomer distribution. These factors can be summarized as those properties contributing to the total viscous (or fluid) component of the elastomer, and those contributing to the total elastic (or spring-like) component. The viscoelastic properties¹¹ are measured by several instruments, which measure the overall viscoelastic properties, but do not, however, fully define the nature of the contributing nuances. Full disclosure of an elastomer's nature requires additional complex and expensive analytical techniques.

## **Acrylonitrile Content**

Acrylonitrile content plays a significant role in processing, in addition to end use performance. The acrylonitrile portion of the polymer chain is thermoplastic, while the butadiene portion is more "rubbery". The higher the acrylonitrile content, the more thermoplastic the nitrile's processing behavior.

#### **Mooney Viscosity**

Mooney viscosity is the other most commonly cited criterion for defining nitrile elastomers. It is the current standard physical measurement of the polymer's collective architectural and chemical composition. Mooney viscosity is measured under narrowly defined conditions, with a specific instrument that is fixed at one shear rate. There are an almost unlimited number of ways to modify polymers to derive any given Mooney number, with little assurance of uniformity in the polymer's true architecture.

#### **Emulsifier System**

The emulsifier system^{12,13} is one of the more important polymer attributes which characterize performance. It is usually next in importance, after ACN content and Mooney. There are three basic systems used: fatty acid, tall oil rosin acid and synthetic-based soaps. These are often further subdivided into blended soap systems. Although the specifics of the emulsifier systems are rightfully proprietary to the polymer manufacturer, generalities should be sought out. Each type of emulsifier system can affect factory processing differently. The effects include mixing, calendering, building tack, extrusion; cure rate, mold fouling and adhesion. Each emulsion system carries its own set of attributes. The synthetic soaps are most expensive, while providing the lowest levels of extractables, for low mold fouling, good adhesion and high shear rates for good filler dispersion. The fatty acid soaps are the least expensive, and yield fast rates

of cure and flow. Negatives include possible problems with adhesion, building tack, and extrusion rates. The tall oil based rosin soaps are intermediate in cost and most processing properties, falling between the fatty acid and synthetic soap systems.

# Stabilizer System

Stabilizer systems consist of chemical additives that provide elastomer stability¹⁴ during storage and mixing. Staining and semi-staining amines, phenolics and complex phenyl phosphites are the antioxidants most commonly used. The correct elastomer/stabilizer selection is based on the final product's application, such as high temperature oil service, FDA requirements or color fastness.

# **Coagulation System**

Coagulants¹⁵ used in making an NBR can affect cure rate and state of cure. Coagulating systems can also influence cured properties, including modulus, compression set, water swell and corrosion. Calcium chloride is one of the most commonly used coagulants. It has the benefit of fast cure rate, high modulus and low compression set. On the negative side, residuals may contribute toward water sensitivity and corrosion in some sealing applications. Other common coagulants include aluminum sulfate and magnesium sulfate. Aluminum sulfate's primary benefit is low water sensitivity coupled with low corrosion contribution. Magnesium sulfate provides some benefit with heat resistance.

## Microstructure

Microstructure is concerned with how monomers are physically assembled within the polymer chains. This includes types of monomers, quantities of each and how they are dispersed throughout the polymer chains. At a given ACN content, the acrylonitrile can be "single charged," providing a benefit with low temperature impact brittleness, or it can be "evenly distributed" providing an improved (lower) T_g. Each distribution is better for some applications, while having deficiencies in others.

The ratios of the double bond types, contributed by the butadiene, have an impact on the behavior of the polymer. There are relatively standard proportions of 1,4 *cis*, 1,4 *trans* and 1,2 butadiene within the polymer backbone. Cold nitriles have a higher 1,4 *trans* content, than is found in the hot varieties.¹⁶ The higher *trans* content is a contributor to the easier processing of cold polymers as compared to their hot counterparts.

## Macrostructure

Macrostructure concerns the structural assembly of the polymer mass. It deals with the polymer's architecture. When NBR is polymerized, molecular chains do not all begin to form at the same time. The rates of chain formation are also not uniform. For practical purposes, at any given instant there is an enormous size differential in the population of constantly growing polymer chains. The physical character of the polymer mass is a summation of positive and negative contributions of all these chain members at the time the reaction is stopped. There is a gradient of molecular chain lengths ranging from very short and plasticizer-like to very long and tough. This summation can be measured, as molecular number, molecular weight and distribution. Molecular weight distribution is the attribute most compounders find of interest. Macrostructure also categorizes the extent polymer chains are linear, branched or gelled.

## Gel

Gel^{17,18} is usually divided into two arbitrary categories. The first, called micro gel, is the crosslinked and solvent-insoluble material caught on a 0.45-micron filter, but passes through a 10-micron filter. The second, macro gel, is that material larger than 10 microns. The possible presence of gel cannot be ignored, particularly if it is a significant part of the polymer content. The presence, or absence, of gel can significantly affect every aspect of factory processing.

A high gel content could be beneficial in one application and detrimental in another. For example, high gel content resists flow and provides green strength desirable for maintaining dimensional stability. The same resistance to flow will make the same nitrile elastomer unsatisfactory for injection molding. Gel can also effect on product performance. Because gel can be a significant part of the product, it must be accounted for, when analyzing any molecular weight data.

## Molecular Weight and Distribution

Molecular weight (MW) and its distribution (MWD) greatly influence how a polymer mixes, extrudes, molds and calenders in the factory. The molecular weight curve is actually a measure of the soluble polymer plus the insoluble polymer smaller than 0.45 microns. The extent to which the curve accurately represents the polymer is inversely proportional to the gel content. The molecular weight correlates directly with viscosity, or toughness. A broad molecular weight distribution lends itself to easier processing on a greater variety of equipment. The lower MW fractions behave as process aids. The medium to very high MW fractions are the strength members. A narrow MWD may not be quite so easy to process. It provides higher green strength and less cold flow, because of relative uniformity in the polymer chain lengths. This sometimes provides a benefit in some hose and molding operations. It may also influence physical properties of finished rubber articles, usually exhibiting higher tensile and modulus. Molecular weight distribution may also reflect shrinkage and nerve. This can occur when a small quantity of very high molecular weight (excluding gel) polymer is mixed in with a significant quantity of lower molecular weight polymer.

Pre-crosslinked nitrile elastomers are excellent process aids. Because these polymers are highly gelled through a difunctional monomer, their tensile properties can be severely diminished. Their rheological properties may also render them unsuited for use as the sole polymer in most rubber recipes. They are generally used as a partial replacement at a 10 to 20 part level for other polymers, such as XNBR, SBR or cold nitrile, in order to stabilize extruded profiles for further processing and to control die swell. They are used in molded parts to provide increased molding forces or "back-pressure", in order to eliminate trapped air. They can also be used to provide increased dimensional stability of calendered goods and improve release from the calender rolls. Other benefits include addition of dimensional stability, impact resistance and flexibility for PVC modification.

# NITRILE ELASTOMER TYPES AND CHARACTERISTICS

# **Hot Nitrile Elastomers**

Hot polymerized nitrile elastomers are highly branched and prone to gel formation. The prevention of gel formation with these types of elastomers requires extra precautions, not usually needed with cold nitrile elastomers. For solvent-based adhesives, a high degree of branching with low gel content is desirable. The branching helps prevent pigments from settling out of the adhesive, and the low gel promotes complete polymer solubility. The combination of low gel content with high degrees of branching also encourages good tack and a strong bond. The physically entangled structure of this kind of polymer also provides a significant improvement in hot tear strength compared with a cold-polymerized counterpart. The hot polymers' natural resistance to flow makes them excellent candidates for compression molding and sponge. Other applications are thin-walled or complex extrusions, where shape retention is important. Extrusion rates however, may be slow and power consumption may be high.

# **Cold Nitrile Elastomers**

The present generation of cold nitrile elastomers spans a wide variety of compositions. Acrylonitrile contents range from 18% to 50% of actual polymer content. Mooney values for bale nitriles range from a very tough 110 to pourable liquids. A Mooney viscosity of twenty is the lowest practical limit for solid material. Pre-plasticized grades are made using polymers in the 120 to 160 Mooney range. Within the normal polymerization temperature range used for making cold nitrile elastomers, the lower temperatures yield more linear polymer chains, while higher temperatures yield more branching. Reactions are conducted in processes known as continuous, semi-continuous and batch polymerization. Each process develops different MWDs.

Cold NBRs can present the rubber factory with significant processing benefits, because linear polymer chains are less viscous and can therefore disentangle themselves more easily than can the highly branched hot varieties. This increased mobility requires much less force to process the stock. The results are lower process temperatures and lower power consumption. The linearity also contributes to the cold nitrile elastomers easily incorporating fillers and plasticizer. The reduced force required for stock flow is a benefit for transfer and injection molding, and highly filled extrusions. The same linearity that allows stock to easily flow during mixing, extruding, calendering and molding, may also allow stock to cold flow or exhibit a shriveling effect, commonly called "nerve". The usual remedies are to blend in some pre-crosslinked nitrile elastomer.

## **Specialty Nitrile Elastomers - Preplasticized**

Preplasticized nitrile elastomers have found a primary niche market for making soft 15 to 35 Shore A printing rolls. These products are also used for other low hardness calendered and molded goods, where quality is an issue. The preplasticized nitrile elastomers, such as Nipol 1082V (containing 50 parts of DIDP), are made from 34% ACN latex having a Mooney viscosity of 140 to 160. This very high Mooney level enables incorporation of the high plasticizer content, while still providing the user with a workable rubber.

#### **Specialty Nitrile Elastomers - Carboxylated**

Addition of carboxylic acid groups to the nitrile polymer's backbone significantly alters processing and cured properties.²² The primary reason for including carboxylation is to provide a network of ionic bonds that supplement conventional sulfur or carbon vulcanization bonds. The additional ionic network is a series of metallic-carboxyl reactions. The result is significantly increased strength, measured by improved tensile, tear, modulus and abrasion resistance.

Carboxylated nitriles are used in high abrasion applications, such as rolls, conveyor belting, hose covers, oil well drilling parts, high modulus wear seals and premium footwear soles. Offsetting these benefits are losses in compression set, heat resistance, resilience and some low temperature properties. Another effect of the carboxylation is a 12 to 16 point hardness increase in most recipes.

Working with carboxylated nitrile elastomers (XNBR) requires special compounding considerations. Customary peroxide or sulfur cure systems, common to conventional nitrile elastomers, react identically with the butadiene network in the carboxylated nitrile elastomers. However, XNBR also contains the acid-base reactions of the carboxylation with metallic oxides, metallic salts, amines, and a wide variety of other acid-reactive materials that form a second crosslinking network. Water is the primary catalyst for the carboxyl-metallic reactions and must be treated as an "ultra" accelerator. Many of the compounding ingredients contain water, including the polymer itself, and this must always be kept in mind when working with carboxylated nitriles. The best way to remove water is by volatilizing it through heat generated during mixing. Desiccants such as calcium oxide do not work, because of high reactivity with the carboxylation, causing premature ionic crosslinking. Figure 1 represents the basic dual nature of the carboxyl-zinc ionic bonds and the sulfur crosslinking.²³



Figure 1: Carboxylated Nitrile Sulfur and Ionic Crosslinks
## PROCESSING CONTRIBUTION OF COMPOUNDING INGREDIENTS

## Plasticizers

Plasticizers are often used to influence processability of nitrile elastomer compounds, in addition to affecting changes in end-use performance properties. There are many plasticizers to choose from, and elastomer compatibility must be assessed to avoid plasticizer bleeding from the cured system or causing other problems. Supplier literature on plasticizers and nitrile elastomers should be consulted in order to obtain the best balance for processing and service.

## Reinforcement

As with most elastomers, fillers are used with nitrile rubbers to achieve optimum properties. Because the filler selection can be very complex and greatly affects processing, assistance from the filler and nitrile suppliers should be sought. A more detailed discussion of this topic is contained in the section on Mechanical Properties.

## **Tackifiers and Lubricants**

Tackifiers, such as coumarone-indene and phenolic resins, are often used to modify process characteristics for calendered and extruded applications where adhesion is an important consideration. Lubricants are mainly used for processes that require the stock not adhere to molds or other processing equipment. Resin and lubricant suppliers are an excellent source of guidance.

## PROCESSABILITY TESTING

Most of the processability testing methods and instruments which are used for determining how compounds based on various polymers will process in the factory are covered in the chapter on "Processability and Curemeters". Note that almost all SBR-applicable processing observations and recommendations also apply to nitriles.

## **MECHANICAL PROPERTIES**

Mechanical properties are usually called physical properties by the industry. These properties are measured by stress-strain and compression tests conducted in a wide variety of ways and conditions chosen to predict actual service performance. The selection of materials for a particular application include the nitrile, filler, plasticizer, processing aids, antioxidants, antiozonants and cure system. Each material contributes differently and shares in the mechanical properties of the finished article.

## **Nitrile Elastomer Selection**

The selection of the nitrile elastomer is normally the first recipe building block, and sets the pattern for the selection and quantity of the rest of the ingredients. The first consideration is the acrylonitrile level, followed by the Mooney, then other factors depending on factory needs or service requirements. Using the standard recipe shown in Table 1, the data in Table 2 show the relative physical properties to be expected, according to the polymer's acrylonitrile content. Note that oil resistance increases but low-temperature performance decreases with increasing acrylonitrile content.

Ingredients	phr	
Nitrile Elastomer	100.0	
N550 Carbon Black	50.0	
Zinc Oxide	5.0	
Plasthall [®] 7050	5.0	
AGERITE [®] RESIN D [®] Antioxidant	1.0	
ETHYL TUADS [®] (TETD) Accelerator	1.0	
Stearic Acid	1.0	
METHYL TUADS [®] (TMTD) Accelerator	1.0	
AMAX [®] Accelerator	1.0	
Spider Sulfur®	0.5	
Total	165.5	

# Table 2: Physical Properties of Nitrile Elastomer Series

Ningl	DNIACCO		DNI2050	DNI2250	DNI2050	N047
<u>NIPOI</u>	<u>DIN4555</u>	<u>DIN4050</u>	<u>DIV3050</u>	<u>DIN3350</u>	<u>DIV2850</u>	<u>N917</u>
Acryionitrile,	45	40	30	33	28	23
Polymer Mooney	55	53	50	50	50	62
ODR Rheometer, 3° ARC @	170°C					
M₋ (dN•m)	6.7	7.5	6.7	8.8	8.3	10.7
M _H (dN•m)	71.2	83.5	82.1	94.0	90.4	77.8
ts 2 (min)	1.2	1.3	1.6	1.6	1.5	1.5
ť 90 (min)	5.3	4.1	4.2	4.2	3.7	3.5
MDR 2000 Rheometer, 0.5°	Arc @ 170	)°C				
M∟ (dN•m)	0.87	0.79	0.80	1.0	1.0	1.3
M _H (dN•m)	12.71	16.5	16.3	18.5	17.2	15.2
t _s 2 (min)	0.91	0.90	0.90	1.00	1.00	1.10
ť 90, (min)	3.1	2.9	2.6	2.9	2.8	2.8
Mooney Viscosity, $M_{\Lambda}$ 1+4 @	100°C					
	66	71	65	73	63	62
Mooney Scorch, M _L 1+30 @	125°C					
Minimum Viscosity	37	44	39	45	41	47
Minutes to 5 pt. rise	11.7	6.8	8.5	9.5	9.5	9.4
Minutes to 35 pt. rise	15.5	10.3	12.7	14.4	15.7	18.7
Original Physical Properties						
Hardness, Shore A	70	70	71	72	71	68
Tensile, MPa	23.9	23.5	18.7	20.6	20.9	20.0
Elongation, %	469	470	382	346	372	306
50% Modulus, MPa	2.3	2.3	2.0	2.2	2.0	2.2
100% Modulus, MPa	4.4	4.4	3.8	4.5	4.0	4.7
200% Modulus, MPa	11.5	11.4	10.1	12.1	10.6	12.3
Tear, Die C, kN/m	36	35	36	36	34	24
Retained Properties After Ag	ing in Air, i	70 hrs. @	100°C			
Hardness, Pts. Change	+6	+4	+2	+3	+3	+4
Tensile, %	99	102	96	104	99	101
Elongation, %	80	79	69	77	80	78

Nipol	DN4555	DN4050	DN3650	DN3350	DN2850	N917
Acrylonitrile,	45	40	36	33	28	23
Polymer Mooney	55	53	50	50	50	62
Retained Properties After Aging in Air, 70 hrs. @ 125°C						
Hardness, Pts. Change	+10	+6	+4	+4	+3	+6
Tensile, %	102	111	99	103	108	99
Elongation, %	68	75	61	73	83	78
Retained Properties After Ag	ging in AST	⁻ M No. 1 C	Dil, 70 hrs.	@ 100°C		
Hardness, Pts. Change	+8	+6	+2	0	0	+2
Tensile, %	101	102	104	112	107	99
Elongation, %	86	79	79	89	91	74
Volume Swell, %	-4.0	-3.7	-3.4	-2.1	-1.2	-1.2
Retained Properties After Ag	ging in IRM	1 903 Oil, 7	70 hrs. @	100°C		
Hardness, Pts. Change	+3	+4	-4	-5	-8	-6
Tensile, %	104	106	101	103	97	83
Elongation, %	-14	-9	-18	-10	-12	-13
Volume Swell,	+0.1	+1.9	+5.3	+10	+16	+33
Retained Properties After Ag	ging in AST	M Fuel C,	70 hrs. @	23°C		
Hardness, Pts. Change	-18	-12	-14	-15	-17	-14
Tensile, %	-48	-49	-57	-51	-57	-84
Elongation, %	-37	-45	-57	-53	-59	-79
Volume Swell, %	+32	+33	+43	+47	+64	+84
Retained Properties After Ag	ging in Dist	illed Wate	r, 70 hrs. (	@ 100°C		
Hardness, Pts. Change	+3	+3	0	0	0	+3
Tensile, %	-7	-1	-6	+5	+5	-5
Elongation, %	-18	-27	-23	-13	-10	-17
Volume Swell, %	+2.2	+0.8	+0.1	+0.4	-0.5	-1.3
Compression Set, Method B						
70 hrs. @ 100°C	20.0	17.7	6.1	14.9	17.4	15.9
70 hrs. @ 125°C	26.3	22.2	20.6	18.9	19.2	21.4
Gehman Low Temperature	Torsion (°C,	), ASTM D	1053			
T - 2	-3	-6	-12	-17	-19	-21
T - 5	-7	-12	-18	-22	-23	-25
T - 10	-11	-14	-20	-24	-26	-28
T - 100	-17	-20	-25	-29	-30	-33

Table 2: Physical Properties of Nitrile Elastomer Series (continued)

The compounds in Tables 3 and 4 show the relative properties expected when a conventional medium acrylonitrile content polymer is blended with a carboxylated nitrile.

Ingredients	phr	phr
Nipol DN3350	100.0	
Nipol NX775		100.0
N660 Carbon Black	40.0	40.0
Dibutyl Phthalate	5.0	5.0
Stearic Acid	2.0	2.0
Wingstay [®] 29	1.0	1.0
METHYL TUADS (TMTD)	2.0	2.0
AMAX	1.0	1.0
Spider Sulfur	0.5	0.5
Zinc Oxide	5.0	5.0
Totals	156.5	156.5

Table 3: Test Compound For Carboxylated Nitrile (XNBR) Elastomers

Conventional nitrile polymers are compatible with XNBR, and are used to modify properties²⁴ and lower cost. The properties, as shown in Table 4, are linearly proportional to the XNBR content.

Nipol DN3350	100	75	50	25	0
Nipol NX775	0	25	50	75	100
Original Physical Properties					
Hardness, Shore A	67	74	80	82	83
Tensile, MPa	18.2	19.7	21.0	23.8	25.5
Elongation, %	500	460	415	420	430
100% Modulus, MPa	1.7	3.1	4.5	5.5	5.2
200% Modulus, MPa	4.8	7.3	10.0	11.4	11.0
Tear. Die C					
@ 23°C, kN/m	48.5	50.4	50.9	52.2	53.4
@ 100°C, kN/m	11.9	11.0	18.8	23.7	26.9
Compression Set, Method B					
70 hrs. @ 125°C, %	15	22	27	31	34
Pico Abrasion Index, %	73	100	159	280	493

Table 4:	Physical	Properties	of XNBR	/ Nitrile	Blends
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Table 5 was developed to show the relative contribution made by zinc oxide to the vulcanized strength of the ionic/conventional crosslinking system used with carboxylated nitrile elastomers. A gum recipe is used to discount the effect of reinforcement fillers, and to focus entirely on the ionic bond strength of the carboxylated nitrile elastomers vulcanizates.²⁵

Ingredients	phr	phr	phr	phr	phr
Nipol NX775	100.0	100.0	100.0	100.0	100.0
Wingstay [®] 100 Antiozonant	2.0	2.0	2.0	2.0	2.0
Stearic acid	0.5	0.5	0.5	0.5	0.5
METHYL TUADS (TMTD)	2.0	2.0	2.0	2.0	2.0
AMAX	2.0	2.0	2.0	2.0	2.0
Spider Sulfur	0.4	0.4	0.4	0.4	0.4
Kadox [®] 911C Zinc Oxide		3.0	4.0	5.0	7.0
Totals	106.9	109.9	110.9	111.9	113.9
Original Physical Properties					
Hardness, Shore A	48	57	64	67	68
Tensile, MPa	3.8	7.2	10.7	14	16.9
Elongation, %	600	515	410	375	365
Compression Set, Method B, 7	70 hrs. @ 100	°C			
%	58	26	18	19	17
Rebound @ 23°C, %	44	49	46	45	45
Rebound @ 100°C, %	65	65	66	58	56

Table 5: Ionic Carboxyl-Zinc Bond Contribution

#### Reinforcement

Reinforcing fillers are used with nitrile rubbers to achieve optimum properties. Carbon black and non-black fillers are used, depending on applications and level of physical properties required. Various fillers affect physical properties differently and selection of any specific filler system can be based on guidance from both filler and nitrile suppliers. A nitrile rubber test recipe for a filler comparison is given in Table 6. Figure 2 provides the effect of four black and four non-black fillers on physical properties when added to this 33% acrylonitrile, 55 Mooney nitrile elastomer. This comparison represents only a small fraction of the available fillers, yet the selection demonstrates general effects that are observed as filler levels in the compound are increased.

Ingredients	phr
Nitrile Elastomer	100.00
Zinc Oxide	5.00
Polystay 100	1.00
Stearic Acid	0.50
Reinforcement Filler	Variable
Cumar [®] MH 2 1/2	10.00
Dibutyl Phthalate	10.00
Spider Sulfur	1.50
ALTAX [®] (MBTS) Accelerator	1.50
UNADS® (TMTM) Accelerator	0.10

#### Table 6: Filler Study Test Recipe





# **Engineering Properties**

Nitrile rubber lends itself to a virtually infinite number of approaches to compounding and compounding materials. The results of this are a wide variety of compounds whose mechanical properties fall somewhere within a wide range listed in Table 7.

Property	Value
Hardness	25 Shore A to 50 Shore D
Tensile	6 MPa to 24 MPa
Elongation	100% to 700%
Compound Density	0.60 to 2.00 g/cc

Table 7: Typical Properties of Nitrile Rubber Compounds

There are several additional physical properties that change as a function of the acrylonitrile level present in the polymer. A number of these acrylonitrile dependent properties are listed in Table 8.²⁷

Table 8: Key Properties Affected by Acrylonitrile Level (Gum Rubber)

Property	% ACN	Value
	15	0.94
	20	0.95
Specific Gravity, g/cc	35	0.99
	45	1.02
	50	1.03
	15	-49
	22	-40
Tg, ℃	30	-30
0	40	-19
	50	-9
	28	0.90
Thermal Conductivity, kJ/(m hour °C)	33	0.90
	38	0.92
Thermal Expansion Coefficient (Linear)	28	175
	33	170
x 10- 11/11. C	38	150
Specific Heat	40	0.00283 <i>T</i> *+ 1.126

* T = temperature °K

## **Electrical Properties**

NBR compounds are typically not well-suited for applications where the very best insulative properties are required. Compounds can be developed which exhibit good electrical conductivity by using the proper compounding materials, such as conductive carbon blacks, and a high acrylonitrile content polymer. Using these techniques, recipes with a volume resistivity of less than 100 ohm-cm can be obtained. Electrical resistance can be increased through the use of hydrophobic mineral fillers and water resistant polymers. Under these conditions, typical electrical properties would be as shown in Table 9.²⁸

 Table 9: Properties Optimized for Electrical Resistance

Property	Value
Volume Resistivity (ohm-cm x 10 ⁹ )	35
Dielectric Constant	13
Dielectric Strength, volts/mil	251

## **Permeation Properties**

By its very nature, nitrile rubber has very good resistance to gas permeation. As the level of acrylonitrile increases in the polymer, the resistance to gas permeation also increases. A 40% acrylonitrile content polymer has permeation resistance on par with that of a butyl polymer. Permeation resistance can be enhanced through the use of platy fillers. Surface treatments of these fillers will serve to further improve the permeation resistance. Comparative gas permeation data are listed in Table 10.²⁹ For reference purposes, natural rubber is arbitrarily assigned a value of 100.

Polymer	H ₂	N ₂	<b>O</b> ₂	Co ₂	He	Air
Natural Rubber	100	100	100	100	100	100
Nitrile Rubber (41% ACN)	15	2.9	4.1	5.7	22	3.4
Butyl Rubber	15	4	5.6	4	27	4.8

Table 10:	Comparative	Gas	Permeability	of	Gum	Vulcanizates	at	25°	°C
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## VULCANIZATION

The vulcanization of nitrile elastomers is accomplished in much the same way as that of other common rubbers (e.g., SBR and natural rubber). While it is possible to employ tire-type thiazole and sulfenamide cure systems in nitrile elastomers, these are not recommended for applications requiring good compression set or high temperature resistance.

For most high temperature applications, the preferred cure systems are the thiurams and organic peroxides. The thiurams may often be modified by using a thiazole or sulfenamide as a secondary accelerator. Organic peroxide cure systems can be modified with coagents and/or sulfur/thiazoles or sulfur/sulfenamides. General information on the vulcanization of nitrile elastomers can be found in the literature.⁵ Chemical suppliers, such as the R.T. Vanderbilt Company, Inc., should be contacted for technical support in providing recommendations for their products. They are most knowledgeable concerning the many factors affecting vulcanization characteristics.

Nitrile polymers are vulcanized using sulfur-based and peroxide-based cure systems. Three subcategories of sulfur-based cure systems would be high sulfur, semi-efficient, and efficient. Examples of these systems are shown in Table 11.

			-		
High Sulfur		Semi-Efficient		Efficient	
Sulfur	1.5	Sulfur	0.5	VANAX [®] A	1.5
ALTAX (MBTS)	1.5	DURAX [®] (CBS)	1.0	METHYL TUADS	1.5
		METHYL TUADS	1.0		
		ETHYL TUADS	1.0		

Table 11:	Sulfur-Based S	ystems
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As sulfur is not highly soluble in nitrile rubber, it is suggested that surface treated versions or sulfur masterbatches be used to insure the best incorporation.

Peroxide cures are used in applications where optimum heat resistance is

required. Peroxide-cured compounds also provide excellent compression set and high modulus vulcanizates. When peroxide cure systems are used, coagents are frequently a part of the cure package. A variety of coagents are available, such as VANAX MBM, methacrylate types and liquid polybutadiene resins. Examples of peroxide cure systems with and with out coagents are listed in Table 12.

Peroxide Cure		Peroxide Cure with Methacrylate Coagent		Peroxide Cure with VANAX MBM	
VAROX® DCP-40KE	3.0	VAROX DCP-40KE Saret [®] SR 500	3.0 1.5	VAROX DCP-40KE VANAX MBM	3.0 0.5

### Table 12: Peroxide-Based Systems

## ENHANCED SOLVENT AND HEAT RESISTANCE

As with any polymer having an unsaturated main chain, vulcanized nitrile elastomer compounds are subject to degradation at high temperatures. Many antidegradants are used in compounding to help protect against high temperature oxidation. In the case of nitrile elastomers, the elevated temperature aging is especially challenging because of their frequent use in extractive media that often remove the antioxidant in the compound. Studies showing the effects of such aging on a variety of stabilizer systems are available.^{31,32} One approach that has been used to minimize this problem is the binding of antioxidant permanently into the polymer molecule during manufacture.^{33,34,35} Such polymers are said not to lose their antioxidant due to either heat volatilization or solvent extraction, so that the useful life of the compounded nitrile elastomer article is extended. Nitrile elastomers having this type of functional modification are available commercially, e.g., Nipol[®] bound antioxidant terpolymers.

## ENHANCED HIGH SPEED PROCESSING

With the advent of high-speed injection molding to improve manufacturing economics of molded products has come the need for compounds that can be "cleanly" processed at molding temperatures in the 225°C (437°F) range. "Clean" processing refers to compounds that do not cause mold fouling, corrosion or undue volatilization during processing, and do not accompany fast cure rate with poor scorch safety.

Although selection of compounding ingredients is very important for satisfactory performance under these conditions, elastomer selection is perhaps the most critical. Many conventional nitrile elastomers may yield acceptable molded articles, but will quickly foul molding equipment, rendering the process inefficient.

Some nitrile suppliers are now providing selected grades of their products with optimized levels of non-elastomeric ingredients that reduce mold fouling under extreme injection molding conditions. This development is part of the nitrile manufacturers' continuing effort to meet the changing needs of nitrile users. Their technical service staffs can provide guidance in proper product selection for various demanding process conditions.

#### POLYMER BLENDS

Nitrile elastomers are generally available in bale form, but some grades are available as particulates. These range from fine powders (<0.1mm) to crumbs (10mm).

Recent years have seen the very rapid growth of products composed of various combinations of plastics and rubbers in the form of blends, alloys, and thermoplastic elastomers. This growth is due to the many special benefits that can be obtained by this approach but, most importantly, to the advantage of processing like a plastic, while possessing rubber-like properties.

Powdered nitrile elastomers have been an important part of this growth, since they are a valuable ingredient for blending in a number of polymer systems, especially with polyvinyl chloride (PVC). PVC products can be made flexible through use of liquid plasticizers, but this approach is limited when service conditions are demanding. Nitrile elastomers have very good compatibility with PVC and the fine powder forms now available greatly extend their usefulness in blends with PVC powders.

The processing of nitrile rubber powder with PVC involves the typical chemicals used in PVC formulations. The nitrile rubber powder is added to the plasticized PVC dry blend at the end of the mixing cycle after the plasticizer and other chemicals are absorbed by the PVC resin. The melt processing is similar to that of plasticized PVC. The dry blends are usually fluxed in extruders and pelletized. The pellets are melt-processed into finished articles. It is also possible to mold or extrude articles directly from a dry blend through use of machines equipped with high shear plasticating screws.

Nitrile rubber crumb and powder are particularly useful for solving problems of permanence of plasticizer, staining, exudation, migration or embrittlement. The presence of the elastomer provides a rubber-like feel to PVC, improved abrasion resistance, compression set, tensile strength, tear resistance and flex fatigue. Also gained with the use of powdered nitrile elastomer are hot melt stability, faster extrusion and calendering speeds, and ability to extrude complex shapes.

Typical NBR levels used to modify PVC are 10 to 30 phr. A variation on this technology is NBR/PVC polyblends. In polyblends, NBR is the continuous phase and 20 to 50 phr of PVC are added to produce a thermoset elastomer with remarkable ozone resistance and enhanced resistance to certain solvents and fuels. While PVC levels as low as 20% are used, the best ozone resistance requires PVC levels of at least 30%. It is essential to precisely control mixing times and temperatures in order to promote fluxing of the two polymers. While this can be accomplished in situ during compound mixing in an internal mixer, the results can be assured through the use of commercially available prefluxed polyblends (e.g., Sivic[®] polyblends). It is important to understand, however, that not all commercially available alloys are fully fluxed products and care should be taken in product selection. It is a simple matter to determine whether or not a material is fully fluxed by examining the T_g of the product. Fully fluxed materials will exhibit only one T_g while unfluxed or partially fluxed products will show at least two distinct T_g's.

### PROCESSING PROCEDURES

Mill mixing, internal mixing, calendering, extrusion, and molding procedures are used in fabrication of nitrile elastomers into a wide variety of rubber products. Procedures for mixing, calendering, extruding, and molding were described in the previous edition of the *Vanderbilt Rubber Handbook*³⁶, and are reproduced below for this issue.

### Mill Mixing

Nitrile polymers handle well in open mill milling, with no unusual requirements. They do differ in certain ways, however, from natural rubber and SBR. Some nitrile polymers are tougher than natural rubber and do not break down as completely. For the higher viscosity types, an initial breakdown occurs followed by a leveling off, rather than the continuous viscosity drop-off of natural rubber. The lower the original viscosity of the nitrile polymer, the less breakdown occurs.

Breakdown on a cold, tight mill is recommended for best results, allowing the batch to drop in the pan between passes to keep the heat down. Five to ten minutes is sufficient before banding and adding the compound ingredients. Nitrile polymers are not crystalline, so filler dispersion must be optimized in order to obtain the best physical properties. The solubility of sulfur is lower in nitriles than in natural or SBR and, while less is used, its dispersion is more difficult. The use of finely divided and surface-treated sulfur is recommended, and it should always be added first after breakdown.

The remaining order of mixing will vary, depending on the type and amount of fillers, but certain points are important. The batch should never be cut with free pigment on the bank, but only after the pigment has either worked in or fallen through to the pan. The items most difficult to disperse should go in first. Examples are zinc oxide, sulfur, and fine particle size fillers such as N220 and N110 carbon blacks, silicas, and aluminas of all types. Plasticizers or waxes should be held out until after the fillers are well dispersed, unless the filler load is excessive and it is necessary to add plasticizer earlier. In the latter situation, only sufficient plasticizer to restore processability to the mix should be added, with the remainder following the addition of the balance of the filler. To achieve the best dispersion, plasticizers should not be added to a batch already containing dry pigment on the bank. When carboxylic nitriles are involved, the zinc oxide should be added last.

Recommended batch sizes for open mill mixing will vary depending on the specific gravity of the final compound, and the cooling capacity of the roll water-system. Generally, the following range will be adequate:

Roll length, inches	48	60	84	
Batch weight, kg (lbs)	13.5-22.5 (30-50)	20.5-34.0 (45-75)	50-72.5 (110-160)	

## **Internal Mixers**

Nitrile rubber may be very successfully mixed in internal mixers such as a Banbury[®], and procedures similar to that used for SBR are generally satisfactory.

The action of an internal mixer, however, is not sufficient to give the same breakdown to nitrile polymers as a mill, and somewhat higher final plasticity will result. This must be considered when shifting a compound from mill mixing to an internal mixer, or problems in final fabrication may arise. Maximum cooling is required, since nitrile compounds generate a lot of heat on mixing and low temperatures improve the breakdown.

The normal procedure is to add rubber and sulfur, close the mixer, and break down the rubber for 1 to 2 minutes. The dry pigments are usually added in one or two increments, depending on their type and amount. Ram pressure is required after each addition. Plasticizers are generally added later, but a portion may be added between the two pigment increments if the batch becomes too hot or dry. Accelerators are added on the dump or sheet off mill to prevent scorching, as the dump temperature will run between 104 and 149°C (220 and 300°F). Dump temperatures in excess of 149°C should be avoided unless necessary for resin fluxing or other unusual conditions. It may occasionally be necessary to use accelerator masterbatches in order to obtain proper dispersion in the mix.

Water quenching is normally used in order to rapidly remove heat, but should be considered carefully if carboxylic nitriles are involved, since moisture accelerates their cure.

### Calendering and Extrusion

Generally, compounds that extrude well will calender well. The same properties of smoothness and lack of nerve are required for both. Nitrile polymers which have these characteristics and provide excellent results are available, with the permanently pre-crosslinked types being preferred in blends with low viscosity polymers. Safe cure systems must be used due to the extra processing steps involved, and are often added at the warm-up mill stage.

Other problems arise which are peculiar to this type of processing. Magnesium carbonate or pyrophyllite is valuable for reducing porosity in the compounds. Optimum breakdown and dispersion are required for both calendering and extrusion, sometimes requiring a remilling operation at least 16 hours after original mixing. Lubricants are sometimes helpful, but must not interfere with the action of the screw, or excess air may be incorporated into the compound. The screw and barrel should be relatively cool at 38 to 71°C (100 to 160°F) while the head should be about 93°C (200°F). Again, conditions will vary depending on the compound. The die itself should be warmer still at 121°C (250°F).

Calender temperatures for unsupported sheet, coating or plying are generally:

Top Roll	77 to 88°C (170 to 190°F)
Middle Roll	60 to 71°C (140 to 160°F)
Bottom Roll	77 to 88°C (170 to 190°F)

Friction compounds are a special case and require special ingredients. High tack and low viscosity nitrile polymers which lend themselves to this type of application are available. Large amounts of ester and coal tar or coumarone-indene are necessary, generally running to 60 parts or more, to improve tack and mechanical adhesion to the fabric. Carboxylic nitrile rubber, while more difficult to friction, adheres better to fabrics, and is often chosen for this reason.

Roll building compounds have much the same requirements of tack and ply adhesion, and nitriles with high-tack and low plasticity should be used. Polymers with high nitrile content have greater inherent tack, but all are inferior to natural rubber. Knitting agents, such as liquid nitrile polymer, are also valuable. No one of these items is sufficient, and combinations are widely used.

## Molding

Three types of molding are widely used: compression, transfer and injection. All require somewhat different compound characteristics. Compression molding is generally done at low temperatures 148 to 170°C (298 to 338°F).

A wide variety of cure systems can be used, but certain viscosity characteristics are necessary for each type of molding. Compression molding operates on the principle that the compound itself will drive all air from the cavity. This requires high compound stiffness at molding temperatures. This requirement, in turn, determines the type of nitrile polymer to be used. High durometer, highly reinforced or stiff compounds can use a medium or low viscosity polymer; but soft compounds, of 50 Shore A hardness or lower, should be based on a high viscosity polymer to improve the "back pressure" and facilitate removal of the air.

The transfer and injection molding processes operate on shorter time cycles and higher temperatures; transfer molding being done at 170 to 193°C (338 to 380°F), and injection molding at up to 218°C (425°F) with clamp cycles as short as 30 seconds. Here, high flow is necessary and the lower viscosity polymers are generally preferred, unless a very soft compound is involved.

## APPLICATIONS

Nitrile elastomers are very versatile because of the unique range and balance of properties they possess. Their increasing use in blends, alloys and thermoplastic elastomers means that their applications are increasing. Summarized below are some of the common applications. Tables 13 and 14 summarize some of their common applications.

Adhesives	Highly loaded Stocks
Cements	Chemically-blown Sponge
Grouts	Oil Field Products
Molded Rubber Goods	Molded Automotive Parts
Hose Tubes and Covers	Roll Covers
Belts	Fuel Hose
Modification of PVC, ABS	Calendered Sheets
Air Conditioning Hose	Flexible Magnets
O-rings	Diaphragms
Seals	Valve Seals
Gaskets	Coatings
Printer Supplies	Flooring
Show Products, Footwear	Auto Crash Pads
Coated Fabrics	Weather Stripping, Cable

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## by D. Rosbottom and M. Jones

Zeon Chemicals L.P. Louisville, KY

## Introduction

The first commercial Hydrogenated Acrylonitrile Butadiene rubber, (HNBR), Zetpol[®] 2020, was introduced in 1984 by Zeon Corporation to serve the automotive need for a higher temperature oil resistant material. HNBR was first commercially manufactured at Takaoka, Japan. Later the same year Polysar, now Lanxess, introduced their Therban[®] HNBR which was manufactured in Orange, Texas.

HNBR is an oil-resistant elastomer consisting of ethylene saturated units, nitrile side groups and a small number of butadiene units to provide carbon to carbon double bonds. HNBR is manufactured by the selective hydrogenation of the olefin segments in NBR.

As expected from its polymer structure, the vulcanizate properties of HNBR best describe it as an elastomer combining the oil and fuel resistance of NBR with the heat and oxidation resistance of EPDM. Compared with other conventional oil-resistant elastomers, HNBR has much better tensile strength, tear strength, wear resistance and low temperature flexibility.

The presence of a small amount of unsaturation in the butadiene unit makes possible easy vulcanization with peroxide. The higher levels of unsaturation in some grades allow for sulfur curing.

## **Chemical Structure**

As shown below, the acrylonitrile unit supplies excellent oil resistance, fuel resistance and good abrasion resistance. The saturated ethylene unit provides heat resistance, chemical resistance and ozone resistance while the unsaturated butadiene units allow for vulcanization.



Figure 1: The Chemical Structure of Acrylonitrile Butadiene

## Method of Manufacture

HNBR is produced by the selective hydrogenation of a specialized nitrile rubber to produce an ethylene-butadiene-acrylonitrile elastomer with unsaturation levels controlled between 1 % and 15 %. In the manufacturing process, NBR is

first ground, dissolved in solvent and then reacted with hydrogen in the presence of a suitable catalyst. It is then coagulated, dried and packaged.



Figure 2: The HNBR Production Process

## **Classification by SAE J200**

The SAE J200 classification system is intended for use in rubber products for automotive applications. Rubber materials are designated on the basis of "type" indicating their heat resistance and "class" designating their oil resistance. "Type" is based on changes in tensile strength of not more than  $\pm$  30%, elongation of not more than  $\pm$  50% and hardness of not more than  $\pm$ 15 points after heat aging for 70 hours at a given temperature. "Class" is based on the material swelling in IRM 903 oil after a 70 hour immersion at temperatures up to 150°C.

The typical HNBR compound can be classified as DH indication a heat resistance of 150°C, and less than 30% swell in IRM 903 oil, as shown below. The classification of HNBR, however, can cover a heat resistance range for Type C to Type F of 125°C to 200°C and an oil resistance range of Class H to Class K of 10 to 30% maximum swell by selecting the appropriate unsaturation level, acrylonitrile content and using various compounding techniques.



Figure 3: SAE J200 Classification of Elastomers

## **Heat Resistance**

HNBR's excellent heat resistance provides for extended service life at elevated temperatures, with the heat resistance increasing as the degree of hydrogenation increases.

The service life of elastomers is based on the criteria that the loss of elongation should be no more than 50% and that no cracking occurs on bending after air aging at the specified temperature. A fully saturated HNBR can be peroxide cured to allow continuous use for 1000 hours at 160°C. When sulfur cured, a 90% saturated HNBR can perform for 500 hours at 125°C.

### **Oil Resistance**

HNBR has excellent oil resistance. With the variety of ACN levels available, 17% to 50%, one must keep in mind that although ACN content controls the oil resistance, it also impacts low-temperature properties; however values typically less than 25% swell in IRM 903 oil are obtained after 70 hours at 150°C.

### Low Temperature

The low temperature properties of HNBR vary with the ACN and unsaturation levels. The ethylene groups do exhibit some microcrystallinity which provides excellent physical properties and improves low temperature properties at medium to high ACN, but also detracts from low temperature flexibility as the ACN content decreases below 35%. To cover the low temperature deficiencies of conventional HNBR's with ACN contents below 35%, special grades with ACN contents of 25% and 17% are commercially available. These HNBR's designed for enhanced low-temperature performance are terpolymers, using a third monomer to disrupt this crystallinity. These polymers have TR10 values

of -33°C and -36°C respectively compared to a typical 36% ACN level HNBR having a TR10 value of -23°C.

Generally, an HNBR elastomer can be compounded to a TR10 value of -30°C although special compounds can be designed for temperatures as low as -45°C.

### **Steam Resistance**

HNBR has excellent resistance to steam, but, as with other elastomers, care should be taken in compound design. Compounding ingredients such as non-black fillers, metal oxides (e.g., zinc oxide), metal salts (e.g., zinc mercaptobenimidazole), and water-soluble process aids should be avoided where ever possible as they detract from the basic properties of the HNBR in this environment. The steam resistance of a 36% ACN, fully saturated HNBR is shown in Table 1.

	150	°C		175°C		
Immersion time (hours)	T _B change (%)	E _₿ change (%)	H _s change (points)	T _B change (%)	E _₿ change (%)	H _s change (points)
72	+9	-5	-1	+5	+5	-1
240	0	0	-1	-	-	-
480	-3	+5	1	+4	+11	0
960	+1	0	0	+15	-5	+4

Table 1: Steam Resistance of Fully Saturated HNBR

T_B = Tensile Strength at Break

E_B = Elongation at Beak

 $H_s$  = Shore A Hardness

### **Abrasion Resistance**

HNBR compounds provide abrasion resistance and wear resistance superior to commonly used elastomers, being between that of regular and carboxylated NBR. The Akron type abrasion index of HNBR produces values in the area of 180 when compared to 100 for NBR, as shown below in Figure 4.



Figure 4: Comparative Abrasion of Elastomers

## Vulcanization

The typical cure systems predominantly used for HNBR are based on either sulfur or peroxide. All the HNBR polymers can be peroxide cured, but only those polymers that contain at least 8-10% unsaturation can realistically be sulfur cured. Peroxide cures are predominately used due to the good heat stability of the crosslinks. Laboratory comparisons of the sulfur/sulfur-donor and peroxide cured compounds demonstrate that peroxide curing provides better compression set and heat resistance, as shown below in Table 2.

Physical Test	Sulfur	VAROX [®] DCP-40C
Compression Set, Method B		
70 hrs. @ 150°C	75	35
Heat Aged in Air, 70 hrs. @ 120°C		
Hardness, Pts. Change	3	3
Tensile, % Change	-11	0
Elongation, % Change	-14	-9

Table 2.	Sulfur vs	Peroxide	Cures	in a	91%	Hydrogenated	
	Sunui vs.	<b>FEIONIUE</b>	Guies	шa	J 1 /0	ingulugenalet	

Due to HNBR's fewer highly reactive allyl position hydrogens versus other diene-based elastomers, (NBR and SBR), it is necessary to add 50-100% more peroxide in order to produce excellent curing characteristics. 8 phr of VAROX 802-40KE is a good starting point.

When compared to SBR or NBR, utilizing a sulphur/sulphur-donor curing system curing speed tends to be slower, therefore, to increase curing speed a secondary accelerator should be employed in combination with the primary accelerator. Long curing times are required when either thiazole-based, ALTAX[®] (MBTS), or sulphenamide-based DURAX[®] (CBS), or AMAX[®] (OBTS), primary accelerators are used. To speed up the curing process, a small quantity of either guanidine-based DPG, or thiuram-based UNADS[®] (TMTM) or ETHYL[®] TUADS[®] (TETD), secondary accelerator may be used in combination with the primary accelerator. Even when using thiuram-based primary accelerator, the addition of a thiazole-based secondary accelerator will shorten the time required for curing. The use of the dithiocarbamate ETHYL ZIMATE[®] (ZEDC), as the primary accelerator is not recommended since the scorch time may be too short. A typical sulfur cure system consists of Sulfur, CAPTAX[®] (MBT) and METHYL TUADS[®] (TMTD).

## Accelerators

Accelerators, such as CAPTAX, are used with sulphur and sulphur-donor systems to increase the rate of vulcanization. Other accelerators such as METHYL TUADS, DURAX and ETHYL TUADS can also be used. These types of sulphur and sulphur-donor accelerators are only used with HNBR polymers containing at least 8% unsaturation.

## Coagents

Coagents are often used to reduce the uncured compound viscosity, improve the state of cure, and/or adjust the cure rate in a peroxide-cured HNBR

compound. The coagents used with HNBR include acrylate monomers, liquid polybutadienes and N,N'-m-phenylenedimaleimide. Coagents tend to increase the crosslink density in an HNBR compound that can typically lead to increased modulus as well as lower compression set, as shown in Figure 5, while lowering the tear and ultimate elongation. The most commonly recommended coagent is a non-nitrosamine inhibited trimethylolpropane trimethacrylate known as Saret SR-517. VANAX MBM and Ricon[®] 153 are also commonly used in HNBR compounding. TAIC, although commonly used in the past, is not recommended today because of its contribution to mold fouling, causing cured articles to tend to stick in the mold.



Figure 5: Effects of Coagent in HNBR

### Fillers

Both black and non-black fillers can be used as reinforcement for HNBR. Usually SRF-type blacks are recommended for HNBR because of the elastomer's inherently high physical properties combined with the fact that there is normally little need for finer particle blacks. However, any of the black fillers (N110 to N990, or graphite) may be used in a HNBR compound if an application demands higher reinforcement or specific performance requirements not typically found with and SRF-type black.

The ideal black filler should be chosen to a balance between the desired physical properties, compound processing, finished goods performance and cost.

When using nonblack fillers, care has to be taken due to their low pH. The low pH in many nonblack filler tends to slow or inhibit peroxide cure systems. Higher pH fillers are advantageous since they can accelerate peroxide cure systems. These high pH fillers are also known to enhance the heat resistance of the compound. Silane coupling agents are suggested to enhance physical properties, and some evidence exists that they enhance water resistance. Of these, the vinyl-type silanes are normally used with peroxide cure systems, while the mercapto-types are used with sulfur-donor type systems. Additionally, processing aids, such as polyethylene glycol, are excellent in wetting the white filler into the elastomer.

Generally, nonblack loaded HNBR compounds exhibit excellent modulus, tensile, elongation and tear properties, while also aging better than their black filled counterparts. However, often the nonblack loaded HNBR compounds will exhibit lower compression set.

Many nonblack fillers are hydrophilic and, as such, will swell in water more than black fillers.

#### Metal Oxides

Regardless whether one uses zinc or magnesium, metal oxides serve a stability role in HNBR compounding. There are numerous different metal oxides which can be used. The most commonly used are zinc oxide and magnesium oxide. Zinc oxide provides the best short-term compression set, while magnesium oxide eventually surpasses zinc oxide in compression set performance when testing is carried beyond the 1,000 hour mark. Zinc oxide and magnesium oxide can be used together in the same compound. The maximum loading recommendations is 3 to 4 phr regardless of type or blending ratio. If higher loadings are used in combination with high-shear molding environments, like injection molding, there is a probability of increased mold fouling during normal manufacturing. Zinc oxide is not recommended for use in compounds that are exposed to high-temperature water or steam; magnesium oxide is recommended.

#### Plasticizers

Plasticizers are commonly used in HNBR to lower hardness, improve lowtemperature performance, or balance swell requirements. Based on the saponification value of a given plasticizer and the ACN content of a given HNBR elastomer, the chemical compatibility between the two materials can be determined. Typically, the higher the ACN level of the HNBR elastomer, the lower the plasticizer level which can normally be incorporated into the compound. While the lower ACN polymers will allow higher levels of plasticizer use, it is often beneficial to use two similar types of plasticizers to help ensure compatibility with the polymer when levels of greater than 10 phr are used. This will help ensure that the cured compound does not exude or "bleed" plasticizer.

Trioctyl trimellitate (TOTM) is the most commonly used plasticizer in HNBR compounding. Although it is a monomeric plasticizer, the mellitate component offers stearic hindrance and good extraction resistance. Other monomeric plasticizers used include various adipates and sebacates. Along with their lower cost, they do improve low-temperature properties, but tend to exhibit a higher level of volatility.

Polymeric plasticizers can also be used. They tend to be less volatile, less extractable therefore more robust than the monomeric plasticizers. However, along with being higher in cost, they are usually more difficult to handle due

to their viscous nature. They also do not provide the desired low-temperature properties typically found by using a monomeric-type plasticizer and have a lower compatibility with the polymer.

## Antioxidants

Due to the saturated bonds in its main chain, HNBR inherently has good resistance to oxygen attack, especially the more saturated grades. Although maximum static heat resistance can be obtained with the most highly saturated grades, this can be further improved by the use of antioxidants. VANOX® CDPA and VANOX ZMTI are currently the best performing antioxidant combination, typically recommended at 1.5 and 1.0 phr, respectively. AGERITE® RESIN D® substituted for the VANOX CDPA improves select dynamic properties. Like Zinc oxide, VANOX ZMTI is not recommended for use in high-temperature water or steam applications. VANOX MTI is more appropriate in applications where water and steam will be encountered.

## **Process Aids**

Process aids are used to improve mixing, mold flow and extrusion. Aliphatic fatty-acid esters tend to be the most effective. Oleamides are excellent internal lubricants.

## Processing

HNBR's can be mixed either on a two-roll mill or with an internal mixer. To improve the consistency of the finished compound and significantly reduce typical two-roll mill mix time, most HNBR's are mixed with internal mixing equipment. HNBR is typically two-pass mixed in an internal mixer with all the ingredients except the cure package are added and dropped out of the mixer at approximately 140°C. The masterbatch is then run through the mixer a second time with the addition of the curatives. The finish pass is dropped at approximately 100–110°C. Between the masterbatch and finish pass, the masterbatch should be allowed to cool to room temperature. The following is a typical HNBR compound mix procedure:

## Masterbatch

Full Cooling/Moderate to Slow Speed

Start	Lift ram, add fillers, all other dry ingredients, and
	polymer, sweep, lower ram
100°C	Raise ram, add oil, sweep, lower ram
120°C	Raise ram, sweep, lower ram
140°C	Drop

## **Finish Pass**

Full Cooling/Moderate to Slow Speed

Start	Add ¹ / ₂ masterbatch,	curatives.	remaining	masterbatch
	,			

- 80°C Raise ram, sweep, lower ram
- 100°C Raise ram, sweep, lower ram
- 110°C Drop

## Milling

The milling of HNBR compound is usually quite easy. HNBR compounds tend to build heat quickly, so full mill cooling is recommended. The normal mill gap setting of approximately 1/4" ensures obtaining the shear action required to finish the mixing process while being thin enough to dissipate any excess heat generated during this process. Use dropped compound from an internal mixer or feed a stored compound one sheet at a time near the ends of the mill. After banding the compound on the mill, crosscutting the compound 5 to 7 times from each end is usually adequate to complete this process. Batching off the mill is normally done by hand or via an automatic system.

## Extrusion

Extruding HNBR for hose or other profiles does take some specific knowledge. Similar to EPDM, HNBR's temperature profile must be at least 10-15°C hotter than a typical NBR compound. Due to its somewhat thermoplastic nature, HNBR also requires enough residence time in the extruder to develop adequate heat to extrude smoothly. Process aids can greatly improve the quality of the extrudate as well as significantly increasing the rate at which it can be extruded. A typical temperature profile for HNBR is provided in Table 3.

Extruder Section	Temperature, °C
Feed Box	75
Screw	85
Barrel (rear)	82
Barrel (front)	90
Head/Die	100

## Table 3: Typical Extruder Temperature Profile for HNBR Compound

## Applications

HNBR is used in applications requiring oil and fuel resistance, with good retention of physical properties after heat aging. Some current applications are listed in Table 4.

Table 4: HNBR End-Product Applications

Water pump shaft seal	Water pump housing seal
Intake & throttle body gaskets	Oil cap seal
Rear crank seal	Timing belts
Oil drain plug	Front cover gaskets
Front crank seal	Fuel hose
Bonded piston seal	Piston lip seal
Printing rollers	Beverage dispenser seals
Hydraulic hose	Cable jacketing
Blow out preventors	Truck hub seals
Constant velocity joint boot seals	Driveline boot seals
Down hole packers	Drill pipe protectors

HNBR suggested starting-point formulations for several applications are listed in the following Tables 5, 6, 7 and 8.

Ingredients	phr
Zetpol 4310 HNBR	100.0
N774 Carbon Black	65.0
Kadox [®] 911C Zinc Oxide	3.0
VANWAX® H Antiozonant	2.0
AGERITE RESIN D Antioxidant	1.0
VANOX ZMTI Antioxidant	1.0
VANOX CDPA Antioxidant	1.5
Plasthall® 226 Plasticizer	10.0
Plasthall TOTM Plasticizer	5.0
VAROX DCP-40KE Peroxide	11.5
Total	200.0

# Table 5: Driveline Boot for Low Temperature Service

## Table 6: 90 Durometer Downhole Packer

Ingredients	phr
Zetpol 2010 HNBR	100.0
N326 Carbon Black	90.0
N220 Carbon Black	25.0
Kadox 911C Zinc Oxide	5.0
VANOX CDPA Antioxidant	1.5
VANOX ZMTI Antioxidant	1.0
Paraplex [®] G-25 Plasticizer	8.0
Ricon 131 Coagent	15.0
VAROX 802-40KE Peroxide	9.0
Total	254.5

# Table 7: 80 Shore A Duro HNBR O-Ring

Ingredients	phr
Zetpol 2010L HNBR	100.0
N774 Carbon Black	65.0
Plasthall TOTM	5.0
Kadox 911C Zinc Oxide	3.0
VANOX CDPA Antioxidant	1.5
VANOX ZMTI Antioxidant	1.0
Saret SR 517 Coagent	6.0
SR 350 Coagent	4.0
VAROX 802-40KE Peroxide	8.5
Total	194.0

Ingredients	phr
Zetpol 1000L HNBR	100.0
N550 Carbon Black	50.0
N990 Carbon Black	45.0
Plasthall 7050 Plasticizer	10.0
Plasthall TOTM Plasticizer	10.0
Kadox 911C Zinc Oxide	3.0
VANOX CDPA Antioxidant	1.1
VANOX ZMTI Antioxidant	0.4
Hycite 713 Acid Acceptor	10.0
TAIC 75% Coagent	2.1
VAROX DCP-40KE	10.5
Total	242.1

Table 8: Diesel / Bio-Diesel HNBR

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### EPICHLOROHYDRIN ELASTOMERS

### by Samuel C. Harber

Zeon Chemicals L.P. Louisville, KY

### Introduction

As part of a broader class of materials known as polyethers, epichlorohydrin elastomers are characterized by fully saturated backbones that contain ether linkages and pendant chloromethyl groups. These characteristics impart unique properties to epichlorohydrin elastomers, including a combination of heat, fuel, oil and ozone resistance, while also maintaining excellent low-temperature flexibility. Additionally, they possess static dissipative properties and excellent permeation resistance to gasses. Dynamic properties range from damping to resilient. The SAE J200/ASTM D 2000 designation for epichlorohydrin elastomers is CH (125°C capable) for the copolymer. The usage of these elastomers has expanded beyond their traditional automotive-related applications such as hoses, seals, diaphragms and air ducts. Their unique, inherent properties have enabled broader application which includes industrial seals and mounts, oil field seals and consumer applications such as computer and laser printer components and industrial respirators.

#### Historical

In 1957 while working for Hercules, Dr. E.J. Vandenberg discovered that organometallic catalysts yielded high molecular weight, amorphous polymers from epoxides¹. On further investigation, when compounded, these were found to possess the unique properties previously described. Commercially viable elastomers were developed from the three basic monomers illustrated in Figure 1. These are a homopolymer of epichlorohydrin (ECH), a copolymer of ECH and ethylene oxide (EO) and a terpolymer consisting of ECH, EO and allyl glycidyl ether (AGE). In Table 1, the designations of these polymers are given as established by the American Society for Testing and Materials (ASTM).

At the time of Dr. Vandenberg's discovery, Hercules was not directly in the rubber business so they licensed the technology to B.F. Goodrich who, in 1965, introduced a commercial material by the trade name of Hydrin[®]. By 1970 Hercules became interested in marketing a commercial epichlorohydrin product so they introduced Herclor[®]. They exited that business in 1987 and sold it to B.F. Goodrich. Finally, in 1989 B.F. Goodrich exited the synthetic rubber business and sold Hydrin[®] to Nippon Zeon, which was headquartered in Japan, and had just formed Zeon Chemicals USA, Inc. as their North American venture. In addition to Zeon, Daiso Company Ltd. in Japan also produces epichlorohydrin elastomers under the trade name Epichlomer[®].²



Allyl glycidyl ether Figure 1: Monomer Composition

## Table 1: ASTM D 1418 Designations for Epichlorohydrin Elastomers

Homopolymer of epichlorohydrin	CO
Copolymer of epichlorohydrin and allyl glycidly ether	GCO
Copolymer of epichlorohydrin and ethylene oxide	ECO
Terpolymer of epichlorohydrin, ethylene oxide and allyl glycidyl ether	GECO

### **Commercial Epichlorohydrin Elastomers**

Production of epichlorohydrin elastomers is based on a continuous solution polymerization process catalyzed by organometallic compounds based on aluminum or tin. The catalysts are combined with monomers of ECH, EO and/or AGE and the reaction proceeds according to a proposed cationic, coordination chain propagation mechanism. Because it is unsymmetrical, ECH monomer will polymerize in a head-to-head, tail-to-tail or head-to-tail fashion. Commercial polymer is 97-99% head-to-tail and is stereo random and atactic in nature. Polymers of CO, GCO, ECO and GECO are amorphous and linear². A typical production process is shown in Figure 2. Basic physical properties of the polymers are shown in Table 2. Commercial types of epichlorohydrin elastomers past and present are shown in Table 3. Compounded epichlorohydrin elastomers have a good balance and broad range of properties as illustrated in Table 4.



Figure 2: Production Process

Polymer	ECH	Chlorine	EO	CAS Reg.	Density	Mooney	T _g ,
	Wt.%	Wt.%	Wt.%	Number		M _L 100°C	°C
СО	100	38	0	24969-06-1	1.36	40-80	-22
GCO	92	35	0	24969-09-3	1.24	60	-25
ECO	68	26	32	24969-10-6	1.27	40-130	-40
GECO	65-76	24-29	13-31	26587-37-1	1.27	50-100	-38

 Table 2: Basic Polymer Properties

# Table 3: Commercial Epichlorohydrin Elastomers

	B.F. Goodrich	Hercules	Zeon Chemicals L.P.	Zeon Corp. Nippon Zeon	Daiso Co.
Co Homopolymer	Hydrin100	Herclor H	Hydrin H45 to H75	Gechron 1000	Epichlomer H
GCo Copolymer	-	-	Hydrin H1100	-	-
ECO Copolymer	Hydrin 200	Herclor C	Hydrin C55 to C95, C2000L, LL, XL	Gechron 2000	Epichlomer C, Epichlomer C55, Epichlomer D
GECO Terpolymer	Hydrin 400	Herclor T	Hydrin T55 to T95, T3000, L, LL, T3100, T3102, T3105	Gechron 3000	Epichlomer CG, CG102, CG140, CG105, CG107, CG109

Property (ASTM D 2000)	Typical	Range
<i>Original Physicals</i> Hardness, Shore A Tensile, MPa Elongation, % Tear Die C, kN/m	70 10 250 35	40 to 90 8 to 18 150 to 600 25 to 45
Compression Set, Method B (Button) 22 hrs. @ 125°C, %	30	25 to 35
Density, g/cc	1.38	1.32 to 1.45
After Heat Aging, 70 hrs. @ 125°C Tensile,% Change Elongation, Change	-30/-50 -30/-50	to 150°C* to 150°C*
After Aging in Oil, 70 hrs. @ 125°C IRM 901 Oil, Volume Swell, % Change IRM 903 Oil, Volume Swell, % Change	1 10	-5 to 5 0 to 12
After Aging in Fuel, 48 hrs. @ 23°C Fuel B, Volume Swell, % Change Fuel C, Volume Swell, % Change	15 35	5 to 25 20 to 45
Low-Temperature Flexibility, °C	-40	to -50

Table 4: General Properties of Epichlorohydrin Elastomers

* Homopolymer

### Compounding

The formulating of epichlorohydrin elastomers is similar in many regards to other common elastomers. Industry-standard carbon blacks, nonblack fillers, plasticizing agents, process aids, metal oxides and antidegradants can all be used successfully. A typical formulation is shown in Table 5.

Differences occur with respect to cure systems. The most common vulcanization reaction can be characterized as acid-base, and care must be exercised concerning the pH of compounding ingredients. Another major difference in formulating is that an acid acceptor / activator must be included, which drives the vulcanization reaction by scavenging and neutralizing HCI formed during vulcanization².

These materials are commonly available and include calcium carbonate, magnesium oxide and calcium oxide. The use of lead, which is unfortunately still associated with these elastomers, has been largely nonexistent for at least 15 years. Since epichlorohydrin terpolymers (GECO) have dual cure sites, conventional cure systems based on sulfur or peroxide can be used with them.

Ingredients	phr	Range (phr)
Polymer	100	-
Filler	70	0 to 130
Plasticizer	10	0 to 25
Antioxidant	1	0 to 2
Process Aid	2	0 to 3
Acid Acceptor/Activator	5	3 to 10
Curative	1	0.3 to 2.0

Table 5: Typical Formulation

#### Fillers

Epichlorohydrin elastomers respond to carbon black much like other elastomers: high-structure carbon blacks provide good tensile strength at lower levels than low-structure blacks. SAF and HAF types provide the best tensile strength; MT types provide low compression set and high resiliency. As a rule of thumb, the compounder can anticipate a response on nearly a point per part basis, as calculated from a base gum with Shore A hardness of about 40. This of course can vary with carbon black structure and cure system. Industry standard charts showing hardness calculations based on chloroprene will often yield close to calculated or desired hardness values. Table 6 shows typical results possible with a copolymer-based recipe and triazine cure system. Compounds containing less than 30 phr will not normally process as well as those with higher loadings.

Nonblack fillers also are usable in epichlorohydrin elastomers. Generally speaking they respond in similar ways as in other elastomers, providing physical properties similar to carbon black filled compounds. Materials such as hydrated and fumed silicas are examples. As in other elastomers, nonblack pigments can be used to reduce cost. Calcium carbonate is an excellent choice in that it will not reduce resilience, is non-reinforcing and has no impact on cures. Hard clays require the addition of extra curative. Examples of nonblack fillers compared to HAF black are shown in Table 7. The use of silane coupling agents is not generally required, but they can be used if needed, as shown in Table 8. Certain types are more beneficial than others and the end use requirements such as compression set and water swell resistance should be considered in their selection.

Carbon Black	phr	Duro Shore A	Duro + oil*	M100 MPa	M100 + oil	Tensile MPa	Tensile + oil	Elong %	Elong + oil
Base Gum	0	42	38	0.9	0.9	4.1	2.8	471	438
N990	25	49		1.4		8.2		415	
	50	58	51	1.8	1.5	9.7	8.1	423	493
	75	65		2.7		9.7		327	
	100	71		3.8		9.6		277	
N762	20	51		1.4		10.3		476	
	35	61		1.9		12.5		493	
	50	66	60	3.0	2.3	14.0	11.7	385	470
	65	75		4.4		13.4		300	
	90	83		7.6		14.2		234	
N550	20	56		1.6		11.6		494	
	35	67		2.7		14.9		462	
	50	78	71	4.9	3.6	15.0	12.9	419	482
	65	87		8.2		14.6		262	
N330	20	61		1.7		16.0		619	
	35	70		2.9		18.0		527	
	50	79	77	5.3	4.3	18.0	15.8	433	559
	65	85		7.3		16.6		358	
N220	20	58		7.2		11.7		423	
	35	69		11.4		17.3		470	
	50	80	73	13.8	3.3	16.6	17.3	409	616
	65	89		15.5		15.7		314	

Table 6: Carbon Black Loading Properties

* 10 phr DBEEA

# Table 7: Nonblack Fillers

Filler	phr	Duro Shore A	M100 MPa	Tensile MPa	Elong %	C/Set, % (Button) 22 hrs. @ 150°C		
Copolymer*								
HAF	50	74	5.9	15.2	230	25		
Hydrated Silica	50	83	3.8	14.1	420	79		
Fumed Silica	50	73	5.2	15.7	360	79		
Terpolymer*								
HAF	50	81	8.6	13.0	140	22		
Hydrated Silica	50	81	5.0	10.6	220	70		
Fumed Silica	50	80	6.3	10.7	210	77		
Calcium Carbonate**	50	44	0.8	6.3	830	not tested		
Calcium Carbonate	100	51	1.1	6.1	770	not tested		
Calcium Carbonate	150	59	1.2	4.3	730	not tested		

*Triazine cure system **Sulfur cure system

Physical Property*	No Agent	Si- 230	Si- 263	Si- 69	A- 189	SCA 98WT	TESPT	Z-6940
Hardness, Shore A	52	59	58	58	60	60	58	60
100% Modulus, MPa	1 3	2 0	2 1	1 9	24	1.9	1 7	2 0
Tensile, MPa	10.1	10.6	8.9	8.4	10.0	8.1	8.7	9.0
Elongation, %	811	648	575	572	450	588	683	593
Die C Tear, kN/m	27.7	41.3	35.9	34.8	39.7	35.4	33.4	38.2
C/S 22 hrs. @ 100°C	20	12	10	25	7	24	25	23
C/S 22 hrs. @ 125°C	33	22	20	37	15	37	39	36
DIN Abrasion, grams	432	301	304	313	230	330	339	335
Water Swell, 70 hrs. @ 100°C	4	37	41	41	44	14	9	54

Table 8: Silane Coupling Agents

*Copolymer 100 phr; hydrated silica 40 phr; coagent 2 phr; triazine cure system

#### Plasticizers

Several types of plasticizers can be used with epichlorohydrin elastomers. The best choices are those closest in polarity to the elastomer, which is very polar. Most commonly these are from the diester and ether classes and include DOP (dioctylphthalate), DIDP (diisodecyl phthalate) and DBEEA (dibutoxy-ethoxy-ethyl adipate). For most applications 10-15 phr of plasticizer is sufficient. Within the compatible types, limitations mainly come into play with respect to loading. These elastomers will not tolerate ultra-high loadings such as are common for example, in EPDM. Typically levels of between 20 and 25 phr are normally well tolerated. Table 9 illustrates several types of plasticizing or softening materials that can be used as well as their impact on physical, low- temperature and volatility properties.

Plasticizer	phr	Hardness Shore A	Tensile MPa	Elongation %	Gehman T100, °C	Air 150°C Wt Δ, %
Control*	0	80	15.4	180	-46	-0.6
Oils						
DOP	10	75	14.4	230	-49	-1
"	20	66	13.5	280	-50	-2
"	30	60	12.4	360	-52	-2
Flexon® 680	12	75	11.6	180	n/a	-1
KP-140 [®]	10	69	13.6	240	-53	-2
"	20	64	11.7	390	-54	-3
**	30	52	10.7	440	-58	-4
Paraplex [®] G-50	20	65	13.7	300	-50	-1
Paraplex G-25	20	65	14.2	300	-50	-0.7
Santicizer® 160	20	65	13.2	330	-45	-2
TP-95	20	65	12.4	300	-54	-3
TP-90B	20	64	13.4	270	-48	-5

Table 9: Plasticizers

Plasticizer	phr	Hardness Shore A	Tensile MPa	Elongation %	Gehman T100, °C	Air 150°C Wt Δ, %
Other Materials						
Cumar® P-10	10	75	13.9	250	-45	-2
"	20	66	13.1	320	-43	-5
Dyphene [®] 8318	20	77	12.5	390	-40	-1
Neophax [®] A	10	75	14	210	-46	-0.9
"	20	71	12	280	-45	-1
£6	30	65	9.4	360	-44	-2
Nipol [®] 1312	10	63	12.4	380	-48	-1

Table 9: Plasticizers (continued)

*Copolymer 100 phr; N550 60 phr; ETU 1.5 phr

#### Antidegradants

Although epichlorohydrin rubbers contain saturated backbones and are considered heat and ozone resistant, the addition of antidegradant packages is recommended for the best service. While sufficient antioxidant is added during polymerization to stabilize the material during storage, antioxidants such as VANOX[®] CDPA and VANOX MTI provide an excellent level of resistance to thermal oxidative aging. Blends generally are used because they have synergistic effects. A good starting point is to use 1.0 phr VANOX CDPA with 0.5 phr VANOX MTI. Other materials such as VANOX NDBC, ISOBUTYL NICLATE[®] and METHYL NICLATE have also been used, although not to the same extent as they once were due to increasing regulatory concerns.

Antiozonants are not normally required as the saturated backbone is not easily attacked. In the last few years however, more aggressive ozone tests have been developed where specimens are placed under high extensions (20% +) and bombarded with very high levels (100 pphm) of ozone for extended continuous periods (568 hours). In these situations, standard antiozonant packages will provide the necessary protection. A package containing a blend of Sunolite[®] petroleum waxes at 2 phr, IPPD at 2.5 phr and AGERITE[®] RESIN D[®] at 2.0 phr is an example of one that has proven very effective.

### Process Aids

The addition of a process aid package is recommended to help alleviate mill and mold sticking. While there are a number of very effective process aids for mill release on the market, the best additive is usually stearic acid. It acts as a very effective mill release agent and is normally added at 1.0 to 1.5 phr. A variety of other materials that are designed for both mill and/or mill/mold release can be used at levels of between 0.5 phr to 2.0 phr. In conjunction with stearic acid they provide a satisfactory level of processability in epichlorohydrin rubbers. Chemically these materials are typically based on condensation products or derivatives of fatty acid esters or amides and metal soaps of fatty acids. Examples of materials found useful in this regard are VANFRE® AP-2, Struktol® WB-222, Struktol® TR-121 and Armoslip® CP.

#### Curatives

Curatives used in the vulcanization of epichlorohydrin elastomers is an area where a more specialized understanding of the polymers is required. The mechanism is nucleophilic substitution, where a chlorine molecule is displaced from the polymer chain and in its place a crosslink is formed. The reaction is an acid and base type and as previously mentioned, the pH of compounding ingredients is of critical importance.

A proposed mechanism for vulcanization with a non-lead containing cure system based on a triazine compound, Zisnet[®] F-PT (2,4,6-Trimercapto-s-triazine) via the chlorine is shown in Figure 3. The curative contains mercapto (S-H) groups, the protons of which are acidic. When activated by heat in the presence of a base, magnesium oxide (MgO) for example, the reactivity of the sulfur anion is enhanced. This then displaces a chloride ion from the chloromethyl group to form a crosslink. Accelerators are of the amine type (DPG) and are organic bases. As such they react similar to MgO to promote formation of sulfur anions thus speeding the reaction. Retarders are acidic in nature and slow the reaction³.



Figure 3: Proposed Mechanism of Triazine Cure

Ideal acid acceptors/activators for use with the Zisnet F-PT system are a combination of calcium carbonate (Atomite[®] Whiting for example), at 5 phr and a high-activity MgO such as Maglite[®] D at 3 phr. This combination is used to replace lead/ETU (ETU is a thiourea). The MgO can also be adjusted to control the activity of cure. Normally the tightest cures are obtained with 3 phr. At this loading some stocks can be too scorchy for certain processes and lower levels would then be used. Alternatively, magnesium trisilicate (Magnesium Trisilicate L[®]) can be used to impart substantial scorch safety even at 3 phr loadings for better processing hose extrusions.

DPG is the preferred accelerator and is normally used between 0.3 and 0.8

phr to adjust cure rate. A retarder is normally added at between 0.3 and 1.0 phr and functions mainly to improve bin scorch stability. Choices include PVI, Retarder Safe[®] and Vulkalent[®] E/C.

Ingredients	Tria	azine Cu	ure	Lead/ETU	Bis-phenol
	phr	phr	phr	phr	phr
Homopolymer Copolymer	100.0	- 100.0	-	- 100.0	- 100.0
N330 Carbon Black VANOX MTI	- 50.0 1.0	- 50.0 1.0	100.0 50.0 1.0	- 50.0 1.0	- 50.0 1.0
Stearic Acid Atomite® Whiting	1.0 5.0	1.0 5.0	1.0 5.0	1.0	1.0
Zisnet [®] F-PT DPG Patarter Safe®	0.8 0.5	0.8 0.5	0.8 0.5	-	-
Poly-Dispersion® GRD-90 (Lead) Poly-Dispersion GND-75 (ETU)	-	-	-	5.0 1.5	-
Dynamar [®] RC-5251Q Dynamar FX-5166 Dynamar FC-5157	- - -	- -	-	- -	15.0 1.8 1.5
Totals	161.6	161.6	161.6	158.5	170.3
*QC formulas for comparisons only					
Mooney Scorch, M _L (1+30) @ 25°C Minimum Viscosity Minutes to 5 pt. rise Minutes to 35 pt. rise	119.0 4.4 8.6	144.0 2.3 4.0	133.0 3.4 6.0	141.0 3.5 5.7	129.0 4.9 >30.0
ODR Rheometer @ 200°C, 100 cpm, 3° Arc ML (dN-m) MH (dN-m) ts2 (min) t' 90 (min)	24.0 105.0 0.9 9.2	35.0 107.0 0.9 8.4	27.0 104.0 1.1 9.3	25.0 109.0 1.1 10.7	23.0 87.0 2.1 12.3
Original Physicals Press Cured 15 mins. @ 2 Hardness, Shore A 100% Modulus, MPa Tensile, MPa Elongation, % Tear Die C, kN/m	00°C 81 8.6 15.3 200 31.5	76 5.8 14.6 220 38.5	80 6.6 13.4 180 31.5	80 7.2 18.8 240 43.8	78 5.5 18.5 350 49.0
Compression Set, Method B (Plied Disc) 22 hrs. @ 125°C,%	30	36	29	26	31
Physical Properties After Heat Aging in Air, 70 Hardness, Pts. Change Tensile, % Change Elongation, % Change	) hrs. @ 7 -4 -40	125°C 6 -3 -23	6 -10 -39	3 -11 -33	5 8 -37
Physical Properties After Aging in IRM 903 On Hardness, Pts. Change Tensile, % Change Elongation, % Change Volume Swell, % Change	il, 70 hrs. -2 -23 -47 9	@ <i>150</i> -1 -19 -28 10	℃ -5 -28 -40 11	-7 -15 -20 11	-1 -14 -36 11
Physical Properties After Heat Aging in Fuel C Hardness, Pts. Change Tensile, % Change Elongation, % Change Volume Swell, % Change	C, 48 hrs -16 -58 -47 38	. @ 23°0 -7 -53 -33 39	C -10 -60 -53 41	-16 -58 -47 38	-10 -48 -19 39

## Table 10: Curatives for Chlorine Cure Site*
Table 10 offers a comparison between common cure systems used in conjunction with the chlorine cure site. (These recipes are for comparison purposes and do not represent optimized factory formulations). Occasionally an adjustment in tensile is needed when doing conversions for lead/ETU cures. This can be accomplished by adding HAF black or silica⁴. Dynamar[®] (Bis-phenol) cures are key to obtaining excellent adhesion between epichlorohydrin and FKM in fuel hose constructions.

Terpolymers (GECO) have dual cure sites consisting of chlorine just like CO and ECO but also contain unsaturation (double bonds) contributed by the AGE monomer. These dual cure sites enable crosslinking or vulcanization of GECO by either chlorine displacement or more conventional means such as sulfur or peroxide.

Conventional cure systems proceed according to mechanisms commonly understood in the industry for other unsaturated elastomers. These cure systems are shown in Table 11. The use of zinc oxide (ZnO) should be avoided when curing through the chlorine and should be held to a minimum in conventional cures (2 to 3 phr is usually sufficient for good activation) if exposure during the service life of the vulcanized compound is to be at or above 125°C. This is because at elevated temperatures the zinc can form zinc chloride (ZnCl₂) a Lewis Acid that will unzip the polymer backbone.

In peroxide cures, the peroxide should be held to a 1 to 3 phr range. Excess peroxide can cause polymer backbone chain scission. Acid acceptors should be either MgO or CaO. ZnO should be avoided because of degradation concerns. Most common coagents can be used with the exception of triallyl cyanurates, trimetallates and phosphates which are ineffective.

Ingredients (phr)	Sulfur	Peroxide
Terpolymer	100.0	100.0
N550 Carbon Black	50.0	50.0
Plasthall [®] 7050	5.0	-
Plasthall 226	-	10.0
AGERITE® RESIN D®	1.0	-
VANOX CDPA	-	1.0
VANOX MTI	-	1.0
Kadox [®] 920C	2.0	-
Calcium Oxide HP-XL	3.0	5.0
Stearic Acid	1.0	-
Struktol® WB-222	-	2.0
Spider [®] Sulfur	0.5	-
AMAX®	1.0	-
METHYL TUADS®	1.0	-
ETHYL TUADS®	1.0	-
SR-517	-	1.0
VAROX [®] DCP-40KE	-	2.0
Totals	165.5	172.0

#### Table 11: Sulfur and Peroxide Cures

	Sulfur	Peroxide
Mooney Scorch, M _L (1+30) @ 25°C Minimum Viscosity Minutes to 5 pt. rise Minutes to 35 pt. rise	55.9 15.9 24.0	58.6 13.7 17.8
ODR Rheometer, 100 cpm, 3° Arc @	(170°C)	(180°C)
M _L (dN⋅m)	11.3	13.3
M _H (dN⋅m)	79.1	67.7
t _s 2 (min)	2.3	1.0
t′ 90 (min)	17.3	15.0
Original Physicals, Press Cured t' 90 @	(170°C)	(180°C)
Hardness, Shore A	72	64
100% Modulus, MPa	4.9	4.2
Tensile, MPa	16.7	16.6
Elongation, %	469	331
Tear Die C, kN/m	52.0	not tested
Compression Set, Method B (Button) 70 hrs. @ 100°C, % 22 hrs. @ 125°C, %	54	- 33
Physical Properties After Heat Aging in Air, 70 hrs. @	(100°C)	(125°C)
Hardness, Pts. Change	7	10
Tensile, % Change	9	7
Elongation, % Change	138	-29
Physical Properties After Aging in IRM 903 Oil, 70 hrs. @	(100°C)	(125°C)
Hardness, Pts. Change	-1	2
Tensile, % Change	10	-45
Elongation, % Change	-31	-63
Volume Swell, % Change	3	4
Physical Properties After Aging in Fuel C, 48 hrs. @	(23°C)	(23°C)
Hardness, Pts. Change	-16	-16
Tensile, % Change	-34	-50
Elongation, % Change	-37	-49
Volume Swell, % Change	36	44

 Table 11: Sulfur and Peroxide Cures (continued)

#### Properties

The properties of epichlorohydrin elastomers can best be thought of in two categories. First are the typical or standard properties such as temperature and chemical resistance. Second are those considered unique and inherent to these elastomers such as excellent permeation resistance, static dissipation and dynamics. Table 4, from earlier in this chapter, provides a good general overview of the former showing typical original physical and aged properties.

The best balance of properties is usually obtained with the copolymer (ECO). Fuel resistance of a copolymer recipe is typically similar to a 50 ACN NBR. An important distinction here is that with ECO the low-temperature flexibility is -40°C, which is not possible with higher ACN-content NBR's. Improved heat and permeation resistance are obtained with the homopolymer (CO) alone or

by blending with ECO. Suppliers can offer a greater variety of grades within the terpolymer (GECO) types where low-temperature and static-dissipative properties are enhanced by adjustments in monomer composition. The level of unsaturation can also be varied.

The inherent, unique and more specialized properties alluded to earlier are more or less dependent on the specific polymer type. In choosing a polymer, the compounder needs to establish not only the application end-use requirement but also those revolving around how the material is to be processed. In Figure 4, some common rationales are shown that illustrate where and how each type would normally be used. In Figure 5, permeation resistance relative to other common elastomers is shown. This shows that the homopolymer has permeation resistance to air exceeding that of butyl rubber. Figure 6 shows electrical properties which that range from highly insulative with a homopolymer (CO) to highly static dissipative with a terpolymer (GECO). Finally, Figure 7 shows the capability of the elastomer relative to dynamic properties. This illustrates performance relative to natural rubber in terms of tangent delta over a range of temperatures. Generally speaking a CO polymer has a higher viscous component than either the ECO or GECO types.



Figure 4: Rationales for Service







**Figure 6: Electrical Properties** 



Figure 7: Dynamics

Blends can be used to enhance properties. All types of epichlorohydrin can be used for blending with other epichlorohydrin rubbers and other common elastomers, as long as cure-system compatibility is considered, e.g., CO and ECO do not have unsaturation whereas GECO does. An example of improving and extending NBR is given in Table 12. In Table 13 a blend with EPDM is shown.

Ingredients (phr)	Peroxide	Sulfur
Nipol DN 3350	70.0	70.0
Hydrin T5010	30.0	30.0
N550 Carbon Black	50.0	50.0
Plasthall 7050	5.0	5.0
AGERITE RESIN D	1.0	1.0
Kadox 920C	2.0	2.0
Calcium Oxide HP-XI	3.0	3.0
Stearic Acid	1.0	1.0
VANAX® MBM	0.5	-
VAROX DCP-40KE	3.0	-
Spider Sulfur	-	0.5
AMAX	-	1.0
METHYL TUADS	-	1.0
ETHYL TUADS	-	1.0
Totals	165.5	165.5

Table 12: Epichlorohydrin Blends With NBR

	Sulfur	Peroxide
Mooney Scorch M _L (1+30) @ 125°C		
Minimum Viscosity	55.9	49.9
Minutes to 5pt. rise	5.0	7.0
Minutes to 35 pt. rise	8.0	10.4
ODR, 30M @ 170°C, Micro, 100 cpm 3° arc		
M _L (dN⋅m)	11.9	9.6
M _H (dN•m)	95.3	90.7
t _s 2 (min)	0.8	1.4
ť 90 (min)	7.8	9.9
Original Physicals Press Cured t' 90 @ 170°C		
Hardness, Shore A	72	71
100% Modulus, MPa	6.3	4.8
Tensile, MPa	20.1	17.2
Elongation, %	246	317
Tear Die C, kN/m	44.1	51.0
Compression Set, Method B Button		
70 hrs. @ 100°C, %	18	26
Physical Properties After Heat Aging in Air, 70 hrs.	@ 100°C	
Hardness, Pts. Change	4	4
Tensile, % Change	7	-5
Elongation, % Change	0	-24
Physical Properties After Aging in IRM 901 Oil, 70	hrs. @ 100°C	
Hardness, Pts. Change	2	3
Tensile, % Change	6	3
Elongation, % Change	-1	-20
Volume Swell, % Change	-3	-3
Weight, % Change	-3	-3
Physical Properties After Aging in IRM 903 Oil, 70	<i>hrs.</i> @ 100°C	
Hardness, Pts. Change	-4	-3
Tensile, % Change	-8	0
Elongation, % Change	-11	-18
Volume Swell, % Change	7	6
Weight, % Change	5	4
Physical Properties After Aging in Fuel C Resistan	nce, 70 hrs. @ 23°0	2
Hardness, Pts. Change	-15	-14
Tensile, % Change	-52	-55
Elongation, % Change	-47	-54
Volume Swell, % Change	48	47
Weight, % Change	32	31
Gehman Low Temp Stiffening Test		
12 Relative Modulus, °C	-20	-18
15 Relative Modulus, °C	-27	-25
I 10 Relative Modulus, °C	-28	-27
1100 Relative Modulus, °C	-33	-34

Table 12: Epichlorohydrin Blends With NBR (continued)

Ingredients (phr)	GECO	GECO/EPDM
Hydrin T3100	100.0	80.0
Vistalon™ 7001		20.0
N550 Carbon Black	60.0	60.0
Plasthall 7006	10.0	10.0
Stearic Acid	1.0	1.0
VANOX CDPA	1.0	1.0
Potassium Stearate	3.0	3.0
Calcium Oxide HP-XL	4.0	4.0
VAROX DCP-40KE	2.0	2.0
Totals	181.0	181.0
Mooney Scorch M _L (1+30) @ 125°C		
Minimum Viscosity	48.8	61.2
Minutes to 5 pt. rise	4.4	7.5
Minutes to 35 pt. rise	8.0	10.6
ODR, 45M @ 170°C, Micro, 100 cpm 3° arc		
M _L (dN⋅m)	7.9	13.6
M _H (dN⋅m)	84.0	88.6
ts 2 (min)	1.0	1.2
ť 90 (min)	14.1	22.3
Original Physicals Press Cured t' 90 @ 170°C		
Hardness, Shore A	67	78
100% Modulus, MPa	4.9	7.8
Tensile, MPa	13.7	14.5
Elongation, %	239	188
Compression Set, Method B, Button		
70 hrs. @ 125°C, %	23	38
Physical Properties After Heat Aging in Air, 70 hrs.	@ 135°C	
Hardness, Pts. Change	15	8
Tensile, % Change	6	8
Elongation, (%) Change	-26	-4
Physical Properties After Aging in IRM 903 Oil, 70 h	rs. @135°C	
Hardness, Pts. Change	3	-17
Tensile, % Change	-18	-68
Elongation, % Change	-47	-59

Table 13: Epichlorohydrin Blends With EPDM

#### Processing

Epichlorohydrin elastomers are processable on all common rubber industry equipment. Although they have an undeserved reputation for being difficult to process, following a few basic rules will alleviate any concern in this regard. The main issue that is reported concerns mill sticking. Aside from inclusion of process aids as mentioned previously, mill rolls that are clean and hot are imperative. Compounds will stick to cold and/or dirty mill rolls. To prepare for milling epichlorohydrin compounds the following procedure should be used. While the mill is still cold, end roll pigs of an abrasive cleaner such as Millathane[®] Glob or Son of Glob[®]. These work extremely well. If unavailable, clean-out stocks based on NR can be used. The scheduling of EPDM compounds containing peroxide cures close to epichlorohydrin rubber production runs should also be avoided. This type of EPDM stock leaves a bluish coating on the roll that is not compatible with epichlorohydrin elastomers. After cleaning the mill rolls, they should be heated to between 60°C and 80°C. If a temperature control unit is not available, the heating can still be done by dropping a very hot, high viscosity masterbatch type clean-out compound on the mill and working this until the rolls are to temperature.

Mixing is done with internal mixers or open roll mills. Compounds that are highly loaded respond well to an upside-down procedure. Since some stocks can be sensitive to scorch, two-pass mixes often give the best result. If single pass mixing is chosen, the drop temperature should be held to no more than 115°C. Batch sizing is also important, and it is the one thing that often contributes to poor results. Batches should be sized to the high side with fill factors in the 70% to 72% range because of the higher density of the polymer and hence the compounds.

Since epichlorohydrin elastomers are somewhat thermoplastic in nature, they are shear sensitive and have a narrow window for optimum shear during mixing. As a result no polymer breakdown period is needed and fillers should be added quickly to take advantage of this narrow window to achieve optimum dispersion. A typical two-pass mix procedure is shown in Table 14. Standard mill mixing procedures work well. A temperature differential of about 10°C should be maintained between rolls, with the front roll cooler. After banding the polymer and allowing it to run 1 minute, metal oxides, process aids and antidegradants should be added. Next, fillers and plasticizers should be incorporated, alternating their addition. Curatives are added in a second operation after the stock has been thoroughly milled, sheeted off and cooled.

Cycle 1	Time (min.)	Temp. °C	Action
Masterbatch			Rotor Speed 20-30 rpm, ram full down
	0	60	Load Polymer, filler, chemicals
	2	90	Scrape and add oil
	4	100	Scrape
	6	120	Drop
Cycle 2			
Final			Rotor speed 30 rpm
	0	60	Load 3/4 MB, curatives, 1/4 MB
	1.5	80	Scrape
	3	105	Drop
			*water on full cooling

Table 14:	Internal	Mixing	<b>Procedure*</b>
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Extrusion of epichlorohydrin rubber will normally yield smooth extrudate at good rates. Since these elastomers are shear sensitive, softening occurs as the compound is worked by the screw. They will process well by cold- or warm-feed extrusion processes. Barrel restrictions such as breaker plates and screen packs can lead to premature scorch. Vacuum is recommended for higher temperature extrusions where air entrapment is more likely. Table 15 shows an excellent all-around starting point set up for extrusion.

Other methods associated with extrusion processes in the vulcanization of epichlorohydrin rubber include autoclave and salt bath. In general, typical processes used for other elastomers are also applied here. In autoclave curing, care should be taken to evaluate the end properties desired from the vulcanizate versus cure system. This is especially true when converting from lead/ETU cures. Some of the alternative cure systems such as triazine-based compounds do not develop optimum properties below 170°C. Salt bath cures are compounded and processed much in the same way as with other elastomers by using cures systems that are very fast and which contain a desiccant such as calcium oxide.

Extruder Setup		
Zone	Temperature, °C	
Screw	54-80	
1	54-80	
2	65-85	
3	70-90	
Head	70-90	
Die	90-110	

Table 15:	Extrusion	Parameters
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Molding of epichlorohydrin rubber can be done with industry standard processes such as injection, compression or transfer. Injection molding is quite common, and the thermoplastic nature of the elastomers lend themselves to provide excellent mold flow and cavity fill. Compounds can be molded at very high temperatures (200°C) without unusual issues. Table 16 shows a typical injection molding setup. For increased life, tooling should be made from a hardened mold steel; stainless for example, works well. Semi-permanent mold releases are recommended, having been adhered to a clean tool using a pre-bake procedure and applied per the manufacturer's recommendation. Types such as McLube[®] 1829, Diamondkote[®] W-59 and Releasomer[®] RR5-EF have been very successfully utilized and provide good release.

Zone	Parameter Setting
Barrel temperature	60° to 80°C
Screw temperature	60° to 80°C
Screw speed	30 to 60 rpm
Injection time	6 to 20 seconds
Injection pressure	11.7 to 13.8 MPa
Hold time	6 seconds
Hold pressure	11.7 to 13.8 MPa
Back pressure	4.1 MPa
Mold temperature	180° to 210°C

Table 16: Injection Molding

Calendering of epichlorohydrin rubber compounds is very common and stocks give smooth, bubble-free sheets even in relatively thick cross-sections. Rolls should be clean and run at temperatures between 60° and 80°C. Avoiding excessive warm-up, feeding small pigs and keeping a rolling pencil bank are all essential. As previously mentioned, a good process aid package should also be included in the compound. However, stocks that are lightly loaded will generally not calender well. Typically these would be stocks containing less than 30 phr of reinforcing fillers (FEF, HAF, etc.) and less than 50 phr non-reinforcing fillers (MT black, whiting, etc.).

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# POLYACRYLATE ELASTOMERS

#### by Joshua R. Kelley

# Zeon Chemicals L.P. Louisville, KY

HyTemp[®] and Nipol[®] AR acrylic elastomers are polymers of acrylic acid esters with added reactive cure site monomers. These saturated elastomers offer excellent resistance to severe environments in thermoset applications. Polyacrylic elastomers are classified as high temperature, oil-resistant, specialty rubbers. They are also often called polyacrylates or simply acrylic rubber. The American Society for Testing and Materials (ASTM International) approved designation is ACM for <u>acrylic monomer</u>. ASTM and the Society of Automotive Engineers (SAE) have developed a classification system, D 2000/J200, designed for elastomers used primarily in automotive applications. ACMs fit within the DF (150°C capable), DH (150°C capable), and EH (175°C capable) oil-resistant elastomer tables of this system. This is appropriate as nearly 80% of acrylic elastomers sold go into automotive components. They are generally formulated with reinforcing, curing, and other modifying agents. These thermoset compositions are processed into parts designed for applications requiring performance over the temperature range of -40°C to 200°C.

The development of polyacrylate rubber was started in the early 1940s at the U.S. Department of Agriculture's Eastern Region Laboratory and at the University of Akron's Government Laboratories. The efforts made by the U.S. Department of Agriculture were intended to result in a polymer product produced from whey, a by-product of cheese production.¹ The first commercially produced polyacrylate polymers became available in 1947 and were produced by B.F. Goodrich Chemical. While their physical properties, even with reinforcing fillers, were only moderate, resistance to heat and hot oils was superior to that of polychloroprene and nitrile elastomers. The first two polymers were marketed under the names Hycar PA and Hycar PA-21. However, the Hycar PA-21 material showed the most promise and later development projects were focused on this grade.² Polyacrylates currently are used in various applications where heat and oil resistance are critical, and there are numerous grades available to fit a variety of functions. Table 1 gives a timeline of the evolution of ACM elastomers.

#### Table 1: Evolution of ACM Elastomers

1947	First commercially produced ACM polymers become available (based upon chlorine cure site/polyamine curatives)
1965	Development of chlorine cure site/soap sulfur curatives technology
1975	Introduction of epoxy cure site technology
1985	Introduction of dual chlorine/carboxyl cure site technology
1994	Introduction of peroxide-curable ACM
2000	Introduction of the HT-ACM products
2004	Extrusion Grade HT-ACM becomes available
2007	Introduction of low-temperature, extrusion-grade HT-ACM

Recent improvements to polyacrylate materials have broadened the functional temperature ranges and environmental constraints of polyacrylate polymers. Improved vulcanization characteristics, through the incorporation of advanced cure sites and curatives, have played a significant role in these improvements. However, the most significant achievements are the result of monomer/polymer construction which has resulted in polyacrylates with improved low and high temperature performance, fluid resistance, and processing characteristics.

#### POLYMER PRODUCTION AND CHEMICAL COMPOSITION

Acrylates can be polymerized in a variety of ways, including bulk, solution, suspension, and emulsion polymerization. The most common methods used industrially are suspension and emulsion polymerization. One of the major reasons for the use of either emulsion or suspension polymerization techniques is the ability of the aqueous phase to aid in the removal of the heat produced during the course of the polymerization. The use of bulk polymerization can cause problems due to the lack of adequate heat removal and because most polyacrylate elastomers are polymerized to high conversions. The use of solution polymerization can cause a problem due to the high viscosity of the reaction medium at high conversions and normal monomer concentrations.

Emulsion polymerization makes use of water-soluble initiators such as potassium persulfate or redox systems to initiate the polymerization. A surfactant, such as fatty acid soap, is added to stabilize the latex particles as they are formed. The amount of surfactant present will determine the number of particles formed, which, in turn, will determine the rate of polymerization.

The rubber is recovered from the latex by coagulation, usually by using a divalent or trivalent metal salt, to form a crumb. The crumb is washed and dried, and then packaged either in a slab or particulate form for consumption by the industry. Because of the high conversions possible with acrylate polymerizations no stripping of the latex is usually required before coagulation to remove unreacted monomer.

#### **Polymer Structure and Chemical Composition**

The first polyacrylate elastomers made were homopolymers of ethyl acrylate. These polymers were saturated and hard to cure, relying on curatives such as sodium metasilicate pentahydrate. The use of this curative caused processing problems and gave poor dispersion. Because of the difficulty of the vulcanization of the ethyl acrylate homopolymers it was decided to add small amounts of crosslinking or cure site monomers to the polymer. The vulcanization reactions could then take place at these reactive sites. This thinking is similar to the copolymerization of small amounts of ethylidene norbornene (ENB) with ethylene and propylene to make EPDM rubber. Therefore there are two different types of monomers used in the production of polyacrylate elastomers: backbone monomers and cure site monomers.

#### **Backbone Monomers**

Backbone monomers account for 95-99% by weight of a normal polyacrylate

elastomer. Some examples of backbone monomers used in polyacrylate are ethyl acrylate (EA), n-butyl acrylate (BA), and 2-methoxy ethyl acrylate (MEA). Their chemical structures are shown in Figure 1. These monomers are responsible for the physical properties of the elastomer, especially the oil swell, low temperature, and heat resistance properties.

As was mentioned previously, the first polyacrylate elastomers were based on ethyl acrylate. These elastomers gave excellent oil and heat resistance. However, the Tg of polyethyl acrylate is approximately -18°C. In many applications lower temperatures are required for the rubber, so other backbone monomers are added to lower the Tg of the polymer.





The copolymerization of n-butyl acrylate with ethyl acrylate gives a polymer that has a lower Tg. The Tg of poly(n-butyl acrylate) is -55°C, which enables production of polymers with brittle points of -40°C. These polymers also give excellent heat aging resistance, with maximum service temperatures of 204°C possible. The major issue with the use of BA is larger volume swell in oil immersion tests. A typical cured compound based on EA/BA copolymer with a brittle temperature of -41°C gives a volume swell of approximately 60% in IRM 903 oil. A similar cured compound based on EA homopolymer gives a volume swell of approximately 10% under the same conditions.

The T_g of n-alkyl acrylates decreases as the length of the side chain is increased up to poly(n-decyl acrylate). At the same time the solubility parameter also decreases, causing an increase in the volume swell of the polymers in oil. Studies show that the use of ether-containing alkoxy acrylates give both low temperature performance and low volume swell. The reason for this is that the length of the side chain of, e.g., 2-methoxy ethyl acrylate, is similar to that of n-butyl acrylate, giving a similar T_g.

However, the substitution of an oxygen atom for a  $CH_2$  group increases the solubility parameter. Therefore both low temperature performance and good resistance to oil swell can be obtained through the use of alkoxy acrylates. Alkoxy acrylates, however, have issues with thermal stability. Their homopolymers lose a substantial amount of their original physical properties after aging for 168 hours at 150°C in an air oven. Figure 2 shows the influence of heat aging on polymers composed of each of the major backbone monomers used in polyacrylates.



Figure 2: Backbone Monomer Comparison

Therefore, the design of the composition of polyacrylate elastomers is a compromise between low temperature performance, high temperature resistance and low volume swell in oil. The low temperature types generally suffer from poorer heat resistance or greater volume swell. The low volume swell/high temperature types generally have poor low temperature performance. The different grades of polyacrylate elastomers are designed with the specific application in mind to take advantage of the strengths of the various monomers while minimizing their weaknesses. The oil swell/low temperature balance of the backbone monomers is shown in Figure 3.



Figure 3: Property Balance of Acrylic Monomers

# **Polymer Synthesis**

Polyacrylate elastomers are typically polymerized through a free radical

reaction mechanism as follows:

Initiation:			
R-00-H	$\rightarrow$	R-O• + HO•	
$R-O \bullet + CH_2 = CH(COOR)$	$\rightarrow$	$R-O-CH_2-CH(COOR)$ • (1)	
Propagation:			
(1) + $mCH_2$ =CH(COOR)	$\rightarrow$	R-O-[CH ₂ -CH(COOR)] _m -CH ₂ -CH(COOR)•	(2)
(1) + $nCH_2$ =CH(COOR)	$\rightarrow$	R-O-[CH ₂ -CH(COOR)] _n -CH ₂ -CH(COOR)•	(3)
Termination:			
(2) + (3)	$\rightarrow$	R-O-[CH ₂ -CH(COOR)] _m + _n + ₂ -O-R	
(2) + X*-H	$\rightarrow$	$R\text{-}O\text{-}[CH_2\text{-}CH(COOR)]_m\text{-}CH_2\text{-}CH_2(COOR) + X\bullet$	

*X can be tertiary hydrogen alone or in the backbone, which can lead to branching or crosslinking points.

#### **Cure Site Monomers**

As previously mentioned, curing of the first commercial polyacrylate elastomer, a homopolymer of ethyl acrylate, proved to be very difficult. For this reason, cure site monomers are copolymerized with the backbone monomers to produce a usable polyacrylate elastomer. Examples of the common cure site functional groups used today are shown in Figure 4.



Figure 4: Common Polyacrylate Cure Site Functional Groups

The largest volume of polyacrylate elastomers produced today contains chlorine cure sites. The other major type of cure site monomer is the epoxy-ring-containing monomers. Epoxy-containing polymers can be cured by ammonium benzoate, blocked diamines, and onium salts.

A novel approach to the cure of polyacrylate elastomers was the development of dual cure sites along the polymer backbone. The two types that have achieved commercial importance are the chlorine/carboxyl and epoxide/carboxyl dual cure sites. The emphasis for the development of the dual cure site polymers was to eliminate the need for postcuring of the rubber article. The dual cure site polymers can give good physical properties, especially compression set resistance, without the use of a post cure. However, in some applications a post cure may still be necessary.

Most recently, Zeon Chemicals has introduced a new family of ACM elastomers known as high temperature polyacrylate (HT-ACM). These HT-ACM materials use the most heat resistance ACM technology to date and, therefore have better heat resistance over traditional ACM materials because of the optimization of

backbone monomers along with improved amid cross linking technology. When aged at elevated temperatures, the unique polymer construction of HT-ACM develops superior compression set stability and physical property retention never before achieved with prior ACM technology.

# MATERIAL CLASSIFICATION

Polyacrylate elastomers (ACM) are classified by ASTM D 2000 and SAE J200 to be in the categories of DF and DH (both 150°C capable), and EH (175°C capable) and are considered to represent one of the specialty elastomer families. Figure 5 compares many common oil and high temperature resistance polymers based upon the ASTM and SAE specification systems. ACM elastomers generally have greater heat resistance than HNBR and improved oil resistance compared to ethylene acrylic polymers (AEM).



Figure 5: Heat- and Oil- Resistant Elastomers

The various specialty elastomer families are rubbery materials that offer some unique physical characteristics that can solve particularly difficult sealing, containment, dampening or environmental protection problems. Table 2 lists some key characteristics of the more common specialty elastomer families.

Elastomer Family	Relative Compound Cost	Maximum Service Temp, °C	Continuous Service Temp, °C	Minimum Service Temp, °C	Oil Resistance
ACM	1	200	175	-40	Excellent
HNBR	5	175	150	-50	Excellent
ECO/CO	1.5	165	135	-60	Excellent
FVMQ	20	260	230	-60	Excellent
FKM	14	290	260	-30	Excellent
AEM	1	200	175	-40	Fair
MQ/VMQ	2.5	310	275	-100	Fair

Table 2: Comparative Properties of Specialty Elastomers

As can be seen, polyacrylates generally offer a lower cost solution as compared to the other oil-resistant, high temperature types such as FVMQ (fluorinated silicone) and FKM (fluorinated hydrocarbon) elastomers. Polyacrylates also offer improved high temperature resistance over HNBR (hydrogenated nitrile) and ECO/CO (epichlorohydrin ethylene oxide) elastomers. Improved oil resistance is their major advantage over the AEM (acrylic/ethylene) and MQ/VMQ (silicone/vinyl functional silicone) materials.

# COMPOUNDING

Nearly all rubber compounds require the gum polymer to be formulated, or combined, with other ingredients. In the rubber industry this is commonly called "compounding". A typical generalized formulation is given in Table 3. The range of physical properties that can be obtained with a polyacrylate compound can be seen in Table 4 below. A more detailed discussion on polyacrylate properties is presented later in this chapter.

Ingredient	phr	Purpose	Typical Example
Polymer	100	Oil Swell/High & Low Temp Resistance	HyTemp 4051, HyTemp AR12
Reinforcing Agents/Fillers (Black or Nonblack)	25-150	Reinforcement	N550, Hi-Sil 233
Retarder*	1 - 6	Increase Scorch Safety	Stearic Acid, HyTemp SR-50, Vulkalent E/C
Process Aid/Lubricant	1 - 4	Improve Mill Release	WB-222, Stearic Acid, (VANFRE [®] VAM, Armeen 18D)**
Antioxidant	0 - 4	Increase Thermal Stability	VANOX [®] CDPA, AGERITE [®] STALITE [®] S
Plasticizer	0 - 20	Softening and Low Temperature Enhancement	Thiokol TP-759, Paraplex G-25, DBEEA
Curatives	1 - 10	Crosslinking	Metallic Soap/Amine, Urea, Sulfur; Isocyanuric Acid; Diamine; Thiadiazole

Table	3:	Tvp	ical	ACM	Com	pound
IUNIO	•••		i o u i			pouria

* Examples given depend on the polymer and cure system.

** Examples given are only recommended for HT-ACM elastomers.

#### Table 4: Physical Properties of Typical ACM Compounds

Physical Property	Range
Hardness, Shore A	40 - 90
Tensile Strength, MPa	7 - 14
Ultimate Elongation, %	100 - 250
Compression Set, 70 hrs @ 150°C, %	5 - 60
Specific Gravity	1.30

# **Polymer Selection**

As explained earlier, the choice of base rubber is the primary determinant of low temperature and oil resistance. This also determines the choice of the cure system. It is necessary to match the cure system with the specific polymer cure site type. As cure site types vary between polymer manufacturers, it is generally not possible to change base rubbers without making additional changes in the formulation. However, polyacrylates in the same family can be blended to achieve the desired physical properties. For example, a high oil-resistant chlorine grade can be blended with a low temperature chlorine grade polyacrylate to achieve a mid-range balance of oil and temperature resistance.

# **Reinforcing Agents/Fillers**

Polyacrylates are not tough or resilient in the gum state, even when vulcanized. Typically, carbon black is added to gain strength and reduce cost. It is also possible to formulate with non-black fillers by using treated silica and clay. However, physical strength and compression set are generally poorer. For special needs, graphite is sometimes used to gain lubricity. In all cases more basic materials are preferred, as both acidic blacks and non-black fillers can retard the cures significantly.

*Carbon Black Reinforcement* – provides the best physical properties. For optimal balance of processing, original physicals, and aging (especially compression set) N550 (FEF) is the most common type. Higher elongation and tensile strength can be obtained by using smaller particle size, lower structure-type blacks. N326 (HAF-LS) is rather unique in this respect.

*Mineral/Non-black Reinforcement* – chemically modified aluminum silicate and blends of these are the most commonly used mineral types of reinforcing agents. Vinyl- and amino-type silane coupling agents also are effective in promoting improved vulcanizate physical properties for silica-reinforced compounds. Highly acidic or basic fillers will affect cure rates.

Synthetic graphite or molybdenum bisulfate is also often used in conjunction with carbon black and/or mineral reinforcing agents. This can improve surface lubricity and abrasion resistance in, for example, a rotary shaft seal application.

Table 5 provides examples of the effect of alternative fillers in a typical, high oil-resistant grade of polyacrylic. For low temperature grades, approximately 20% higher filler loadings are required to gain equivalent hardness. With proper choice of filler and level it is possible to formulate compounds with about 40 to 90 Shore hardness. The effect of filler particle size and structure is essentially the same as with other elastomers.

					Clay/	
Ingredients	None	N326	N550	Clay	Silica	Graphite
HyTemp 4051EP	100	100	100	100	100	100
Stearic Acid	1	1	1	0	0	1
Struktol WB-222	2	2	2	2	2	2
AGERITE STALITE S	2	2	2	2	2	2
Sodium Stearate	4	4	4	6	6	6
HyTemp NPC-50	2	2	2	3	3	3
Filler Type:						
N326, HAF-LS	0	65	0	0	0	0
N550, FEF	0	0	65	0	0	70
Nulok 321	0	0	0	140	70	0
Zeolex 23	0	0	0	0	45	0
Asbury 22U Graphite	0	0	0	0	0	20
Totals	111	176	176	253	228	204
Mooney Scorch, ML1+30 @ 10	0°C					
Mooney Viscosity	20	65	62	52	66	55
Minutes to 5 pt. rise	13.0	11.0	9.0	18.5	>31	3.8
Minutes to 35 pt. rise	>31	17.5	14.5	>31	>31	8.5
ODR, Micro Die, 3° Arc, 100 cp	m @ 190	Э°С				
M∟ (dN•m)	0.6	1.4	1.2	1.1	1.0	1.0
M _H (dN∙m)	2.4	7.3	7.3	6.3	6.6	6.0
t _s 2 (min)	0.7	0.6	0.5	0.9	1.3	0.4
ť 90 (min)	5.2	5.0	3.9	6.4	8.1	2.2
Original Physicals, Press Cured	l 4 mins.	@ 190°	0			
Hardness, Shore A	23	68	68	70	71	65
100 % Modulus, MPa	0.40	4.00	6.00	10.80	7.70	4.80
Tensile, MPa,	1.3	16.2	12.6	11.4	9.7	8.0
Elongation, %	280	280	220	120	140	170
Compression Set, 70 hrs. @ 15	50°C					
Plied, %	12	42	26	38	59	30

Table 5: Filler Systems

# Antioxidants

Polyacrylate elastomers are inherently resistant to oxidation. However, the use of low volatility antioxidants provides improved dry heat aging resistance. Certain diphenylamines, such as VANOX CDPA, are quite effective at preventing loss of elongation after hot air aging.

## **Plasticizers and Processing Aids**

Generally, large amounts of plasticizers are seldom used in polyacrylate compounds. Effective low temperature types tend to volatilize in the severe high temperature environments where polyacrylates are often used. However, they are sometimes added at low levels (5 to 10 phr) to gain improved processability and/or marginal improvement in low temperature resistance. Low molecular weight-types will aid flow during processing, and polymeric types can improve tack and mold knitting characteristics. The monomer ether/ester plasticizers are the most commonly used types.

Standard process aids are commonly used to improve mixing, mill release, and flow characteristics. Stearic acid and metallic carboxylate soaps (e.g., sodium stearate), when used as a part of the cure system, also function as process aids.

Plasticizer/process aids can affect cure characteristics and resultant physical properties. Therefore, it is important to follow manufacturer's recommendations and not substitute functional equivalents unless thoroughly evaluated. Excessive levels of lubricant (above 3 phr) should also be used cautiously as this may cause bonding or knitting problems. Table 6 summarizes characteristics of some commonly used types of plasticizers and processing aids.

Trade Name	Principal Function	Chemical Type	Typical Level	Volatility	Extractability
Thiokol TP-759	Improve Low Temp.	ether-ester	5 to 10	moderate	high
Paraplex G-25	Reduce viscosity	polyester	5 to 10	low	low
Struktol WB-222	Improve mixing/flow	fatty acid salt	1 to 3	low	moderate
VANFRE VAM (HT-ACM Only)	Mill Release /Improve mixing/flow	organic phosphate ester, free acid	0.5 to 2	moderate	high
Armeen 8D (HT-ACM Only)	Mill Release /Scorch Retarder	octadecyl amine	0.5 to 1	moderate	high

#### Table 6: Commonly Used Plasticizers and Processing Aids

# Retarders

Retarders are used to keep the compound from crosslinking prematurely before manufacturing of vulcanized articles. The chemistry of polyacrylate is basic in nature, therefore adding weak acids will tend to retard the cure mechanism(s). Since retarders adversely affect compression set and sometimes heat aging performance, the amount used is often small. The choice of retarder depends on the cure system that is being used. Stearic acid is the universal retarder for polyacrylates; it also serves as an effective processing aid.

# **Cure Systems**

In order to facilitate cure most commercial polyacrylic rubbers have a low level of reactive cure sites. This varies between commercially available types. Since there is no universal cure system for all commercially available acrylic rubbers, cure systems must be matched with the type of reactive cure site. Typically, the polymer manufacturer will recommend an appropriate cure system.

In the U.S., soap/sulfur systems developed in the earlier 1960s are still very common. They offer good scorch safety, cure rate, and physical property balance. They also are relatively low in mold corrosion even for chlorine functional

polymers. In Japan, the older ammonium benzoate and adipate remain very popular. They are slower curing but offer very good scorch safety and non-water sensitivity for extruded steam cured hose.

In order to develop low compression set resistance most polyacrylates require a post cure (temper). Newer cure systems have been developed in order to reduce, or in some cases, eliminate the need for this post cure. In the late 1970s soap/amine/urea systems were developed for dual chlorine/carboxyl functional polyacrylics. These have become the most popular systems in Europe. In the late 1980s even more efficient cure systems were developed in the U.S., Europe, and Japan. The HyTemp NPC-50 cure package, which is marketed by Zeon Chemicals in the U.S., uses this technology and provides for faster cures and lower compression set, with or without a post cure. The HyTemp NPC system can also yield excellent physical properties, and cure rheology can effectively be used to determine an appropriate cure time and temperature based upon T' 90 values.

HT-ACM polymers are cured with hexamethylene diamine carbamate (HMDC) and a highly alkaline accelerator such as VANOX[®] DOTG. As mentioned earlier, this cure system offers superior compression set stability and physical property retention even when aged at temperatures approaching the limit of ACM operating conditions. Because of the recent concerns over health risks associated with VANOX DOTG and other guanidine chemicals, DOTG-free formulations are also available. As with many of the other ACM cure systems, a post cure is recommended to achieve the best compression set and high temperature performance that this outstanding cure system has to offer.

Retarders are often used to increase scorch safety and shelf stability of polyacrylates. Stearic acid is the most common scorch retarder for ACM, and it also acts as a processing aid. Other common scorch retarders are also used. As mentioned earlier, the cure sites used in polyacrylates are quite reactive even at room temperature; therefore, care should be taken to prevent premature curing or scorch. Depending upon the cure system and climate, the shipping and storing of compound in refrigerated environments may be used to prolong a polyacrylate compound's shelf life. Shelf stability is highly dependent on the specific formulation and storage conditions. Storage stability can vary from a few days to several months.

Because the cure mechanism of most acrylic rubbers is alkaline they are accelerated by basic materials, e.g., magnesium oxide, and retarded by acidic materials, e.g., stearic acid. Polyacrylate non-black compounds can be formulated to achieve fast curing and low compression set characteristics. Increased curative levels are often required to overcome the acidic retarding effect of the nonblack fillers.

#### PROCESSING

Polyacrylates can be processed in all standard rubber-type equipment. However, because of their inherent rheological characteristics and different cure mechanisms, acrylic elastomers are more process sensitive than some other elastomers. This requires that a fairly rigid processing procedure be followed and maintained to ensure mix-to-mix quality and uniformity.

Polyacrylates are relatively soft and thermoplastic in nature and, because of this, tend to exhibit steep reductions in viscosity with increase in temperature. Therefore, it is important to incorporate fillers earlier in the mix cycle to gain good dispersion because of the rapid loss of shear resistance upon mixing. Efficient cooling also contributes to maintaining polymer integrity during the initial, and critical, phase of mixing.

## Scorch

Of the processing problems associated with acrylic rubbers, most are scorch related. Polyacrylate elastomers, while scorchy, tend to be slow curing, hence the necessity of post cure. However, with the development of the diamine curable HT-ACM grades, relatively fast cure rates are possible. Also, the HyTemp NPC (No Post Cure) cure system yields excellent physical properties without the need for a post cure. When using the NPC cure system, the compound must be maintained below its 85°C threshold activation temperature during mixing and shaping operations.

With most acrylic compounds, scorch manifests itself by way of increased viscosity. A severe scorch problem can render the stock completely useless. A more moderate scorch condition is not always recognizable because the premature crosslink density is relatively small and breakdown occurs readily with subsequent work. The fact that a rough extruding or poor mold-flowing stock is smoothed out on remilling does not indicate the absence of a scorch problem. Scorched stocks, particularly those that have been reworked, could also produce worse than normal vulcanizate physical properties. For investigative purposes, determination of the mean viscosity of the master mix (without curatives) can be of value in determining the degree of scorch in the finish mix (with curatives). It is recommended that Mooney viscosity and cure rheology test methods be employed as quality control tools. The Mooney viscometer serves to provide a sensitive measurement of viscosity/scorch related behavior at processing temperatures. Cure rheology can give an indication of cure behavior at a given cure temperature.

#### **Polymer/Compound Storage Stability**

Raw acrylic elastomers exhibit excellent (at least 24 months) shelf stability when stored in their original packages under normal room temperature and in dry conditions.

Shelf lives of finished (mixed) compounds are primarily dependent upon the choice of cure system and storage conditions. In general, refrigerated storage can dramatically extend shelf life.

#### Zinc and Zinc Salts

It is important to use an adequate process aid for good mill release. When mixed stocks are sheeted or stripped off for subsequent processing, care should

be taken in the choice of anti-stick used. Zinc stearate should be avoided as it can be pro-degrading. Standard clay or calcium stearate types are recommended.

# Mill Mixing

Internal mixing is generally recommended for best efficiency because polyacrylic elastomers do not lend themselves to open mixing as a result of problems associated with release. However, it is possible to mill mix. The mill should be run with full cooling on both rolls. It will tend to split and stick to both rolls. There is no need to give the polymer a breakdown period or to get the polymer all to one roll prior to beginning the filler addition. Once the majority of filler is added, the batch will tend to go to the fast roll. Dependent on the specific polymer type and loading, total mix time will vary from about 15 to 45 minutes. A typical mixing procedure is:

- 1. Band polymer on room temperature mill with full cooling water.
- 2. Adjust nip to provide a high rolling bank.
- 3. Add reinforcing filler in several increments and open nip as required to retain rolling bank.
- 4. Cut and work stock as necessary to allow polymer to accept the filler.
- 5. Add antioxidant, retarder, lubricant, process aid, etc.
- 6. Add plasticizer.
- 7. Cut and blend until uniform appearance is obtained, then end pass a minimum of six times.
- 8. On second mill step, form rolling bank and add the curatives.
- 9. Cut and blend until uniform appearance obtained, then end pass a minimum of six times.

If the formulation is known to have excellent scorch safety, and the mill has sufficient cooling ability to prevent an excessive increase in compound temperature, a one step procedure can be used. This is generally not recommended because of the high reactivity of the ACM cure chemistries. In this case the curatives would be added after any plasticizer.

# **Internal Mixing**

A two step internal mixing procedure is normally recommended. Although not recommended, compounds can be mixed in one pass if the formulation has been optimized for scorch safety. If the mixer is well sealed it is possible, and often desirable, to use an upside-down mix procedure, i.e. adding polymer last. A combination of time and temperature is commonly used to control the addition sequence. For highly loaded stocks that may show irregular temperature spikes during mixing, using integrated power can be a useful control technique. Optimum cooling and rotor speed are dependent on the particular mixer. As a result of their steep reduction in viscosity with increasing temperature, a high rotor speed is desirable to achieve the best filler dispersion early in the mixing process. Maximum curative dispersion will be obtained if the master compound is aged 16 to 24 hours prior to the cure addition step. Polyacrylate master batches are typically indefinitely stable.

For the curative addition step, care must be taken to prevent excessive heat buildup as this can lead to scorch. The timing between the first and second pass is important. As the compound cools, the viscosity of the compound will increase. Under ideal conditions the master batch should be allowed to cool for 12 to 24 hours for optimal viscosity and recovery from the prior mixing step. During the second pass the increased shear helps the curative to disperse. The second pass is often mixed at a slower speed to minimize rapid temperature increases. A typical two-step mix cycle is shown below:

# Step 1 Master Batch:

<u>Time</u> 0'	<u>Temp</u> -	<u>Procedure</u> Add reinforcing filler, antioxidant, retarder, process aid(s), etc.
1/2'	-	Add polymer
4'	110°C	Add plasticizer
5'	130°C	Bump and brush ram
6'	150°C	Dump to cool mill*
Step 2	Cure Addition (/	After 12 to 24 Hours)
0'	-	Sandwich add 1/2 master, curatives, 1/2 master
2'	-	Dump to cool mill*

*Dump temperature dependent on cure system - 85 to 95°C. At least two complete cut downs for blending and/or end passes is recommended.

# Extrusion

Polyacrylic can be formulated for excellent appearance and fast extrusion. Ram-type Barwell extrusion is often used for preform preparation. Care must be taken not to generate excessive heat on mill warm-up of pigs for the Barwell, especially in fast curing compounds. Generally, higher structure blacks, higher filler loadings, and addition of process aid and plasticizer will give best results. The choice of polymer is a very important factor. Lower viscosity (lower Mooney) polymers will extrude faster, but may not exhibit as high a green strength. Zeon Chemicals offers various polymers that are identified as EP, or easy processing grades.

Extruder temperature profiles should be set for a polymer that exhibits relatively high sensitivity to temperature and shear. A typical initial profile for a cold feed extruder is shown in Table 7.

Extrusion Parameter	Setting
Head & Die Temperature, °C	95-105
Screw Temperature, °C	50-70
Hopper Temperature, °C	50-60
Barrel Zone 1 Temperature, °C	60-70
Barrel Zone 2 Temperature, °C	70-80
Typical Screw Speed, RPM	5-10
Typical Feed Strip, mm	120-150
Typical Die Land Length, mm	10-20

 Table 7: Typical Cold Feed Extruder Setup

The list below addresses many common recommendations and topics for the successful extrusion of polyacrylate compounds:

- The screw and barrel temperatures should be kept as low as possible, thus allowing the compound to retain viscosity. This enables adequate transition of the material down the screw and barrel and maintains back pressure.
- Hot head and die temperatures (95°C to 105°C) impart a smoother surface finish on the extrudate.
- The amount, or number, of extruder feed strips should be optimized to prevent rubber from backing up in the throat of the extruder. It is recommended that the rubber strip width going into feed of extruder be less than the screw flight width. Polymer-rich compounds have more of a tendency to "ball up".
- The use of a spider or breaker plate is recommended because it converts the rotational flow of the material to linear flow.
- A long die land length (~10 mm) helps maintain a smoother extrudate surface finish.
- When extruding hose, there is a chance the hose may collapse on exiting the die. Applying air pressure inside the hose via the extruder can prevent this from occurring.
- For a hose application, adhesion of the rubber covering to the textile is very important for dynamic performance.
  - Some manufacturers warm the braided hose before the cover is applied, often by the use of a hot air oven.
  - Some manufacturers apply an adhesive to the fabric before the cover is applied. The adhesive must be allowed to dry thoroughly before the cover is applied.
  - Others use a solvent bath dip located after the braider. Recommended solvents include, but are not limited to, acetone, methanol, methyl ethyl ketone (MEK), and toluene.

# Calendering

The stock should be banded on a warm-up mill and blended for several minutes for calendering applications. However, care should be taken to prevent the stock from getting above 80°C. Two, three, or four roll calenders can be used. It is generally not necessary to re-calender in the second nip on three and four roll machines. A starting temperature profile on a three roll calender would be as follows:

Calender Roll	Temperature (°C)		
Тор	60 to 70		
Middle	70 to 80		
Bottom	80 to 100		

Additional surface lubricants, as recommended by the polymer supplier, should be added to get good release from the mill. As polyacrylates can be relatively nervy it is also important to have the calendered sheet well cooled prior to winding on a roll. A poly-type liner is also recommended, but non-zinc stearate talcs are sometimes used.

## Molding/Curing

Compression, transfer, and injection molding techniques are all currently used with polyacrylic compounds. In recent years the trend has been to move to the injection molding method, and this process now accounts for between 50% and 70% of molded applications. For extruded tubing and reinforced hose, the batch steam autoclave process is most common. In some cases pressureless continuous vulcanization (CV) techniques such as salt bath and microwave are used.

Typical cure cycles are given in Table 8. These cycles can vary depending on the mass and/or configuration of the molded product. It is important in compression molding to build back pressure to force out trapped air and prevent blistering. This can be accomplished by the use of fast curing systems and/or allowing preforms to age 12 to 72 hours prior to molding. Generally, using the compound the same day as stripped, or mill freshening prior to processing, is advised for injection molding or extruded applications.

# Postcure

In most cases a postcure is required to gain optimal compression set. The postcure process is generally carried out in a circulating air oven at maximum air flow. This varies from 3 to 24 hours at 150°C to 200°C. It is generally recommended not to exceed postcure temperatures above 205°C.

Method	Time (min.)	Temperature (°C)
Compression	0.5 to 4	170 to 210
Transfer	4 to 8	160 to 180
Injection	0.5 to 2	180 to 210
Steam Autoclave	20 to 60	150 to 160

Table 8: Typical Cure Cycles

## Bonding

Acrylic compounds provide excellent bonds to metals and other substrates with various types of commercially available adhesives. Bonding is customarily carried out during vulcanization. Recommended adhesives, substrate preparation, and application procedures are provided by the adhesive manufacturers.

# POLYACRYLATE PROPERTIES

As previously discussed, polyacrylic elastomers are classified as high temperature, oil resistant, specialty-type rubbers. The chemical construction of ACM gives this material many useful and interesting properties, many of which are outlined as follows:

- Broad temperature range dependent upon the polymer grade: -40°C to >175°C continuous and >200°C short-term heat exposure
- Excellent long-term high temperature resistance obtainable with HT-ACM
- · Excellent resistance to new semi and fully synthetic engine oils
- · Excellent resistance to petroleum-based lubricants and greases
- · Excellent resistance to transmission fluids
- Resistance to aliphatic hydrocarbons
- Inherent ozone resistance
- Resistance to ultraviolet (UV) radiation
- Low noise/vibration transmission
- · Resistance to diesel and biodiesel fuels

# Characteristic Temperature Resistance

The mechanisms of thermal and oxidative degradation of acrylic gums have been studied in detail. Thermal degradation begins near 300°C. Oxidative degradation initiates with oxygen attack at the tertiary carbon atoms to form hydroperoxides. These subsequently decompose to form molecular fragments. Depending on the choice of cure system, some initial reversion may be observed, but all acrylic compounds will eventually fail by embrittlement.

High temperature resistance is highly dependent upon the specific grade of polyacrylate base polymer used in a particular application. They are generally considered to have 200°C intermittent and 175°C continuous upper use temperatures. This is typically based on maintaining at least 50% of original

tensile and elongation and passing a 180° bend test (when tested at room temperature) after 70 hours at 200°C and 1000 hours at 175°C in air. Strength at elevated temperature, including hot tear, is fair. When tested at 150°C, ultimate elongation, tensile strength and tear strength properties range from 20 to 40% of room temperature values.

Low temperature resistance is also very dependent on the specific grade of polyacrylic gum rubber. As with high temperature resistance, low temperature performance is dependent upon the choice and variety of monomers used during polymerization. The glass transition temperatures (Tg) of polyacrylates typically range from -40 to -15°C without plasticizer. Low-temperature plasticizer use is limited as it tends to be volatile at the 175 to 200°C expected high temperature range and/or extracted in functional fluid environments. However, the use of 2 to 15 phr monomeric ether/ester-type plasticizers can improve low temperature capability up to 5 to 10°C.

The specific test procedure can have a significant effect on the low temperature rating. Polyacrylics exhibit a more gradual shift to a glassy state than do most other elastomers. They also tend to be rather weak in the glassy state. This results in better low temperature ratings by flexibility tests like mandrel bend, or torsional (Gehman) stiffness methods. They look worse on impact brittleness type tests. The proper choice of coolant is also important as the use of alcohols can effectively plasticize the test specimens and lead to false results. Specific examples of high and low temperature resistance are illustrated below in Table 9.

HyTemp Polymer	<u>4051 EP</u>	<u>4052 EP</u>	<u>4053 EP</u>
	Oil	Low	Ultra Low
Typical Application	Resistance	Temperature	Temperature
Ingredients	phr	phr	phr
Polymer	100.0	100.0	100.0
Stearic Acid	1.0	1.0	1.0
Struktol WB-222	2.0	2.0	2.0
N550, FEF Carbon Black	65.0	80.0	80.0
AGERITE STALITE S	2.0	2.0	2.0
Sodium Stearate	4.0	4.0	4.0
HyTemp NPC-50	2.0	2.0	2.0
Totals	176.0	191.0	191.0
Specific Gravity	1.31	1.32	1.31
Mooney Viscosity, ML 1+4 @ 1	00° C		
Mooney Viscosity	55	53	60
Minutes to 5 pt. rise	6	8	5
Minutes to 35 pt. rise	11	31	9

Table 9: Physical Properties at Typical High and Low Temperatures

	(		
ODR, Micro Die, 3° Arc, 100 cpr	т @ 190°С		
M _L (dN•m)	1.3	1.3	1.8
M _H (dN•m)	7.5	5.9	6.9
t _s 2 (min)	0.5	0.6	0.5
ť 90 (min)	3	2.3	2.6
Original Physicals, Press Cured	4 min. @ 190°C		
Hardness, Shore A	66	67	65
100 % Modulus, MPa	6.5	5.6	6.3
Tensile, MPa,	11.9	9.5	9.3
Elongation, %	200	170	140
Original Physicals, Tested @ 17	7°C		
Hardness, Shore A	58	53	55
Tensile, MPa	1.2	1.6	1.2
Elongation, %	50	50	50
Compression Set, Plied, 70 hrs.	@ 150°C		
%	26	30	30
Test Results After Postcuring 4	hrs. @ 177°C		
Original Physicals			
Hardness, Shore A	67	67	64
100% Modulus, MPa	6.5	5	6.2
Tensile, MPa	12.3	8.8	9
Elongation, %	210	180	140
Retained Properties After Heat	Aging in Air, 70 hrs	s. @ 204°C	
Hardness, Pts.	3	12	14
Tensile, %	-30	-38	-35
Elongation, %	-10	-65	-50
180° Bend	Pass	Pass	Pass
Retained Properties After Heat	Aging in IRM 903	Oil, 70 hrs. @ 150 C	>
Hardness, Pts.	-9	-17	-15
Tensile, %	2	-3	-20
Elongation, %	-15	0	-14
Volume Swell, %	10	16	24
180° Bend	Pass	Pass	Pass
Compression Set, Plied, 70 hrs.	@ 150°C		
%	12	19	16
Low Temperature Flexibility, AS	TM D 1053		
Pass, °C	-18	-32	-42
Low Temperature Brittleness. A	STM D 2137		
Pass, °C	-12	-26	-34
-			

# Table 9: Physical Properties at Typical High and Low Temperatures (continued)

#### **Characteristic Fluid Resistance**

Polyacrylics are known to have outstanding resistance to hot oils, including those containing enhanced performance additive packages. These additives often contain sulfur, zinc and other chemicals that can act as curatives and/or degradants for many rubbers. Hypoid (EP, extreme pressure) gear lubricants

used in the differential of cars, trucks and buses will quickly attack most alternative sealing-type rubbers. Polyacrylics also perform very well in petroleum-based engine lubricating oils and automatic transmission fluids.

However, polyacrylics have only fair resistance to water and most aromatic hydrocarbons. This may be sufficient for occasional contact, i.e., so-called splash-up resistance. They are not recommended for direct, long term contact with strong acids, bases, alcohols, glycols, or steam. ACM materials perform quite well in applications involving diesel fuel contact. However, ACM materials are not used in applications where gasoline contact is likely. Lower molecular weight hydrocarbons such as iso-octane are more readily soluble in the ACM polymer matrix. A more complete listing of general fluid resistance is given in Table 10.

Fluid Type		Fluid Type	
Automatic Transmission Oil	E	Gasoline	Р
Aliphatic Hydrocarbons	E	Hydraulic oil - petroleum base	Е
Aromatic Hydrocarbons	F/P	Hydraulic oil - silicate ester base	G
Acids - dilute/concentrated	F/P	Hydraulic oil - phosphate ester base	Р
Alkali - dilute/concentrated	P/P	Ketones	Р
Alcohols	Р	Lubricating oil - petroleum base	Е
Chlorinated Hydrocarbons	Р	Lubricating oil - diester base	G
Ethylene Glycol	Р	Steam	Р
EP Greases	Е	Water	F-P
E = Excellent	G = Good	F = Fair	P = Poor

Table 10: Polyacrylate Fluid Resistance

# Flex Fatigue and Abrasion Resistance

Polyacrylics, in general, are not considered to have outstanding flex fatigue or abrasion resistance. However, good flex life can be obtained by choosing cure and reinforcing systems that yield low modulus and high elongation. Abrasion resistance can be dramatically improved by formulating with graphite, highly reinforcing blacks, and silicas. Dynamic rotating shaft seals (often with dust boots) that have a spring retainer behind a sealing lip are an example of an application where polyacrylics meet demanding abrasion and flex requirements.

# Weathering, Ultraviolet, and Ozone Resistance

Polyacrylates are ideal for applications involving weather and ozone resistance. Without the addition of any protective agent, typical formulations easily pass standard ozone and weathering tests, i.e., 168 hours of exposure to 100 pphm ozone at 49°C and six months of roof exposure under 20% stretch test conditions. Extended outdoor agings have been conducted showing no visual changes and elongation losses of only 25% or less after 10 years in Illinois and Alaska, or 6 years in Panama.

#### **Electrical Properties**

Polyacrylics can be considered for applications requiring either an insulating or conducting rubber member. The reinforcing agent chosen is the key to gaining the desired result. Typical filler systems and the resultant electrical properties are given in Table 11 below.

Property	Insulating Compound	Conductive Compound	
Reinforcing Agent	Silica, Silicate	CF Carbon Black N-294	
Volume Resistivity	7 X 1012 Ohm-cm	5 to 20 Ohm-cm	
Dielectric Strength	800 Volts/Mil	—	
Dielectric Constant	10 (60 cycles)	_	

Table 11:	Polyacrylate	Electrical	Properties
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# **Corrosion Resistance and Mold Fouling**

The specific grade of base rubber and the cure system are the prime determinants for mold corrosion and fouling. There are generally two areas to consider:

- 1. In-process molding surfaces
- 2. Metals in contact with the finished cured part

Mold fouling occurs when the metal mold surface becomes discolored or, in the extreme, pitted. It can be the result of compound components adhering to the metal, true corrosion, or a combination of the two. With regard to cured parts, the metal in contact with the rubber is the area of potential concern, e.g., a fitting on a hose or mating wear surface on a rotary seal.

Metal corrosion requires the presence of moisture and a catalyst such as a halogen source. Non-chlorine and low chlorine functional base rubbers are, therefore, generally the least corrosive. The less water sensitive the cure system the better. Properly formulated, polyacrylates generally are not considered highly corrosive. On the GM 9000-P corrosion test, ratings of 1 to 2 (0 being the best and 5 the worst) are obtainable with chlorine functional base polymers and 0 to 1 with carboxyl- or diamine-curable base polymers.

# Flame and Radiation Resistance

Polyacrylics find some small but interesting applications because of their unique chemistry. They consist of almost 99% by weight carbon, hydrogen, and oxygen. The oxygen content ranges from 20 to 30% by weight. Therefore, they burn quite readily and leave very little residual ash. This, combined with their ability to act as a binder for high loadings of powders, makes them valuable as a binder for propellant or explosive mixtures.

Their stable backbone structures also make them reasonably radiation resistant. Exposed to a  $5 \times 10^7$  Roentgen dosage, an ethyl acrylate type lost a high (60 to 70) percent of tensile strength and elongation properties, but did not harden excessively and retained a high degree of flexibility.

#### POLYMER SELECTION

Recent advances in polyacrylate (ACM) polymer development continue to result in new, easily processed polymers. These technical advances have coincided with new temperature and warranty demands from major automobile manufacturers worldwide. The result is increasing demands for more flexible and efficient curing systems for ACM compounds. To meet these demands, Zeon Chemicals continues to develop new curing technology enabling polyacrylate polymers to be safely compounded, bin stored, and vulcanized using a variety of processing equipment. These curatives not only provide the compounding chemist with safety and convenience, but with excellent cure rates and physical properties as well.

Selecting the right polymer for a particular application is the most important step to developing a successful polyacrylate application. This section describes the characteristics of each ACM polymer family, as well as the particular characteristics of each polymer grade. The information presented here is by no means a complete representation of all the technical data available, but can be used as a means to better understand the general characteristics of each family of ACM elastomers.

As explained previously, the characteristics of ACM are dependent, as with most polymers, upon the monomers that make up the polymer backbone of the particular grade of ACM elastomer. Zeon Chemicals offers ACM polymers from four different families of polyacrylates. A family, as defined here, is a class of polyacrylate elastomers that share common reactive cure sites and can be vulcanized by using the same, or similar, cure system chemistry. Polymer grades from the same family can be blended to achieve a desired balance of physical properties and/or processing characteristics.

Choice of polymer is primarily dependent on low temperature considerations. The ethyl acrylate-type grades provide the best overall balance of processing characteristics, heat and oil resistance, and physical properties but possess limited low temperature performance. The lower temperature grades sacrifice some of this balance proportional to the glass transition temperature of the polymer.

#### **Chlorine Cure Site Family**

The HyTemp/Nipol AR70 series elastomers incorporate the use of a chlorine cure site monomer. The largest volume of polyacrylate elastomers produced today contain chlorine cure sites. This monomer has a reactive chlorine atom that allows the use of mild curatives such as a fatty acid soap/sulfur system, ammonium benzoate, or trithiocyanuric acid. Historically, the soap/sulfur system is the most common curing method.

In general terms, the chlorine cure site family offers a range of performance from approximately -40 to 175°C. They are well known for their resistance to high temperatures, but their compressive stress relaxation (CSR) properties, resistance to compression set, and the need for a post cure for optimum

compression performance have led to the development of more advanced curing site technology as described later.

#### **Dual Chlorine/Carboxyl Cure Site Family**

One approach to the cure of polyacrylate elastomers was the development of dual cure sites along the polymer backbone. The emphasis for the development of the dual cure site polymers was to eliminate the need for postcuring of the rubber article. The dual cure site polymers can give good physical properties, especially compression set resistance, without the use of a postcure. However, in some applications a postcure may still be necessary.

All of the 4050 types offered by Zeon Chemicals have identical dual chlorine/ carboxyl cure sites, respond to the same cure systems, and can be blended in all proportions. The most appropriate polymer grade for a given application is dependent on the required balance of operating temperature range, oil resistance, cost, and processing.

The dual cure site series of polymers incorporates both carboxyl and chlorinefunctional cure monomers. This particular combination of cure sites requires unique curatives to provide ultimate physical properties. Traditionally used cure systems for this series of polymers are Sodium Stearate/Diuron-80 (Diuron), HyTemp NPC-50 (NPC), and HyTemp SC-75 (SC-75).

#### Peroxide-Curable Polyacrylate Family

Peroxide curing is a popular method for crosslinking elastomer formulations. Zeon Chemicals provides a peroxide-curable polyacrylate known as HyTemp PV04. It incorporates proprietary cure sites and does not require postcuring. However, like many ACM cure systems, a postcure can improve the material's compression set performance. HyTemp PV04 is suitable for O-rings and gaskets that do not require a high degree of physical strength, ultimate elongation, or compression set. HyTemp PV04 should not be considered for dynamic applications requiring high tensile strength or elongation at break. It is most suitable for binders, adhesives, caulks, and plastic modification. HyTemp PV04 processes very similarly to other ACM elastomers; however, like many peroxide-cured polymers, hot tear strength can be an issue.

# High Temperature ACM (HT-ACM) Family

Automotive-related demands on elastomers continue to become more severe. This is a trend that appears to be continuing unabated. Not only are the temperature demands increasing, the specification-related constraints both in time and newer test techniques, such as compressive stress relaxation (CSR), are also more demanding. This combination is requiring suppliers to turn to increasingly more exotic, yet cost-effective, polymers and cure chemistry in order to fulfill modern automobile specifications.

In order to assist the industry in this regard, Zeon Chemicals has developed and commercialized the new family of polyacrylic polymers known as hightemperature ACM, or HT-ACM. This family exhibits an improved level of heat and compression set resistance heretofore not seen in ACM elastomers. These improvements are achieved without sacrifice in strength, low temperature properties, or oil resistance. The superiority of these new elastomers over traditional ACM elastomers has been demonstrated in many under-the-hood applications, including valve cover and oil pan gaskets, seals, hoses, and air ducts. Zeon Chemicals' HyTemp AR12 has become a leader in these highly aggressive sealing applications. HyTemp AR12 compounds can easily exceed most CSR requirements with greater than 50% force retained at 1000 hours, and have better percent force retention than the chlorine and dual cure-site polymer grades.

When aged at elevated temperatures, the unique cure sites used in the polymer construction of HT-ACM provide superior compression set stability and physical property retention. HT-ACM elastomers generally offer a lower cost solution versus the other oil-resistant, high temperature polymer types such as FVMQ (fluorinated silicone) and FKM (fluorinated hydrocarbon) elastomers.

## APPLICATIONS

The most important properties of polyacrylate elastomers are heat and oil resistance; they therefore find use in a wide range of automotive applications. Automotive seals, gaskets and hoses represent the largest application for polyacrylics. They find more limited use in adhesives and as binders for propellants and flexible magnets. Typical applications are summarized in Table 12.

Seals/Gaskets	Other
Cork Binder	Flexible Magnets
Crankshaft	Spark Plug Boots
Grommets and Packings	Vibration Damping
Oil Pan	Belting
O-Rings	Adhesives
Pinion	Dust Boots
Rocker Cover	Rolls
Sponge	Fabric Coating
Transmission	Oil Cooler Hose
Valve Stem	Transmission Oil Cooler Hose

 Table 12: Typical Polyacrylate Applications

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# by E. McBride and M. A. Stewart

DuPont Performance Elastomers Wilmington, DE

# Introduction

Ethylene Acrylic elastomers are sold commercially under the trade name Vamac[®] by DuPont Performance Elastomers and are classified as 'AEM' in accordance with ASTM D 1418. The AEM designation follows where the 'A' stands for acrylic monomer, the 'E' for ethylene and the 'M' is for the saturated polymethylene backbone. Parts made from these elastomers have a good balance of properties including:

- Good heat and UV resistance because the backbone is fully saturated.
- Good fluid resistance to engine oils and transmission fluids because of the acrylic monomer. The preferred acrylic monomer for good fluid resistance is methyl acrylate, which is relatively polar for an acrylic monomer.
- Good low temperature properties. The balance of ethylene and acrylic monomer in the polymer determines the low-temperature properties.

Most AEM elastomers include a third monomer that is a cure site monomer and it allows the polymers to be crosslinked by reaction with diamines. The diamine-cured compounds require a postcure step. Some AEM elastomers do not contain a cure site monomer, and they can be crosslinked with peroxides. The peroxide-cured compounds may not require a post cure.

ASTM D 2000 establishes guidelines for rating elastomeric compounds resistance to heat and fluids. Compounds made from AEM polymers typically are rated as acceptable after 70 hours at 175°C which makes them Type E compounds. The fluid resistance in IRM 903 can range from 20% up 70% so they can be rated from Class J to Class E – typically they are rated as Class F (60% or less swell in IRM 903).

# **HISTORY and PRODUCT GRADES**

In the early 1970s there was a significant effort at DuPont to develop a polymer that would be cost-effective yet have good resistance to engine oils and transmission fluids, as well as good high and low temperature properties. This work led to the commercialization of Vamac elastomer in 1975. Improvements in the manufacturing process led to the commercialization of Vamac G in 1980, which is considered the "standard" grade. The product offering has continued to expand and now seven grades are available. The expanded grades have some of the following features:

- Better fluid resistance
- Higher viscosity for increased green strength
- · Improved low temperature properties
- · Better dynamic properties for hoses
- Better heat resistance
The manufacturing process was further upgraded to produce much lower levels of residual methyl acrylate monomer in the finished polymer.

The volume of sales for AEM elastomers has grown because of the desire for higher heat resistance and longer service time compared to many of the "traditional" elastomers such as natural rubber, SBR, nitrile rubber, CPE and ECO. Smaller, more compact engines have resulted from automotive industry trends for greater fuel efficiency and temperatures in and around the engine compartment continued increase. As an example, an application that required testing for air aging for 70 hours at 120°C may now require aging for 6 weeks at 150°C. AEM compounds can meet a specification of 6 weeks at 150°C, and they have replaced lower cost/lower performance polymers in automotive under-the-hood applications.

New developments for AEM elastomers are under way with the focus on further improving the processability of AEM compounds and properties of parts made from AEM compounds.

#### **Commercial AEM Elastomers**

AEM elastomers are sold as Vamac, and a list of the available grades are shown below in Table 1.

Mooney Viscosity Cu		Tg of	Vo Increa	olume ase, % in	Commont
ML (1+4) @ 100°C	System	Polymer* (DSC, °C)	ATF**	SF 105***	Comment
16.5	Diamine	-30	15	25	Standard Grade
18.5	Diamine	-23	6	11	Low Swell
26	Diamine	-30	15	25	High Viscosity
17.5	Diamine	-31	18	27	Improved Flex for Hoses
29	Diamine	-30	15	25	Improved Molding
11	Diamine	-40	33	45	Better Low Temp.
22	Peroxide	-30	15	25	Peroxide Cure
* Plasticized compound Tg will be lower. Most AEM compounds can meet a low temp. spec of -40°C.					
** Standard compounds with nominal hardness of 70 Shore A tested in Dexron [®] VI automatic transmissions fluid for one week @ 150°C.					
	Viscosity ML (1+4) @ 100°C 16.5 18.5 26 17.5 29 11 22 ed compound d compounds ons fluid for o	Viscosity ML (1+4) @ 100°C 16.5 Diamine 18.5 Diamine 26 Diamine 17.5 Diamine 29 Diamine 11 Diamine 22 Peroxide ed compound Tg will be low rd compounds with nomina ons fluid for one week @	Viscosity ML (1+4) @ 100°C       Cure System       Tg of Polymer* (DSC, °C)         16.5       Diamine       -30         18.5       Diamine       -23         26       Diamine       -30         17.5       Diamine       -30         17.5       Diamine       -30         11       Diamine       -30         22       Peroxide       -30         24 compound Tg will be lower. Most AEM of cons fluid for one week @ 150°C.       150°C.	Viscosity (@ 100°C         Cure System         Tg of Polymer* (DSC, °C)         Increation           16.5         Diamine         -30         15           18.5         Diamine         -23         6           26         Diamine         -30         15           17.5         Diamine         -31         18           29         Diamine         -30         15           11         Diamine         -40         33           22         Peroxide         -30         15           cd compound Tg will be lower. Most AEM compound rons fluid for one week @ 150°C.         70 Shore /	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

Table 1: List of Commercial Grades of Vamac

*** Standard compounds with nominal hardness of 70 Shore A tested in Service Fluid 105, a representative mineral-based engine oil, for one week @ 150°C. VI is usually less in synthetic engine oil.

#### **AEM Polymers**

AEM is produced by free radical polymerization of ethylene with methyl acrylate and optionally with an alkenoic acid cure site monomer. The resulting random copolymer is isolated, finished and packaged. Finishing includes devolatizing to remove residual methyl acrylate monomer. Low levels of methyl acrylate, however, remain in the polymer; consult the product Material Safety Data Sheet and guide for 'Safe Handling and Processing of Vamac and Vamac Compounds'.⁷ Vamac is packaged in 25 kg bales with either a strippable polyethylene liner or a fluxible liner. The strippable liner must be removed prior to processing.

The AEM elastomer has a relatively low Mooney viscosity with low nerve response, making it desirable for ease of processing. The combination of low viscosity and polymer composition provides good interaction with fillers for ease of compounding. The AEM polymer is amorphous and 'cold flows', with bales formed as a solid mass that is clear to opaque. The tops of bales may not be as fully massed as the bottom and the top portion may appear friable. The bale will continue to mass over time. Care must be taken to completely remove the strippable liner from bales, including from folds in the polymer. Fluxible liners are based on films made from compatible copolymers, and they may be processed with the compound if desired.



Figure 1: AEM Process Flow Diagram

# **AEM Polymer Structure**

The AEM backbone is fully saturated and provides good stability for long shelf life, processing and use in demanding applications. Vamac contains no halogens and generates low smoke upon burning.



Figure 2: AEM Polymer Structure

# **Future Trends**

The development of new AEM elastomers continues as the automotive market demands improved performance at a combination of higher and lower temperatures, resistance to new synthetic fluids, resistance to engine oils that contain low levels of fuel and longer service life in dynamic applications. Improved processability is also important for the mixing, molding and/or extrusion processes used to make finished parts.

# APPLICATIONS

Most AEM parts are either extruded hoses or molded gaskets. There are also many other parts made from AEM compounds.

## Hoses

Automotive hoses are a major end-use market for AEM compounds. They are used where the hose has to provide long service life when exposed to elevated temperature, low temperature, different fluids and dynamic loading. Some typical end-use hose applications include:

- · Turbocharger hoses for diesel engines
- Turbocharger hoses for gasoline engines
- · Transmission oil cooler hoses (TOC) for automatic transmissions

*Turbocharger Hoses* - One of the major uses for AEM compounds is in turbocharger hoses. The use of turbocharged engines has grown significantly in the past 20 years, with most of the growth being in Europe where diesel fuel is used in more than half of the new cars. Future growth is predicted in other regions of the world for passenger cars with diesel engines.

The use of turbocharged engines is growing for gasoline engines because of regulations on fuel efficiency and emission control standards. The increased fuel efficiency also reduces the amount of greenhouse gases. The growth of turbocharged gasoline engines is forecasted to be a global trend.

In order to reduce emissions, the positive crankcase ventilation (PCV) fumes are recycled into the fresh make-up air to the engine. In some cases, a portion of the actual exhaust gas is recycled; and some projections show that up to 50% of the exhaust gas will be recycled in the future. As the PCV fumes and the exhaust gases are recycled there is a build up of impurities – many of which are acidic in nature. AEM shows clear advantages where the turbocharger hose must withstand the PCV fumes and acid condensates. A turbocharger hose needs a balance of properties, including:

- good heat resistance
- good fluid resistance including acid condensate
- · good low temperature properties
- good dynamic properties

AEM hoses meet these criteria.

*Transmission Oil Cooler (TOC) Hose* - The automatic transmission fluid (ATF) in an automatic transmission heats up during use and must be cooled. TOC hoses route the hot ATF from the transmission to the radiator and then back again. Most of the radiator is for the antifreeze but there is a separate compartment in the radiator for the transmission fluid. The hose must have good resistance to automatic transmission fluid, good heat resistance, good low temperature properties and good flex properties. AEM hoses meet these criteria.

# Seals and Gaskets

Automotive powertrain seals and gaskets are another major end-use market for AEM compounds. Requirements include long service life at high and low temperatures when the part is exposed to engine oils or transmission fluids. Some typical end-use applications include:

- Engine oil pan gaskets
- Transmission oil pan gaskets and O-rings
- Bonded pistons seals in an automatic transmission

Several factors are driving the use of AEM compounds for these applications, including:

- Longer warranty times
- Higher engine temperatures
- Less volatiles allowed (California LEV requirements)
- More synthetic oils and more synthetic ATF's. In general, AEM compounds have lower swell in synthetic fluids compared to mineral-based fluids.

It is not always easy to predict how a compound will perform in the end-use such as a gasket or a seal. Compression set tests and fluid aging tests have been used for many years. Compressive Stress Relaxation (CSR) testing is becoming more important as a way to predict end use performance. AEM compounds perform very well in this test.

# **Other Applications**

AEM elastomers are also used in a wide variety of other applications, including:

- Wire and cable compounds where there is a need for halogen-free compounds with good flame resistance and fluid resistance.
- Torsional Vibration Dampers for automotive engines AEM compounds are used because they have the required heat and fluid resistance and because they have a relatively flat and desirable tan delta over a wide temperature and frequency range.
- Adhesives where the AEM elastomer acts as a toughener, particularly for cyanoacrylate and epoxy adhesives.
- CV joint boots where the combination of good heat resistance, good low temperature properties, good flex properties and good grease resistance are needed.

# COMPOUNDING

There are many different AEM compounds used commercially. AEM compounds normally consist of a cure package, carbon black filler, low levels of plasticizer, an antioxidant and a release package.

Starting point formulations for hose, seal and gasket compounds are provided in Tables 3 and 4 at the end of this chapter.

# Cure Package – Diamines

More than 90% of AEM compounds are cured with diamines. Hexamethylene diamine carbamate (HMDC) is the standard curative added to compounds. As the compound is heated (or exposed to moisture) the HMDC is converted to hexamethylene diamine (HMDA) and carbon dioxide.

$$H_3^+N - (CH_2)_6 - N \swarrow H_2 - H_2 + CO_2$$

HMDC

HMDA

#### Figure 3: Conversion of HMDC to HMDA

The HMDA is the actual curative that reacts with the acidic cure site in the polymer — and it does so in two steps. In the first step, an amide bond is formed, which gives dimensional stability to the part or hose. In the second (postcure) step, an imide bond is formed, providing good physical properties and compression set. The imide bond has good thermal stability and helps impart good heat resistance to the compound.

For AEM compounds, two factors that can lead to blistering problems during processing are the relatively low viscosity of the compound and the volatiles (including moisture) that are generated during the cure step. In order to prevent problems with blisters, the initial curing step must be done under pressure. For molded parts, the initial cure is achieved under pressure in the injection molding machine, whereas for hose, the initial curing is done in a high pressure steam autoclave. The postcure step can be done at ambient pressure. For the best properties, the diamine-cured compounds are normally postcured.

#### Accelerators

For many years the two most common accelerators for AEM compounds have been DOTG (diorthotolyl guanidine) and DPG (diphenyl guanidine). Compounds based on DOTG have fast cure rates and good compression set properties. This combination is attractive for seals and gaskets. Compounds based on DPG do not cure quite as fast as DOTG but they have better flex properties, so DPG is used in many hose compounds. A blend of the DOTG and DPG provides a balance of good compression set and good dynamic properties and the combination is often used in hoses. Much of the earlier literature for AEM compounds is based on DOTG as the accelerator.

There are issues with the decomposition products of DOTG and to a lesser extent with DPG and many of the newer AEM compounds do not contain DOTG.⁸ The most commonly recommended accelerator now for AEM compounds is DBU (diazabicyclo undecene). Compounds based on DBU have about the same cure rate as DOTG-based compounds but there is a slight increase in compression set and a slight reduction of elongation. These can be resolved mostly through compounding.

### Cure Package – Peroxides

Compounds produced from AEM dipolymers containing no acidic cure site monomer are cured with peroxides by using conventional peroxide cure chemistry.¹⁴ The AEM polymers containing the acidic cure site can also be peroxide cured but the acidic cure site interferes somewhat with the peroxide cure.

The standard peroxide used to cure AEM compounds is bis (tertbutylperoxyisopropyl) benzene (VAROX[®] 802-40KE). Sometimes dicumyl peroxide (VAROX DCP) is used but a concern with this peroxide is the formation of the decomposition product acetophenone, which has a strong odor.

A type 1 coagent like N,N'-m-phenylenedimaleimide (VANAX[®] MBM) is recommended for molding applications because this coagent speeds up the peroxide cure and helps provide good compression set properties.

For hose applications, a type 2 coagent like trimethylpropane trimethacrylate (Sartomer[®] SR 350) is recommended. The cure rate is slower, but the dynamic properties are improved.

# Fillers

*Carbon black* is used as the filler in a very high percentage of AEM compounds. The trends seen with carbon black in AEM compounds are very similar to trends seen in other elastomers and these include:

- As the black level increases there in an increase in viscosity, hardness, modulus and compression set. There is also a decrease in elongation and scorch time.
- As the particle size of the carbon black is increased (as in going from N550 to N770) and if the black level is held constant, there is a decrease in viscosity, hardness, modulus and an increase in elongation.

Some AEM compounds require a color other than black and work has been done with *white fillers*. Some of the white fillers that have been evaluated include:

- · Fumed or Precipitated Silica
- Titanium Dioxide
- Calcium Carbonate
- Magnesium Silicate (talc)

As a general rule, white fillers should be added at about the same volume level as carbon black filler. The white fillers are usually higher in density so a "typical" AEM compound with 50 phr black would require about 70 phr of silica to achieve similar physical properties. However, silica can increase the compound viscosity, rapidly leading to potential scorch issues, so care must be taken in formulating the compound. In general, white fillers do not provide properties equivalent to those provided by carbon black even at the same volume percent.

The properties of white-filled compounds can be improved if an adhesion promoter is used to improve compatibility between the filler and the polymer. A combination of an amino silane with silica filler has better properties than just using silica filler alone.

#### Plasticizers

Plasticizers are used in many AEM compounds and they provide a variety of benefits, including:

- Better low temperature properties
- · Better fluid resistance
- Lower cost
- Lower viscosity
- Lower hardness

Formulating the AEM compound with a combination of plasticizer and additional carbon black will allow for a constant hardness at lower cost, lower viscosity and improved fluid resistance. The compression set, however, will increase, and there may be more processing issues compared with the same hardness compound that contains no plasticizer and less black. As a guideline, if the plasticizer is increased by 10 phr, then the carbon black (N550) should also be increased by 10 phr to maintain the same hardness.

Most AEM compounds are post cured for 4 hours at 175°C to provide good heat resistance (for example: 6 weeks at 150°C). The types of plasticizers that can be used with AEM compounds are limited by exposure to high temperature in the end-use applications. A plasticizer like DOS (dioctyl sebacate) will significantly reduce the Tg (glass transition temperature) of an AEM compound, but most of the DOS will be lost from the compound in the postcure oven and whatever remains will be lost upon heat aging. After heat aging there is no benefit to the low temperature properties from using DOS.¹⁶

The plasticizers that are used with AEM compounds are those that have low volatility, good heat resistance and some polarity. Typical plasticizers used with AEM include mixed polyether/ester plasticizers and polyester plasticizers. Typical levels range from 5 to 20 phr.

AEM polymers are relatively low in Mooney viscosity compared to many other commercially available elastomers, and this limits the amount of plasticizer that can be used in a compound. High levels of plasticizer will cause processing issues because the viscosity will be very low, which can lead to mold fouling for injection molding or poor green strength in hose production.

## Antioxidants

AEM compounds are used because they have good heat resistance in air, and this attribute is improved with a good antioxidant. TGA studies of AEM compounds have been run in air and in nitrogen.¹³ Results show that in nitrogen, AEM compounds have significantly higher thermal stability, indicating that oxygen is the main cause for compound aging. The standard antioxidant for AEM compounds is VANOX[®] CDPA, 4,4'-bis( $\alpha,\alpha$ -dimethylbenzyl) diphenylamine, added at 1 to 2 phr. It is a staining antioxidant, but this is usually not a problem for AEM compounds because they are based on carbon black.

Other antioxidants that are used include hindered phenols. These types are non-staining and are sometimes used in mineral-filled compounds.

## **Release Package**

A release package is recommended for AEM compounds to improve processability in the mixing step and in the molding step. A good release package is especially important for compounds with high levels of plasticizers and/or low hardness values. A typical release package is shown below:

- 1.5 phr stearic acid
- 1.0 phr alkyl phosphate (VANFRE[®] VAM)
- 0.5 phr octadecyl amine

These ingredients are compatible with the compound at mixing temperatures (about 100°C), but they have relatively poor compatibility at room temperature, and they tend to bloom to the surface.

## Miscellaneous

Scorch Retarder - The octadecyl amine also acts as a scorch retarder for the diamine-cured compounds. It is a monoamine, and if it reacts with the cure site monomer it will not produce an effective crosslink. The cure rate slows as the octadecyl amine level increases.

Flame Retardants - AEM compounds are used in selected applications that require flame resistance. One of the key reasons that AEM polymers are used for these applications is that they do not contain any halogens. Standard flame retarders can be used, such as aluminum trihydrate or magnesium hydroxide.

# **COMPOUND PROPERTIES**

Like other elastomers, AEM compounds can exhibit a wide range of properties that depend on how they are formulated and cured. A range for some properties is shown in Table 2 below.

Physical Property Test	Typical Properties
Shore A Hardness, points	40 - 90
Tensile Strength, MPa	7 - 18
Elongation, %	100 - 500
Die C Tear, N/cm	18 - 45
Comp Set, 168 hrs. @ 150°C, 25% deflection	
- As Molded (press cured), %	20 to 80
- Post Cured, %	10 to 40
T _g by DSC, °C	-25 to -45
Volume Increase, %	
- ATF - Dexron VI	5 to 35
- Service Fluid 105	10 to 45
- IRM 903	20 to 90

**Table 2: Range of Physical Properties** 

The usual trends are seen with changing filler levels, plasticizer levels and state of cure. Refer to the section on compounding ingredients for more information.

## Heat Resistance in Air

Heat aging studies have been done with AEM compounds in air and in nitrogen. The AEM compounds have higher heat resistance in nitrogen than in air.¹³ The addition of 2 phr of a hindered-amine antioxidant such as VANOX CDPA will improve the life of the compound. Higher levels of the antioxidant do not appear to help.

Heat aging is a function of time and temperature, and there are different methods for assessing the heat aging of a compound. One method to rate compounds is time to 50% loss of original elongation, and another one is time to 100% absolute elongation. AEM compounds generally have elongation values of about 300% or greater, so they will have a higher rating if the guideline is time to 100% absolute elongation.

Some typical ratings for AEM compounds (time to 50% of original elongation):

- 12 weeks at 150°C
- 6 weeks at 165°C
- 3 weeks at 175°C
- 3 days at 200°C

If an AEM compound is highly plasticized, then the heat ratings will drop because the plasticizer volatizes during the aging step.

## Fluid Resistance

AEM compounds generally age well in engine oils and in automatic transmission fluids. These types of fluids are constantly being reformulated, and a general trend is that they are moving from mineral-based oils to synthetic-based oils. This trend is favorable to AEM compounds because they have lower swell in the newer synthetic-based oils.

Table 2 shows the fluid resistance range for SF 105, Dexron[®] VI and IRM 903. IRM 903 is included in many specifications, and it is a reference oil that has a significant aromatic content. Most of the engine oils and transmission fluids have low aromatic content, so the IRM 903 specifications do not reflect how AEM compounds will perform in the actual fluid that will be used.

AEM compounds are used in select boot applications where there is contact with grease. The AEM compounds are usually chosen for applications that need good heat resistance, and this means that the grease has to be rated for the higher temperatures experienced by the boot. AEM compounds generally age well in the high temperature greases, but they do not always age well in some of the lower temperature greases. AEM compounds are not recommended for direct contact with certain fluids, including:

- gasoline
- biodiesel
- antifreeze such as OAT (organic acid technology) coolants
- esters
- steam

AEM compounds will swell when exposed to gasoline, but if they are given time to dry out they will still have good physical properties. They are used in some commercial applications where there is limited exposure to gasoline vapors.

# Low Temperature Properties

There are many different ways to measure low temperature properties, and most tests will give different ratings for these properties. Some of the tests include:

- Glass Transition Temperature (Tg) by DSC (Differential Scanning Calorimeter)
- Tg by DMA (Dynamic Mechanical Analyzer)
- Temperature of Retraction TR10 or TR30
- Brittle Point
- Gehman
- Mandrel bend

The best predictor of how an AEM part will perform at low temperature is to run an actual bench test. However, this is not an option for compound evaluations.

Most AEM compounds contain some plasticizer, and plasticizers will provide better low temperature properties. Some plasticizer will be lost upon heat aging, so some of the low temperature properties will not be as good after heat aging in air. Most AEM compounds are used in contact with oil/ATF, and they will absorb some of the fluid—which will improve the low temperature performance.

Figure 4 shows the low temperature properties of a "standard" compound of Vamac G with no plasticizer and another compound with 20 phr plasticizer. A compound with 10 phr of plasticizer would have values halfway between the two compounds.

Figure 4 also includes the results for a static O-ring test that simulates the low temperature requirements for an O-ring. This is a test used by DuPont Performance Elastomers.¹¹

As a guideline, the low temperature values for a compound made with Vamac GLS will be about 5 to 8°C higher than the equivalent compound made with Vamac G. The Tg by DSC for a compound with Vamac GLS and 10 phr plasticizer will be about -30°C. Likewise, the values for a compound of Vamac Ultra LT will be about 10°C lower than those of the equivalent compound made from Vamac G. A compound made with Vamac Ultra LT and 10 phr of plasticizer will have a Tg by DSC of about -48°C.

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### Low Temperature Properties of Vamac G Compounds With 0 or 20 phr plasticizer

Figure 4: Low Temperature Properties vs. Plasticizer Levels

## Compression Set and Compressive Stress Relaxation (CSR)

Compression set is a very important test for elastomers, and it can be run in different ways. Most AEM compounds are tested for compression set at 150°C, and the time can vary from 70 hours to 6 weeks. The 150°C temperature usually represents the high end of most of the operating temperatures for an engine or transmission. Other applications require higher end-use temperatures, and sometimes the test temperature can be set at 175°C, with the time being less, ranging from 22 to 168 hours. Different test fixtures can be used, but most of the AEM data are based on ASTM or ISO fixtures.

Most AEM compounds use the diamine cure system, and they must be postcured to have good compression set properties. The compression set values for a diamine compound that is only press cured may be as high as 90% when tested for one week at 150°C. The postcure step will reduce the value down to about 20% to 30%.⁹ Six week compression set values at 150°C can be less than 50%.

The compression set values depend on many factors, including the curative level, the accelerator type and level, the plasticizer level, the black level, the scorch retarder level, and the grade of AEM that is used. The compounds can be designed so as to meet a specification of less than 25% (1 week at 150°C).

Compression set is a test run in air, but most seals and gaskets made from AEM compounds are exposed to fluids in the end use. Fluid aging is also a very important test, but the samples are not compressed as they will be in the end-use application. In order to overcome some of these testing issues the compressive stress relaxation (CSR) test was developed and is used to predict end-use performance for seals and gaskets.^{17, 18} Many different CSR test procedures have been used with more and more of the testing being done with Dyneon (modified Wykeham Farrance) fixtures.

AEM compounds generally perform well in CSR testing in engine oil or in ATF. Some results of CSR with AEM compounds in the Dyneon fixtures are shown below. The test fluid was Service Fluid 105 and the testing was stopped after six weeks at 150°C. Compounds of Vamac can retain above 60% of their initial sealing forces in these fluids when properly formulated.



Figure 5: Compression Set Retention in SF 105

# **Damping Properties**

AEM compounds are used to make torsional vibration dampers. It is very difficult to use laboratory data to predict how a finished part will perform in the end use. AEM compounds are specified because they have the required fluid resistance and more importantly because they can meet the high and low temperature requirements. They also have relatively constant damping properties over a wide temperature range, which is important to the part designer.

Dynamic Mechanical Analysis (DMA) tests were run on a "standard" compound made from Vamac Ultra IP with no plasticizer, at a frequency of 1 Hz and 10 Hz over a temperature scan of -100°C up to +150°C. The data in Figure 6 indicate that the tan delta is relatively flat from 10°C to 150°C at 1 Hz and 10 Hz. The low-temperature performance can be improved by using Vamac Ultra LT and/or by adding 10 to 20 phr of plasticizer. The value of the tan delta can be changed by modifying the formulation.



Tan Delta by DMA of Vamac Ultra IP Compound Without Plasticizer @ 1 and 10 Hz, Temp Sweep -100 to +150°C

Figure 6: Tan Delta by DMA

# PROCESSING

## Mixing of AEM Compounds

AEM compounds can be mixed in an internal mixer or on a two-roll mill. Most commercial compounds are mixed with an internal mixer. There are a few key items to consider for mixing AEM compound successfully. These include:

- AEM polymers are relatively low in viscosity compared to many other commercially available elastomers. A typical Mooney viscosity for an AEM polymer measured at 100°C is between 15 to 22 MU (ML (1+4) @100°C).
- The viscosity of the AEM polymers drops quickly with temperature and with shear rate. A graph of viscosity versus shear is shown in Figure 7 for an AEM G compound with no curative.¹⁰ The viscosity change resulting from shear rate may have more effect on the viscosity compared with the change in temperature (Ref. 15, pg. 132).
- Typically the best mixing between an AEM polymer and carbon black occurs at high viscosity (Ref. 15, pg. 105).
- In order to minimize scorch problems, the diamine cure system used for AEM terpolymers should not be exposed to temperatures above 100°C in the mixing step.
- A good release package is needed for a low viscosity compound with relatively high plasticizer levels.



Figure 7: Viscosity vs. Shear Rate - AEM G Compound Without Curative

Guidelines for compound mixing of AEM terpolymer include:

- Upside-down mixing procedure, where the filler and the release package are added prior to the polymer.
- Ample cooling on the mixer to keep the temperature low (and viscosity high).
- Low mixer RPM to minimize the shear rate (and maximize viscosity), which in turn slows down the rate at which the temperature increases.
- Dump temperature of 100°C check that the actual compound temperature is not too high. If the compound temperature is high there will be scorch problems, and one way to correct that problem is to lower the dump temperature.

The combination of good cooling and a low RPM for the mixer will lead to a longer batch time. However a good quality mix will save much time in downstream processing (i.e. extrusion, injection molding, etc).

High viscosity compounds can be mixed in two passes. The dump temperature of the first pass can be as high as 135°C. The curatives are added in the second pass, where the dump temperature should be kept below 100°C.

# Extrusion

AEM compounds can be extruded at high speed to make hoses with a good surface quality. There are a few key items to keep in mind when extruding AEM compounds and these include:

 Use a general-purpose rubber screw. Screws such as a mixing screw, a vented screw or a barrier screw should not be used because they have high shear regions that can lead to a sharp increase in temperature, and this can cause scorch problems. The diamine cure system is relatively stable at temperatures below 100°C, but it is scorchy at temperatures above 100°C. The localized temperature in a high shear region will be significantly higher than in a low shear region.

- The L/D for the screw can have a wide range and can vary from 10/1 up to 20/1. The important factor is that the temperature needs to be kept low.
- The temperature setting for the extruder should be set based on the overall process parameters. A lower temperature setting will minimize scorch problems, and it will also increase green strength (because of the higher viscosity). A higher temperature will help adhesion between layers of a hose – for example between a tube and cover. A typical temperature profile would have a temperature that ranged from 50°C to 80°C.

Hoses are typically mandrel-cured in a steam autoclave for 20 to 30 minutes at 170°C or higher. A pressurized cure system is needed to prevent blister formation, so hot air cure systems are not recommended. Some hoses are pan cured, and the compounds typically have a higher viscosity so as to minimize flat spotting. The terpolymer cure system uses a postcure to get optimum compression set properties. For some hose applications a postcure step is not needed with terpolymer compounds because the compression set requirements are less than that needed for seals and gaskets.

Fiber reinforcement is used in hoses to improve the pressure rating of the hose. Most AEM hoses are used where good high temperature properties are needed, which limits the type of fiber that can be used. Peroxide-cured compounds can use either polyester or aramid fibers, with aramid fibers being used when higher temperature performance is required. Diamine-cured compounds cannot use polyester fibers because the cure system degrades the polyester fiber, so aramid fibers are used with these compounds.

## Molding

AEM compounds are molded for many applications such as seals, gaskets, dampers, etc. Injection molding is the most common molding process, but compression molding and transfer molding are also used. Most AEM compounds have a relatively low viscosity, and this helps them to be easily injection molded. Some large size air ducts are also injection molded.

Typical injection molding conditions for AEM terpolymers are from 1 to 3 minutes at a temperature of 170°C to 190°C. The part is then postcured to ensure good compression set properties. Typical postcure conditions are 4 hours at 175°C. The molding time for compression molding is longer than for injection molding, with the time ranging from 2 to 5 minutes, and it is also followed by a postcure step.

Mold fouling can be a problem with some AEM terpolymer compounds. Several steps are recommended to minimize fouling problems.⁴ These include:

- Good internal release package
- Proper application of external mold release
- Proper material of construction for mold
- Avoiding high temperatures

A dipolymer compound requires a peroxide cure, is typically injection molded for about 2 to 4 minutes at 190°C, and may not require postcuring if the properties are developed to meet the specification. The slightly longer molding time and the higher temperature will help ensure that the part has good compression set properties.

	"Standard" Vamac G + 10 phr plasticizer	Vamac GXF (Extra Flexible Compared to G)	AEM HT (Excellent Flex and Improved Heat Resistance)	Vamac DP Peroxide- Cured
Ingredients	phr	phr	phr	phr
Vamac G	100.0			
Vamac GXF		100.0		
AEM HT*			100.0	
Vamac DP				100.0
N550 Carbon Black	56.0	55.0	52.0	55.0
TP-759 Plasticizer	10.0	5.0		
Stearic Acid	1.5	1.0	1.0	1.0
VANFRE VAM	1.0	1.0	1.0	0.5
Octadecyl Amine	0.5			
VANOX CDPA	2.0	2.0	2.0	1.0
Diak [™] No.1	1.2	1.2	1.0	
DBU Accelerator	2.0	1.0	1.0	
DPG		2.0	2.0	
VAROX 802-40C				5.0
Sartomer SR 350				3.0
Totals	174.2	168.2	160.0	165.5
<i>Mooney Viscosity</i> M _L (1+4) @ 100°C	41	47	73	46
Mooney Scorch, MS @ 121° Minimum Viscosity	C 13	17	26	16
Minutes to 3 pt. rise	6.5	7.0	9.4	21.5
Minutes to 5 pt. rise Minutes to 10 pt. rise	8.4 12.2	9.5 14.3	13.1 19.5	22.5 25.2

 Table 3: 70 Shore A Duro Hose Starting Point Formulations

MDR @ 177°C, 0.5° arc, 20 min.						
M _L (dN•m)	0.4	0.5	0.8	0.7		
M _н (dN•m)	14.0	8.1	8.8	13.6		
ts 2 (min)	1.0	1.2	1.4	1.4		
ť 50 (min)	2.5	2.1	2.6	2.9		
ť 90 (min)	8.7	9.6	9.3	6.6		
Original Physicals						
Press Cured, °C	5 min. @ 175	5 min. @ 175	5 min. @ 175	15 min. @ 180		
Postcured, °C	4 hrs. @ 175	4 hrs. @ 175	4 hrs. @ 175	None		
Hardness, Shore A	70	68	70	73		
50% Modulus, MPa	2.2	1.8	1.9	2.5		
100% Modulus	5.1	3.7	3.5	5.5		
200% Modulus	10.4	8.8	8.6	12.3		
Tensile, MPa	13.6	15.0	17.1	15.8		
Elongation, %	332	436	513	288		
Tear, Die C, kN/mm	36	41	41	31		
Compression Set, Method B,	168 hrs. @ 15	0°C				
%	24	46	42	34		
DeMattia Flex Test						
Relative Ranking	Good	Very Good	Excellent	Fair to Good		
* Developmental Polymer						

# Table 3: 70 Shore A Duro Hose Starting Point Formulations (continued)

Table 4: Seal and Gasket Starting Point Formulations

	"Standard" Vamac G + 10 phr plasticizer	Vamac GLS for Improved Fluid Resistance	Vamac Ultra IP for Injection Molding	Vamac DP Peroxide- Cured
Ingredients	phr	phr	phr	phr
Vamac G	100.0			
Vamac GLS		100.0		
Vamac Ultra IP			100.0	
Vamac DP				100.0
N550 Carbon Black	56.0	53.0	32.0	55.0
TP-759 Plasticizer	10.0	10.0	3.0	
Stearic Acid	1.5	1.5	1.5	1.0
VANFRE VAM	1.0	1.0	1.0	0.5
Octadecyl Amine	0.5	0.5	0.5	
VANOX CDPA	2.0	2.0	2.0	1.0
Diak No.1	1.2	1.3	1.0	
DBU Accelerator	2.0	2.0	1.0	
DPG			2.0	
VAROX 802-40C				5.0
VANAX MBM				2.0
Totals	174.2	171.3	144.0	164.5

Mooney Viscosity	41	39	45	50
Mooney Scorch MS @ 12	21°C			
Minimum Viscosity	13	12	17	16
Minutes to 3 pt_rise	6.5	57	9.9	-
Minutes to 5 pt. rise	8.4	7.2	-	-
Minutes to 10 pt. rise	12.2	9.65	16.5	-
MDR @ 177°C. 0.5° arc.	20 min.			
M ₁ (dN•m)	0.4	0.4	0.4	0.7
М _н (dN•m)	14.0	13.4	8.1	14.9
ts 2 (min)	1.0	1.0	1.3	0.6
ť 50 (min)	2.5	2.3	1.9	1.2
ť 90 (min)	8.7	9.7	7.5	4.4
Original Physicals				
Press Cured, °C	5 min. @ 175	5 min. @ 175	5 min. @ 175	15 min. @ 180
Press Cured, °C Postcured, °C	5 min. @ 175 4 hrs. @ 175	5 min. @ 175 4 hrs. @ 175	5 min. @ 175 4 hrs. @ 175	15 min. @ 180 None
Press Cured, °C Postcured, °C Hardness, Shore A	5 min. @ 175 4 hrs. @ 175 70	5 min. @ 175 4 hrs. @ 175 69	5 min. @ 175 4 hrs. @ 175 54	15 min. @ 180 None 72
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa	5 min. @ 175 4 hrs. @ 175 70 2.2	5 min. @ 175 4 hrs. @ 175 69 2.1	5 min. @ 175 4 hrs. @ 175 54 1.1	15 min. @ 180 None 72 2.3
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9	15 min. @ 180 None 72 2.3 6.0
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3	15 min. @ 180 None 72 2.3 6.0 14.5
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9	15 min. @ 180 None 72 2.3 6.0 14.5 15.2
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa Elongation, %	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6 332	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4 330	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9 543	15 min. @ 180 None 72 2.3 6.0 14.5 15.2 212
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa Elongation, % Tear, Die C, kN/mm	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6 332 36	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4 330 35	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9 543 33	15 min. @ 180 None 72 2.3 6.0 14.5 15.2 212 28
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa Elongation, % Tear, Die C, kN/mm Compression Set, Method	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6 332 36	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4 330 35	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9 543 33	15 min. @ 180 None 72 2.3 6.0 14.5 15.2 212 28
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa Elongation, % Tear, Die C, kN/mm Compression Set, Methoo 168 hrs. @ 150°C, %	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6 332 36 7 B 24	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4 330 35 25	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9 543 33 24	15 min. @ 180 None 72 2.3 6.0 14.5 15.2 212 28 18
Press Cured, °C Postcured, °C Hardness, Shore A 50% Modulus, MPa 100% Modulus 200% Modulus Tensile, MPa Elongation, % Tear, Die C, kN/mm Compression Set, Method 168 hrs. @ 150°C, %	5 min. @ 175 4 hrs. @ 175 70 2.2 5.1 10.4 13.6 332 36 7 B 24 <i>g</i> ) by DSC	5 min. @ 175 4 hrs. @ 175 69 2.1 4.6 10.2 14.4 330 35 25	5 min. @ 175 4 hrs. @ 175 54 1.1 1.9 5.3 18.9 543 33 24	15 min. @ 180 None 72 2.3 6.0 14.5 15.2 212 28 18

## Table 4: Seal and Gasket Starting Point Formulations (continued)

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#### SILICONE ELASTOMERS

## by Joseph C. Caprino* and Theodore D. Johnson**

*Consultant-Silicone Rubber Schenectady, NY

**Wacker Chemical Corporation Adrian, MI

Since the first patent application in 1944, silicone rubber has become a very well recognized specialty elastomer with worldwide sales of well over 100 million pounds. The original two suppliers, General Electric and Dow Corning, have been joined by other domestic and foreign producers, and it is now manufactured worldwide.

The increased use reflects the development of many new applications for this very versatile material. The unique properties of silicone rubber over a wide temperature range (-65 to 315°C) were recognized at an early date. However, engineers have discovered many other properties which are significant in today's people-oriented, safety- and environmentally-conscious world.

Two broad classifications of compounds are available: heat-cured rubber (HCR) products, which are vulcanized by exposure to heat, and room temperature vulcanizing (RTV) materials. Both types offer the same fundamental properties.

## Chemistry

The special properties of silicone polymers result from their molecular structure. They are unique in combining some of the features of silica, silicate minerals and organic compounds. The basic difference between silicone and organic polymers is shown by the following structures:

Organic Polymer (Natural Rubber)



Organic polymers have a backbone of carbon-to-carbon atoms; the silicone backbone is composed of alternating silicon-oxygen linkages. This chemical bond is found in other high-temperature materials, such as quartz, glass, and sand. These familiar products share silicone's immunity to the deteriorating effects of ozone, corona, weathering, and other forces. However, organic side-chains attached to the silicon atoms (such as the methyl groups, CH₃, shown in the above structure) incorporate a flexibility unmatched by most materials. This inherent flexibility permits the design of compounds without the use of liquid plasticizers.

Many organic polymers contain some degree of unsaturation where carbon atoms are joined together by double bonds. These sites are susceptible to attack by ozone, which is encountered in service, in electrical fields or at high altitudes. The silicone chain contains no double bonds; it is extremely resistant to ozone even in high concentrations and over long periods of time.

The silicone molecules are tailored by the chemist to achieve specific properties. The methyl groups are fundamental to this process. By replacing small quantities of these methyl groups with phenyls and/or vinyls, significant variations in properties can be achieved.

The addition of phenyl groups improves low temperature flexibility and resistance to gamma radiation. Vinyl side-chains improve vulcanization characteristics and the compression set resistance of the cured rubber. While a double bond represents a potential area of ozone attack in organic rubber, the vinyl side-chains in silicone rubber become saturated during vulcanization, so that ozone resistance is retained.

The American Society for Testing and Materials, in ASTM Designation D 1418-01a, has established the following classification and codes for silicone polymers:

MQ = Methyl Silicone VMQ = Methyl-Vinyl Silicone PMQ = Methyl-Phenyl Silicone PVMQ = Methyl-Phenyl-Vinyl Silicone FVMQ = Fluoro-Vinyl-Methyl Silicone

Room temperature vulcanizing silicone rubber compounds are based on polymers with similar molecular structures. The chains are usually terminated by silanol groups, which tend to be relatively unstable, or by hydrolyzable groups which react with moisture in the air and contribute to the vulcanization of the rubber via a condensation reaction. Two-part RTV compounds may also be cured by a platinum-catalyzed reaction, which is discussed later in this chapter.

The molecular weights of the basic RTV polymers are lower than those used in heat-cured rubbers (10,000-100,000 vs. 500,000-1,000,000). Some RTV compounds are relatively free-flowing liquids.

#### Manufacture

Silicone polymers or gums are produced by a complex series of chemical reactions, starting from sand and alkyl or aryl halides.

The sand or quartz is first reduced to elemental silicon by heating it with carbon in an electric furnace:

 $SiO_2$  + 2C  $\longrightarrow$  Si + 2CO

The transformation of silicon into silicone can be done in several ways. The most widely used procedure, designated the "direct process", was developed by Dr. Eugene G. Rochow at the General Electric Research Laboratory. In this operation, silicon and copper powder are heated in a tube with methyl chloride gas passing through it. A mixture of methylchlorosilanes is produced.

2 CH₂Cl + Si 
$$\longrightarrow$$
 Mixture of methylchlorosilanes

The predominant ingredients are:

 $(CH_3)_3$  SiCl - Trimethylchlorosilane  $(CH_3)_2$  SiCl₂ - Dimethyldichlorosilane  $CH_3$  SiCl₃ - Methyltrichlorosilane

Dimethyldichlorosilane is the basic intermediate in the manufacture of dimethyl silicone gum. It is separated from the other components by the process of fractional distillation. The silane is subsequently hydrolyzed to form silanol-stopped siloxanes, which are converted into dimethyl gums by condensation polymerization under carefully controlled conditions. More commonly, cyclic dimethyl siloxanes can be produced and converted to high molecular weight gums by a ring-opening, base-catalyzed reaction.

 $\begin{array}{rcl} & & Hydrolysis \ Reaction \\ (CH_{_3})_2 \ SiCl_2 \ + \ 2 \ H_2O & \longrightarrow & (CH_{_3})_2 \ Si(OH)_2 \ + \ 2 \ HCl \\ & & Condensation \ Polymerization \ Reactions \\ n \ (CH_{_3})_2 \ Si(OH)_2 \ \longrightarrow & -[-CH_{_3})_2 \ SiO \ -]-_n \ + \ H_2O, \ or \\ & & base \\ [ \ (CH_{_3})_2 \ SiO]_x \ & \longrightarrow & -[-CH_{_3})_2 \ SiO \ -]-_n \end{array}$ 

Manufacturing processes must be closely monitored in order to obtain the almost 100% purity required to make very high molecular weight polymers.

To introduce phenyl or vinyl constituents into the polymer, small quantities of phenyl and/or vinyl intermediates are copolymerized with the dimethyl intermediates (Figure 1).



Figure 1: Flow Chart for Silicone Rubber Manufacture

## Properties of Silicone Elastomers

Fabricated silicone rubber exhibits thermosetting characteristics, whether vulcanized with organic peroxides or platinum at elevated temperatures, or at room temperature by RTV technology. It will not soften when subsequently exposed to elevated temperatures. If used as an electrical insulation, it will not soften, melt or drip under conductor overload conditions.

The realities of the marketplace mean that silicones fall into the category of specialty elastomers – products that are frequently selected because of a unique property desired in a specific application. However, experience has shown that silicones can compete with other materials in more routine applications. Product re-design, and longer service life with less need for product maintenance and repair, frequently make silicone rubber more cost-effective than competitive materials.

In discussing the following specific properties, it should be noted that certain qualities are generic to all silicones, while others derive from the expertise of the rubber chemist and will vary from one compound to another. Consultation with the silicone supplier is recommended.

High Temperature Stability – The inherent heat resistance of silicone rubber is well-known. Specific compounds will offer useful service life at temperatures up to 315°C. Actual service life at a given temperature will vary with such application requirements as continuing flexibility, shrinkage restrictions, etc.

Using Arrhenius aging techniques, service life spans of 40 years and more at 90°C have been estimated, where only moderate flexibility is required. As a general rule, if heat is the only criterion, silicone rubber will last longer than most other elastomers at any temperature up to 315°C. It should also be noted that, if tensile strength measurements are performed at elevated temperatures, silicone rubber frequently surpasses other elastomers in this characteristic.

*Flexibility* –All silicone rubber compounds are very flexible at room temperature and, under repeated flexing, will demonstrate excellent resistance to flexing fracture. MQ and VMQ silicones maintain flexibility at temperatures as low as -55°C; phenyl-containing polymers (PMQ and PVMQ) can yield compounds that are flexible at -100°C. These same products maintain normal stability at elevated temperatures.

*Combustion* – The silicon-oxygen backbone results in a polymer with a lower carbon content than organic polymers. In combination with the predominant use of inorganic fillers, the result is that silicone compounds contain a lower level of combustible components, and generate less smoke than most organic counterparts.

Conventional silicones have been classified as slow-burning. Their combustion products consist predominantly of silicon dioxide, oxides of carbon, and water vapor. Additive, flame-retardant technology has been developed which is available in specific compounds. Silicone rubber has a unique advantage over organic materials in that flame-retardance does not usually involve the use of halogens such as chlorine, bromine or fluorine, either in the molecule or as a flame-retardant additive. Consequently, corrosive or toxic products containing these halogens are usually not evolved during combustion. The amount of smoke generated during combustion has been found to be greater than that emitted by Teflon[®] or Kapton[®], but significantly less than that given off by most organic elastomers.

*Electricals* – Good elastomeric insulation typically provides high resistivity and dielectric strength. The power factor and dielectric constant are low, but their variation according to frequency has limited their use in coaxial cables. Ozone and corona resistance are excellent. The silicon dioxide ash formed during combustion displays insulating qualities that enable conductors insulated with silicone rubber to maintain the integrity of electrical circuits even under very severe fire conditions. Electrically conductive compounds are available for the design of non-metallic conductors, shielding and similar products.

*Physical Strength* – Stress-strain properties vary with composition. As a general rule, silicones offer less resistance to tear and abrasion than organic compounds.

*Compression Set* – Silicone rubber is superior to other available elastomers in its resistance to compression set.

*Biocompatibility* – Compounds containing only additives and fillers that comply with the Food and Drug Administration's regulations are biocompatible. They

are resistant to bodily fluids and cause no significant tissue reaction. Specific materials must be tested for compatibility with tissues prior to use.

*Fungus* – Properly cured silicone rubber will neither kill nor support the growth of fungus. Most compounds do not contain fungicides, nor do they provide any nutritional support.

Radiation Resistance – Radiation introduces additional crosslinks, causing increased durometer and reduced elongation. The ultimate mode of failure is embrittlement. The maximum service dosage level that can be tolerated will vary according to the flexibility requirements of the application. Silicone compounds have been rated as performing satisfactorily at dosage levels of  $5 \times 10^7$  to  $2 \times 10^8$  rads. Increasing the phenyl concentration in the base polymer has been shown to improve radiation resistance.

Vibration Damping – The ability of silicone rubber to absorb energy over a wide range of frequency and temperature, as well as its virtually constant loss angle from -50 to 65°C, makes it ideal for use in vibration control devices. This property of silicone rubber allows it to perform in a more consistent and predictable manner over a much wider temperature range than other polymers.

*Weathering* – Silicone rubber provides resistance to the deteriorating effects of sunlight, ozone, oxygen, moisture, and other environmental factors. Long term stability is superior to that of most other elastomers.

*Thermal Ablative* – Silicone rubber may withstand temperatures of up to 5000°C for a brief period. During exposure, a surface char is formed, while the underlying portion, insulated from the heat by the char, can remain elastomeric. Some advanced compounds can form a hard ceramic material that acts as emergency electrical insulation for up to two hours in a fire at temperatures as great as 1100°C, maintaining the utility of vital electrical equipment. UL 2196 is the applicable standard

Release – Surface characteristics serve to prevent the adhesion of sticky materials. This property is used in the manufacture of silicone rubber-coated rollers, which are used to process such products as hot polyethylene and adhesives.

*Permeability* – Permeability to gases is greater than that exhibited by other polymers. However, while being permeable to water vapor, liquid water absorption is very low with proper filler selection.

*Vacuum* – Silicone rubber, when properly compounded and processed, will exhibit very low outgassing when measured at 100  $\mu$ Pa and 125°C.

## Compounding

Silicone rubber compounds can contain as few as three ingredients: a gum, a reinforcing filler and a vulcanizing agent – and still be processed into products with desirable properties. The silicone polymer possesses inherent flexibility, oxidative stability and the ability to vulcanize rapidly. Consequently, there is no

necessity for the plasticizers, antioxidants, and cure accelerators frequently used in organic rubber formulations. However, increasingly advanced technology has resulted in more complex recipes, with emphasis on specific improvements in processing and performance characteristics.

#### Gums and Reinforced Gums or Bases

Methyl and methylphenyl gums were used as the base for compounds in the early days of the industry. While these gums are still available and used in certain applications, today's compounders rely heavily on polymers modified by the incorporation of small concentrations of vinyl groups. These reactive sites permit the more efficient use of curing agents, enabling an appreciable reduction in catalyst levels. In addition, it is possible to use vinyl-specific, higher activation temperature catalysts, such as dicumyl peroxide (VAROX® DCP) and 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (VAROX DBPH). These catalysts decompose without forming significant quantities of acidic by-products. Consequently, "no postcure" compounds have become feasible, and the need for oven baking to optimize properties has become less important. Improvements in compression set, resistance to reversion and insulation resistance have also resulted.

Fabricators desiring to do their own mixing can start with the pure gum. However, a more widely used, more convenient approach is represented by reinforced gums or gum bases. These products are combinations of a polymer, a reinforcing filler and processing aids or other additives. By proper reinforced gum selection, compounds can be produced to satisfy specific fabrication or performance targets.

The domestic suppliers of silicone gums and reinforced gums are Dow Corning, GE Silicones, Shincor Silicones, Inc., and Wacker Chemical Corporation.

#### Fillers

Very fine particle sized fumed silica and precipitated silica are the major reinforcing fillers used to develop tensile and tear strength. Carbon blacks are generally avoided for reinforcement because of their tendency to degrade peroxide catalysts. Fumed silica contributes to the excellent electrical characteristics of silicone rubber.

Semi-reinforcing fillers – ground quartz, calcium carbonate, diatomaceous earth, metallic oxides, etc. – impart only moderate strength but offer other advantages, such as improved processing and performance characteristics, or reductions in cost.

Acetylene carbon blacks and metals such as silver are used to produce electrically conductive compounds.

#### Curing Agents

Silicone rubber can be vulcanized with heat with a peroxide cure or a platinum cure. In the case of compounds based on RTV polymers, at room temperature via a condensation cure or with a platinum cure.

### **Thermal Vulcanization**

#### Organic Peroxide

Heat-activated organic peroxides form crosslinks by reaction with the vinyl or methyl groups. One proposed mechanism is shown in Figure 2. The by-products of this type of cure depend on the curing agent used, and are mostly acidic in nature.



R denotes alkyl group on peroxide

denotes a free radical

## Figure 2: Polyaddition Reaction Initiated by a Radical (Peroxide Cure)

Variations in the rate and method of curing can be obtained by varying the type and amount of catalysts. The selection of the curing agent is generally determined by the forming process required for the fabrication of the part, i.e. compression, transfer or injection molding, extrusion, calendering, etc. Typical peroxides used in thermal vulcanization are listed in Table 1.

Peroxide	VAROX	Recommended Use	Cure Temperature, °C
2,4-dichlorobenzoyl	DCBP-50	Hot air vulcanization	90-125
benzoyl peroxide	ANS	Molding, Steam cure	120-140
dicumyl peroxide	DCP	Thick sections	160-175
2,5-dimethyl-2,5-di	DBPH	Thick sections, and	165-180
(t-butyperoxy)nexame		Carbon black Stocks	

Table 1: Popular Peroxides Used to Crosslink Silicone Rubber

Peroxides are available in many forms, ranging from solids and liquids with 100% concentrations of active ingredients to powders, paste and polymer master batches with lower concentrations of the crosslinking agent. Care in weighing and mixing is essential to ensure proper dispersion, because the quantities of

peroxides used in most formulations are small. Safety considerations should also be kept in mind when storing and working with these materials. Information with regard to the selection and concentration of peroxides, as well as details on their safe handling and use, can be obtained from suppliers.

## Platinum Cure

Another method of curing certain types of silicone rubber containing vinyl units is through an addition cure which gives off no by-products, since the components merely combine under the influence of a catalyst such as platinum. The mechanism is shown in Figure 3.



Figure 3: Polyaddition Cure Initiated by a Platinum Catalyst

Note that a crosslinking molecule (H - Si containing group) is necessary to bridge the polymer chains. This reaction occurs at room temperature, so an inhibitor is usually employed.

# Room Temperature Vulcanization

Vulcanization of the RTV family of silicone rubber compounds can result from either a condensation or an addition reaction.

A condensation reaction requires the presence of a crosslinker such as ethyl silicate, and a metallic salt catalyst such as stannous octoate. One postulated vulcanization process is as follows:



In one-component RTV silicone rubber, the crosslinker is a hydrolyzable material like methyltriacetoxy silane. Atmospheric moisture is essential to induce rubberlike properties.

#### Additives

While essential ingredients are few in number, actual formulations are relatively complex due to the use of additives to enhance specific processing or performance properties.

Low molecular weight silicone fluids retard the development of structure, or nerve, in uncured rubber, thereby extending its workable life between the milling and forming operations. These process aids are normally incorporated in the reinforced gum masterbatches, and are available from silicone suppliers.

Low molecular weight phenyl silicone fluids are added to many compounds to produce a self-lubricating effect. The fluid's solubility in the polymer is such that after curing, the fluid will become incompatible enough to bleed and form a film on the surface of the molded article. These compounds are useful in automotive electrical connectors, where they provide the necessary lubrication to enable wires to be easily inserted though the holes in the grommets.

Inorganic pigments are used to color silicone rubber. Masterbatches in silicone oil or gum are usually cleaner to work with and easier to disperse.

Minute quantities of specific non-halogenic ingredients will improve resistance to flame propagation. Hydrated aluminum oxide is also used for this purpose. At high temperatures, the material is dehydrated and three equivalents of water are evolved.

$$AI_2O_3 \cdot 3H_2O \xrightarrow{H\Delta} AI_2O_3 + 3H_2O \uparrow$$

Inherent high temperature stability is further increased by adding specific oxides and octoates. One example is presented in Table 2.

Ingredients	phr	phr
ELASTOSIL® R401/40	100.0	100.0
ELASTOSIL HTM-3		1.5
VAROX DBPH-50	1.0	1.0
Totals	101.0	102.5
Original Physicals Hardness, Shore A	36	37
100% Modulus, MPa	0.6	0.6
Iensile, MPa	9.4 740	9.3
Physical Properties After Heat Aging to ASTM D 573, 70 hrs. @ 225°C	740	705
Hardness, Shore A	31	35
Tensile MPa	0.5 4 Q	0.5
Elongation, %	606	767
Physical Properties After Heat Aging to ASTM D 573, 70 hrs. @ 275°C		
Hardness, Shore A	84	30
100% Modulus, MPa		0.5
Tensile, MPa	1.7	3.6
Elongation, %	1.7	639

Table 2: Improved Resistance to Heat Aging with Heat Resistance Additive

Additives are available that improve resistance to reversion, either during processing or in service.

Physical and electrical properties, bondability, sponging and other characteristics are all influenced by additive technology.

## **Commercial Compounds**

Most manufacturers prefer to purchase silicones in the form of compounds instead of mixing their own formulations. Several variations in finished compounds are available:

- Uncatalyzed products, which give the manufacturers maximum flexibility in the selection of a curing agent that conforms to the processing equipment and products. Manufacturers must add their own peroxide, usually on a rubber mill, prior to fabrication.
- 2. Catalyzed compounds with a relatively short working life which must be milled as the initial production step to obtain a uniform processable viscosity.
- Catalyzed compounds which are specially formulated to enable the fabrication of finished products without the preliminary milling operation. The wire and cable industry in particular has adopted this approach because of its preference for coil-form or pelletized products ready for direct-feed into extruders.
- 4. In recent years Liquid Silicone Rubber (LSR) products have become

available, which produce silicone rubber with similar properties to the solid types, but can be pumped into molds. Their use will depend mostly on the economics of the application. Small precision parts with production cycles as short as 15 seconds are easily manufactured with the proper tools, pumps and presses. These parts may have little or no flash, due to the low injection pressure and the process precision that is possible with recently developed presses.

A wide range of compounds is available to meet the demands and specifications of industry. Table 3 indicates the spread in the typical values of key properties offered by standard compounds, grouped on the basis of significant property or application. Silicone suppliers can recommend products for specific applications, or to meet given specifications.

	Range of		% C/S	Tempera	ture, °C	
Class	Duro, Shore A	Tensile, MPa	Elongation, %	22 hrs. @ 150°C	Min.	Max.*
General Purpose	30-80	4.83-6.90	100-400	15-50	-50	260
Low Comp. Set	50-80	3.45-6.90	80-400	10-15	-50	260
Extreme Low Temp.	25-80	5.52-10.34	150-600	20-50	-100	260
Extreme High Temp.	40-80	4.83-7.58	200-500	10-40	-50	315
High Strength	30-70	5.52-10.34	300-1000	20-40	-50	260
Coating Pastes	_	—	—	—	-50/-100	315
Wire & Cable	50-80	4.14-10.34	100-500	20-50	-50/-100	260
Food & Health	25-75	5.52-9.65	300-700	20-40	50/-100	—
Fuel Resistant	25-80	4.83-9.65	200-600	15-35	-100	200

#### Table 3: Properties of Classes of Silicone Elastomers

* Performance requirements and the desired service life can cause major variations in these values.

#### Processing

*Mixing* – Mills, dough mixers, Banburys and similar conventional rubber equipment may be used.

Open roll mills should be water-cooled and have friction ratios of 1.2:1 to 1.4:1. Whereas organic rubber will work on the slower roll, silicone rubber will usually transfer to the faster roll during milling. Since uncured silicone has less cohesive strength than most organic rubber compounds, the fast roll of the mill is frequently equipped with a doctor or scraper blade to simplify removal of the stock.

The use of internal mixers enables the production of larger, more uniform batches, with concurrent savings in power and manufacturing costs.

The temperature of the batch should be carefully monitored during the addition of curing agents which can be activated by heat. Maximum permissible temperatures will vary depending on the selection of the vulcanizing agent.

By allowing the mix to shelf-age for 24 hours or more prior to use, the filler surface is "wetted" by the polymer and improvements are obtained in batch-tobatch uniformity.

Special precautions which should be taken during the compounding of silicone rubber include: using care in working with fine particle-size silicas (minimizing skin contact, avoiding inhalation, etc.), following the manufacturer's instructions for the handling of peroxides, and cleaning to prevent contamination by organic materials which either may be present in the environment or may have not been completely removed from the equipment.

*Freshening* – This term is used to describe the reworking and softening of a compound before catalyzing or other processing, the purpose of which is to optimize processing qualities. Freshening is usually done on a rubber mill. Compounds with low green strength and weak cohesion generally require a wide setting of the mill rolls with a gradual tightening or reduction of the space between the rolls; higher green strength silicone rubber is usually given initial passes through tight roll settings, with subsequent gradual separation of the rolls. Inadequate freshening will result in flow lines during molding or surface roughness during extrusion. Excessive freshening can cause increased tackiness and loss of green strength.

*Molding* – Both compression and transfer molding techniques are employed at temperatures ranging from 115 to 200°C and pressures of 5.5 to 10.3 MPa (800 to 1500 psi). Injection molding requires temperatures of 170 to 235°C and pressures between 69 and 82.7 MPa (10,000 and 12,000 psi). Each molding technique has its particular advantage. Compression molding is the simplest and most flexible, and is therefore widely used; transfer molding is suitable for complicated parts and multi-cavity, high volume molding; injection molding requires very short cure cycles and offers uniformly excellent properties and adaptability to high volume production.

Steel, bronze, brass and aluminum can be used in making compression molds. Where a high finish is desired, chrome plate is recommended. In transfer and injection molding, chrome-plated steel is desirable. Gates for both transfer and injection molding should be at least 25% larger in area than those normally used with organic rubbers. If it is necessary to use a mold release agent during fabrication, a 0.5% water solution of DARVAN[®] WAQ can be applied using a spraying technique. The silicone mold release agents that are widely used in the manufacture of organic rubber parts react with silicone rubber, and are therefore unsuitable for use when molding it.

Standard rubber industry methods may be used to finish parts. Whereas dry ice tumbling is used to remove trim for organics, the extreme low temperature capability of silicones requires the use of liquid nitrogen in the tumbling operation.

*Extrusion* – Standard rubber equipment may be employed to extrude silicone compounds. Screws with compression ratios ranging from 1:1 to 4:1 have

been used successfully. Length/diameter ratios of 12:1 to 16:1 work well. The incorporation of a positive pressure feeding roller in the throat of the extruder will give more steady throughput and help maintain uniform diameter. Stainless steel screens are desirable to produce back pressure and remove contaminating particles. A 1:1 ratio of die orifice to land is typical for wire constructions, with the orifice conforming to the desired insulated wire diameter. Drawdown is usually avoided. Cooling water is used to control frictional heat build-up and consequent compound scorching.

Extrusion is useful in the manufacture of rods, channels, tubing, wire and other continuous shapes. It is also used to prepare "preforms" for molding operations. Extruded parts are normally in-line vulcanized by short exposures to saturated steam, hot air, or heated fluidized beds immediately following the extrusion process. Low green strength, with the resultant ease of deformation, precludes taking up unvulcanized silicone rubber on a reel for vulcanization in an off-line radiation curing system.

When it is desirable or necessary to cure extrusions with hot air, the most common peroxide used is VAROX DCBP-50. This substance will leave an acid residue that can bloom. Compounds cured in this manner will tend to have an excessive compression set. Extrusions will usually receive an oven postcure to dissipate the residue. ELASTOSIL Stabilizer R is an additive which, when added to these compounds, can eliminate the need for postcure. It gives lower compression sets and often eliminates bloom.

Ingredients (phr)	Α	В	С	D
ELASTOSIL R401/40	100.0	100.0	100.0	100.0
Min-U-Sil [®] 10 Micron		100.0		100.0
ELASTOSIL Stabilizer R			1.5	1.5
VAROX DCBP-50 Paste	1.5	1.5	1.5	1.5
Totals	101.5	201.5	103.0	203.0
Original Physicals; Press Cured 5 min. @ 116°C, No Postcure				
Hardness, Shore A	41	66	41	66
100% Modulus, MPa	0.8	3.3	0.9	3.1
Tensile, MPa	8.5	6.1	8.5	6.1
Elongation, %	540	235	550	300
Compression Set, to ASTM D 395 Method B				
22 hrs. @ 177°C, %	63	69	35	36

Table 4: Compression Set in Non-Postcured Extrusion Compounds

In Compounds A and B shown in Table 4, the silicone rubber base is merely catalyzed with acid peroxide, or has an extending filler added to it along with the peroxide. The addition of ELASTOSIL Stabilizer R is shown in Compounds C and D. The result is that, even without an oven postcure, the compounds containing ELASTOSIL Stabilizer R have substantially lower compression set. Often the presence of the extending filler will eliminate bloom, but the addition of ELASTOSIL Stabilizer R will eliminate bloom without the filler.

*Calendering* – Silicone rubber can be handled on production calenders with no greater difficulty than that encountered with other rubber materials. To control the amount of work (energy) put into a compound, it is best to under-freshen during the initial milling, and to rely on the calender to complete the freshening operation. The preference of silicone rubber for the faster or cooler roll should be taken into account when setting up a calender. If an "inverted L" four roll calender is used, for example, where the vertical rolls are all 1.1 times faster than the first roll, sequentially reduced temperatures on the second, third, and fourth rolls will produce proper transfer.

The following temperatures are recommended for the vertical calender rolls: the top roll should be at about 50°C, the middle roll at room temperature, and the bottom roll should be water-cooled. Start-up speeds should be about 30 to 60 cm (1 to 2 feet) per minute, with normal running speeds of 1.5 to 3 meters (5 to 10 feet) per minute. Liners of Holland cloth, polyethylene sheeting, coated paper, etc. may be used. When curing calendered sheet stock in roll form, it is recommended that the thickness of the roll not exceed one foot.

Bonding – The bonding of silicone rubber to another material may be required during the forming process. The surface release characteristic of silicones may present some difficulties here. Specially designed primers and adhesives are frequently used. Self-bonding compounds contain special additives which promote adhesion to many surfaces. One-component RTV silicone rubbers are particularly versatile in obtaining good bonds to various substrates.

Silicone oil in paste catalysts may migrate to the rubber-substrate interface and diminish bond strength in molding operations. High activation temperature, non-acid producing, dry catalysts are recommended for best results.

It is very important that the surface to be bonded be prepared by sand blasting, solvent washing, vapor degreasing, etc. wherever possible. Oven-curing will frequently maximize bond strengths.

Sponge – By adding suitable blowing agents to specially formulated compounds and reinforced gums, it is possible to develop silicone rubber sponge which can be fabricated into sheets, extrusions, or molded parts. Service temperature limits are similar to those of conventional silicone products.

*RTV Compounds* – These room temperature vulcanizing silicones are available in a wide range of viscosities, varying from pourable liquids to thixotropic pastes. They are processable by means of standard sealing, caulking, encapsulating, flow-molding and potting techniques.

#### **Oven Curing**

The vulcanization of organic rubber compounds rarely involves an oven postcure. Oven cures are not required with certain silicone rubber products and applications. However, in many instances such a cure is desirable to optimize the properties of the fabricated parts. Oven-curing eliminates catalyst decomposition products and low molecular weight silicone polymers, with resultant improvements in electrical properties, resistance to compression set and reversion, reduced smoke evolution and outgassing, etc. Aging properties are also stabilized.

The degree of oven cure depends on the desired properties and intended application. As a general rule, the lowest compression set will be achieved using a 24 hour cure at 250°C. For most applications, a cure of one or more hours at  $28^{\circ}C$  (50°F) above the service temperature is effective.

Electric ovens having a minimum circulation rate of 0.5 m³/minute fresh air per kg of rubber, or 1.65 ft³ fresh air/minute/pound of rubber, are recommended. The oven should preferably be arranged for horizontal air flow and contain sufficient baffles to prevent air pockets. A fully loaded oven should be capable of reaching 150°C within two hours of a cold start. The maximum temperature level should be at least 315°C. Indirectly fired gas or oil ovens have also been used.

#### Major Applications

Automotive Industry — The largest growth area for silicone elastomers in the past 10 years has been the automotive industry, both original equipment and replacement parts. Silicone rubber's heat resistance is the chief contributing factor to this growth.

As emission standards for domestic automobiles grew more stringent in recent years, the under-the-hood temperatures also increased many times as a result of the added bulk, attributable to pollution-control devices, in the engine compartment. The demand for more power options by car buyers also added to this heat buildup.

Ignition cables insulated and/or jacketed with silicone rubber have become standard equipment in most new cars. These cables not only resist the higher under-the-hood temperatures, but also have high dielectric strength at elevated temperatures, which enables them to withstand the higher voltage – peaking at 35 to 40 kV (AC) – of modern electronic ignition systems.

Silicone rubber has also found wide use in coolant and heater hose, O-rings, cylinder liner seals, and other seals used in transmission, lubricating, and hydraulic systems.

Automotive engineers have found many ways to take advantage of the versatility and convenience of RTV silicones – in the potting of electronic voltage regulators, ignition systems and spark control computers, formed-in-place gaskets, adhesives, repair kits, etc.

Aerospace – Silicone's resistance to temperature extremes has caused it to be used in air frame opening seals, connectors, dust boots and shields, aerodynamic seals, gaskets, cushions, blankets, anti-icing hoses, and other places. Aircraft engines use silicone O-rings, seals and gaskets because of its low compression set at elevated temperatures. Silicone's resistance to oxidation has led to its use in oxygen masks, tubing, control regulators, etc. Silicone ablative coatings have been used on aerospace missiles and re-entry devices. Clear RTV rubber has found application in interlayers for windshields. Jet engine manifolds have been thermally insulated with RTV. Special products with low outgassing features have been used as sealants.

Appliances – The television industry uses RTV silicone rubber to encapsulate high voltage transformers. Its resistance to moisture, corona, ozone and flame was a significant factor in the design of safer compounds, such as anode caps. High voltage endurance and flame-resistance has caused silicone rubber to be used in wire insulation.

The list of appliance applications is a long one, and includes O-rings and seals in small appliances, oven door gaskets (both the conventional and the new semiconducting variety), and defroster wire for refrigerators.

*Electrical* – Wires and cables insulated with silicone rubber are used by electric utilities in both the generation and transmission of electricity. Long service life in nuclear and conventionally-powered generating station environments, and safety considerations under design basis event conditions, are significant factors. When exposed to fire, silicones offer circuit integrity, have low smoke evolution, and are halogen-free. Properly designed cables will satisfy IEEE-383 flame propagation test requirements. Utilities also seal penetrations with RTV silicone sealants.

These same characteristics are also important for naval shipboard cable applications: communication, power, and control. It can be anticipated that industries serving the public, such as mass transit, will turn to silicone rubber in future cable designs.

*Gasketing* – One-component RTV compounds have been used successfully as gasketing materials. Their substitution for pre-cut gaskets saves money per part and, because of the excellent balance of properties possessed by silicones, increased reliability frequently results. Many industries, including the automotive, truck, electrical, and appliance, have used this gasketing concept. Advances have recently been made in silicone's resistance to axle lubricants, which have resulted in better sealing performance. In Table 5, a new RTV silicone compound, T2000, is compared to an older compound, T209. The application is axle sealant. T209 was not resistant to the newer lubricants with friction reducing additives; T2000 was developed to have the necessary resistance.
	T209	T2000
Original Physicals, Cured 168 hrs. @ Room Temp. and 50% Relative Humidity		
Hardness, Shore A	44	44
Tensile, MPa	2.3	2.2
Elongation, %	435	310
Specific Gravity	1.58	1.60
Lap Shear Strength, MPa	1.6	1.5
After Aging in Texaco 2224 Gear Lubricant for 168 hrs. @ 150° C		
Hardness, Shore A	-	2.4
Tensile, MPa		1.1
Liongalion, %		191
Volume Change, %	-	18
Lap Shear Strength, MFa	0.7	1.1
After Aging in Texaco 2224 Gear Lubricant for 1008 hrs. @ 150° C		
Hardness, Shore A	-	19
Iensile, MPa		0.9
Elongation, %		173
Volume Unange, %		7
Lap Snear Strength, MPa		1.1

Table 5: Lubricant Resistance of RTV Silicone Rubber Compounds

Food and Health – Baby bottle nipples, conveyor belts for food, tubing for liquids and other similar applications derive from silicone's inherent inertness and simplicity of composition. Expansion into medical fields has been made possible by the development of special formulations fabricated in extremely clean manufacturing facilities. Medical applications have included prosthetic devices, subdermal implants, surgical tubing and blood oxygenation apparatus.

*Furniture Molding* – RTV liquid rubbers are used extensively for molding purposes. One interesting application involves the manufacture of parts from plastics such as polyurethane, polyester resins, acrylics, etc. Silicone rubber molds provide excellent replication of pattern details. The molds are easy to manufacture and extremely durable. The molded parts simulate wood and are used in a multitude of applications. The finished cost is much lower than that of their carved, wooden counterparts.

*Construction* – Silicone sealants are widely used by the construction industry in glazing, roof-coating, and sealing applications, where they compete successfully with organic alternatives.

#### Silicone Rubber Compounds

Extending fillers for silicone can be used to reduce costs. The base used should be capable of accepting large amounts of extending filler. The compound should not become excessively stiff, making processing difficult. After curing, it must also retain acceptable mechanical properties.

As the level of ground quartz filler (Min-U-Sil 10) is increased (Table 6), the compound does not increase in viscosity to a level that would hinder processing. The compound loses tensile strength as the amount of filler increases, but

elongation and tear resistance are maintained. Compression set is fairly constant as the filler loading increases. The unfilled compound has a tendency towards reversion. However, as the filler amount increases, this tendency is reversed. Overall, cost is reduced while essential properties are maintained.

Ingredients (phr)	Α	В	С	D
ELASTOSIL R2000/30	100.0	100.0	100.0	100.0
Min-U-Sil 10		50.0	100.0	150.0
VAROX DBPH-50	1.0	1.0	1.0	1.0
Totals	101.0	151.0	201.0	251.0
Williams Plasticity (1 day age, 3min. test)	166	173	212	262
Original Physicals Hardness, Shore A 100% Modulus, MPa Tensile, MPa Elongation, % Tear, Die B, kN/m Specific Gravity Compression Set, ASTM D 395, Method B 23 bm @ 177° C %	31 0.5 6.9 933 16.5 1.10	39 0.7 5.7 930 19 1.34	49 1.0 4.0 818 19 1.52	59 1.3 3.1 687 20 1.65
Retained Properties After Heating Aging in Air, 70 hrs. @ 225° C Hardness, Pts. Change Modulus, % Tensile, % Elongation, %	-8 59.4 57.8 97.6	-1 81.1 60.1 62.0	+2 91.8 79.0 39.7	+5 106.3 103.5 31.6

#### Table 6: Low Cost Molding Compounds

#### Liquid Silicone Rubber

Liquid silicone rubber (LSR) has been available for 25 years, but only in recent vears has this molding method become a major process for producing precision parts. LSR products are available which have similar properties to HCR silicone in most respects. The use of LSR will mostly depend on the economics of the application. Small precision parts can be easily produced with cycles as short as 15 seconds, using the proper tools, pumps and presses. If the production volume is great enough, the economics favor the use of LSR despite the higher cost of the material. Parts produced from an advanced process will have no significant flash, due to the low injection pressure, the very fast cure, the high quality molds specifically developed for LSR and the precision that is possible with recently developed presses. These four factors, properly applied, combine to produce low-cost, precision molded parts. Such a process usually provides savings by eliminating secondary operations as well as inspection, with parts often going directly into shipping containers. The result is that for small parts with high production volumes, LSR can reduce overall costs below that of HCR silicone and even below that of organic rubber.

Four elements are critical to the successful development of a production process for LSR: the press, the pumps, the material and the mold.

#### Presses

The press for LSR will be similar to a press used for molding thermoplastics, but there are several important differences. As the material is a soft paste rather than hard pellets, the hopper must be replaced with a pipe coupling. Seals must be installed in the rear section of the screw to prevent leakage of the rubber from the barrel. The nozzle must have a hydraulic shut-off to prevent drool when the barrel is retracted. The barrel and screw tip must have a water-cooled jacket to prevent premature curing. To retain precision in the injection stroke the shot size should be 30% to 80% of barrel capacity. The tonnage requirement is 1.5 - 2 tons of clamp force for each square inch (800 to 1100 MN/m²) of exposed area. Press manufacturers can advise on the selection of suitable presses for LSR.

#### Pumps

Pumps must be designed to accurately and consistently meter and mix the two components through a static mixer usually mounted directly above the barrel. Constant pressure must be maintained throughout the cycle to achieve proper dosing. The pumps may also be called upon to supply a metered dose of a color masterbatch from a "color pot" which is a part of the pumps. The color masterbatch will be mixed along with the metered "A" and "B" components in the static mixer. There are several manufacturers producing suitable pumps for LSR.

#### LSR Material

The material itself may consist of any of a number of commercially available products, as shown in Table 7. LSR materials are available from all the major silicone rubber suppliers.

LSR Type	Hardness Range	Appearance
Oil Resistant Grades	40-80 Shore A Duro	Opaque
Self-Lubricating Grades, low and high bleed	30-70 Shore A Duro	Translucent
General Purpose Grades	5-80 Shore A Duro	Transparent
Health Care Greades	20-80 Shore A Duro	Transparent
High Strength Grades	45 Shore A Duro	Transparent
Fast Cure Grades	20-70 Shore A Duro	Clear or Opaque

Table 7:	Commercially	Available	LSR	Grades
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All LSR products are two-component platinum cure materials. The "A" side contains the platinum catalyst and the "B" side contains the H-Si crosslinker. Once mixed, the vulcanizing reaction is spontaneous, but is moderated by inhibitors. Cure time can be extremely fast when temperature exceeds 150°C. For some small parts, mold temperature may be set at 200°C or greater. Pot life will vary with different manufacturers and with some materials. Barrels and static mixers will require purging as often as every day, or as little as once per

week when not in use, depending upon the LSR material.

# Molds

LSR molds should be electrically heated to reach 200°C or greater. At these temperatures hardened steel at least R50 is necessary. A vapor-honed finish is preferred, since a highly polished finish tends to cause sticking. Part ejection is possible and should be considered early in the project. Knockout pins designed for rigid plastic parts will almost never work for LSR. Mold vents are very small, typically 0.0002 to 0.0005 inches (0.005 to 0.127 mm) deep. Runners should be kept as small as possible for economy. A good cross section is a half-round 3/32 to 1/8-inch (2.4 to 3.2 mm) diameter. There are a number of more costly cold-runner systems available that save material. These may be justified if part volume is great enough. Cavitation in cold-runner molds has increased from a maximum of 6 a few years ago to over 100 for some small parts today.

LSR technology is progressing at a fast pace, and has now become a major method for the efficient, cost-effective production of molded parts. Applications that would not have been considered for LSR a few years ago are eagerly pursued today.

#### FLUOROSILICONE ELASTOMERS

## by Michael A. DiPino

Dow Corning Corporation Midland, MI

#### Introduction

The unique physical properties of fluorosilicone elastomer materials (ASTM designation FVMQ) have never been in greater demand than they are today. Most noted for service in applications requiring contact with jet or automotive fuels, solvents and/or engine oils, fluorosilicones are finding increased usage in a number of high-volume automotive and aerospace (commercial and military) applications. Today, fluorosilicone elastomers occupy a unique segment of the rubber family, identified as much by its unique performance characteristics as the chemistry that allowed it all to happen. Once, a very specialized material, the demanding environments of the transportation market have brought the use of fluorosilicone elastomers to high volume mainstream fabricators and end users.

#### History

Fluorosilicone Elastomers or FSRs were developed by Dow Corning in the late 1950's. They combine the high resilience, low-temperature performance



and outstanding ozone and weathering resistance of silicone rubber with the fuel, oil and solvent resistance of a fluorinated polymer. The most common FSR is based on poly (3,3,3-trifluoropropylmethyl siloxane). Similar to Dimethyl Vinyl Silicones (VMQ), they require particle reinforcement for strength, typically silica. Fluorosilicones are very competitive when an application requires wide operating temperatures and fluid resistance. Fluorosilicones are equally competitive when low temperatures and fluids make for harsh application conditions. FSRs are widely used in the automotive and aerospace industries in diaphragms, valves, O-rings and seals. In the case of turbocharger hose (TCH) liners, the combination of high temperature stability and fluid resistance requirements

together with adhesion to the VMQ cover compounds make fluorosilicones a natural choice.

Chemically, a typical fluorosilicone can be represented by the chemical structure in Figure 1.



Figure 1: The Chemical Structure of Fluorosilicone

The use of the chemically stable, trifluoropropyl pendant substitution results in the polymer being very polar, which in turn gives the siloxane backbone resistance to non-polar liquids such as fuel, solvent, and many oils. The inorganic silicon-oxygen backbone contributes greatly to the elastomer's low temperature flexibility as well as high temperature, thermal stability.

The earliest fluorosilicone elastomers had good fuel and oil resistance, but only moderate physical test characteristics. A typical 40 durometer material would exhibit a tensile strength of approximately 5.5 MPa, with low tear strength and elongation. The newest fluorosilicone versions at the same durometer can achieve tensile strength values of 12.4 MPa, elongation greater than 500%, and excellent tear strength (Tear Die B of 45 kN/m). As higher performance systems were developed (particularly in the automotive and aerospace markets), these newer, high performance fluorosilicone elastomers were necessary.

There are three major suppliers of fluorosilicone elastomer polymers and bases that can be used to compound into a variety of products:

- Dow Corning Corporation
- Momentive Performance Materials Inc.
- · Shin-Etsu Chemical Co., Ltd.

# COMPOUNDING FLUOROSILICONE

#### **FSR Base**

In most cases, the pure FSR polymer or 'gum' is not a typical compound starting point. As with VMQ silicones, FSR suppliers take the polymer and mix it with fillers, treating agents and other performance enhancing ingredients. These 'base' products are developed to obtain certain optimal performance characteristics or to meet particular industry specifications. The other characteristics represented by fluorosilicone bases could include high tear strength, low compression set, high tensile strength, just to name a few. Generally, these bases are available in multiple hardnesses that can be blended to achieve intermediate values. Some are developed to accept high levels of extending filler to improve finished part economies. The FSR base is then used with the appropriate curing system (at

a minimum) to convert to an FSR compound. The FSR compound can be either mixed in-house or supplied ready-to-use by custom compounders familiar with the flexibility and value they can contribute to the fabricator and end user.

# Fillers

Although not necessary, additional fillers may be added to a fluorosilicone base to improve performance, in-process handling, or end part economies. Common fillers for FSR compounds are usually silica based (fumed, precipitated, or ground), but other types can and are used.

# **Pigments**

As with VMQ silicone elastomers, most fluorosilicone bases are translucent or off-white and are easily pigmented. This allows for easy color matching when required. Pigment masterbatches are typically used due to the low shear rates developed in mixing fluorosilicone compounds. These pigment masterbatches can be supplied in silicone fluid, silicone gum, or fluorosilicone gum or base.

## Additives / Modifiers

Similar to VMQ silicone elastomers, small amounts of additives can be used to improve the processing or performance of fluorosilicone compounds. There are a number to choose from. The affect of using modifiers include high temperature improvement, acid neutralization (due to some peroxide by-products), green strength increase or decrease, flame retardants, and the like. Table 1 contains examples of the types of modifiers that are available from one manufacturer.

Modifier	Function
AN-3 Modifier*	Neutralizes acidic by-products
FR-1 Modifier	Enhances flame-retardancy
FR-2 Modifier	Enhances flame-retardancy
FR-3 Modifier	Enhances flame-retardancy
HA-1 Modifier	Stiffening handling additive
HA-2 Modifier*	Softening additive used with extra fillers
HA-3 Modifier	Stiffening handling additive
HT-1 Modifier	High temperature additive
MRA 2 Modifier*	Mold release additive
TM-1 Modifier	Tensile modifier used with extending fillers

Table 1: Silastic[®] Modifier Selection Guide

*Contains FDA compliant ingredients.

# **Cure System**

Organic peroxides are the primary materials used to crosslink fluorosilicone compounds. Fluorosilicones, in general, can use the same peroxide types and levels as VMQ type silicones. The choice of which peroxide is best suited depends on the fabrication process and other process and/or temperature limitations. In addition to peroxide cure systems, some commercial fluorosilicone bases can

be addition (or platinum) cured. Through the optimal selection of a fluorosilicone base and the end application, an oven postcure may not be necessary. Similar to VMQ type silicone compounds, the cure system employed is based on the fabricator's process and the end-user performance requirements.

## PROCESSING FLUOROSILICONES

In the mixing and fabrication of fluorosilicone rubber, it is essential to understand the relationship between current compounding technology and the various fabrication processes employed. Whether starting from standard fluorosilicone bases and developing compounds for internal use or buying a 'ready-to-use' material that is fully-compounded, pigmented and catalyzed, the more information at hand, the better. Even in the absence of mixing equipment suitable for fluorosilicone compounding, a fundamental understanding of the ingredients used and their potential process effects will always be helpful, especially when troubleshooting end-product manufacturing problems. Even if troubleshooting efforts fail to resolve a specific or unique problem, a basic knowledge of fabrication and compound dependencies will help in defining the problem to your fluorosilicone supplier technical service resource, and aid in resolving the problem quickly and minimizing downtime.

As with many other endeavors, there is no single correct way to optimize manufacturing or solve a problem using fluorosilicone compounds in any one of the many processes currently employed. The recommendations made here may be used to help provide direction toward resolving a specific issue, but are not meant to cover all situations. Fluorosilicone rubber compounds can present unique challenges in matching particular compounding technologies to various fabricating processes. For example, what works for an extrusion operation may not apply to injection molding. Likewise, calendering fluorosilicone rubber on fabrics brings a different set of issues than solution (dispersion) coating FSR on the same fabric. Things may also be further complicated by products supplied from different manufacturers or compounders to meet the same specification. These products may act completely different on a specific piece of equipment.

The versatility of fluorosilicone compounds offers a wide range of processing flexibility. Processing fluorosilicones is very similar to VMQ silicone. Millable fluorosilicone compounds can be used in the following processes.

#### Molding

Fluorosilicone compounds can be fabricated in methods similar to organic thermoset compounds. In some cases, the same molds can be used. There are three primary types of molding methods to fabricate fluorosilicone rubber parts: compression, transfer and injection molding. All three methods are similar in that they form the rubber into a finished part through the application of heat and pressure. Differences between the methods relate to the mold loading techniques and reliance on manual labor vs. automation. For insert molding, appropriate primers can be recommended to improve bonding to most substrates.

Compression Molding Techniques and Tips – While the compression molding process is well understood, the following are important considerations when

molding fluorosilicone compounds:

- When using molds designed to mold organic rubber for fluorosilicone, the fluorosilicone may exhibit more shrinkage than an organic compound. Filler loading (high loading results in less shrinkage) and cure temperature (high temperature increases shrinkage) are variables that can be used to offset shrinkage for tight-tolerance parts. Ask the peroxide supplier or custom compounder about cure temperature ranges for your specific compound.
- Preforms should be uniform in shape and contain enough material to fill the cavity and produce a small amount of flash. In many molds, a weight of 5 to 10% over actual part weight is adequate.
- Mold surface finish can also affect material flow in compression molding. Highly polished steel normally facilitates good flow. Chrome or other finishes may also improve part removal time, and are particularly helpful in transfer and injection molding of fluorosilicone compounds.

*Transfer Molding Techniques & Tips* - This method is particularly well suited for large numbers of small parts where flow is difficult to design into the mold or where the part configuration tends to trap air. A well-designed mold can generate nearly flashless parts (although not completely waste free).

- If at all possible, it's preferred to have the transfer pot thermally separate from the mold. A water-cooled transfer pot is even better.
- If using a warm or hot transfer pot, try to minimize the time that the fluorosilicone compound is in contact with heat before it fills out the mold. In most cases, the compound will not require warming to improve flow.

Injection Molding Techniques and Tips - Short cure times and low viscosity (good flow) make injection molding an excellent fit for fluorosilicone compounds. Mold design and sprue size/location are critical factors in optimizing the injection molding process. Due to the high pressures and quick mold fill, short cure dwell times can be designed into a fluorosilicone compound.

- Whether using a stuffer box or strip feed, the feed section generally doesn't require added heat; viscosity reduction is unnecessary.
- In multi-cavity molds, balancing the gates is important for optimizing mold flow. Gate location and number should be evaluated to ensure good flow and quick fills, designed to match cure scorch.
- Due to the quick fill and short scorch times, vents (with or without vacuum) may be necessary to eliminate trapped air.
- Highly polished steel, chrome or other plating can be beneficial in shortening overall mold cycles by reducing part removal time.
- Reduced injection speed (ram pressure) should be used in highly-filled compounds to control frictional heating through the sprues. Lower mold temperatures may also be needed to balance the effects of frictional heat.
- Cold runner systems are strongly recommended.
- · Generally, the fresher the compound, the easier the flow and the quicker the

# fill. Refreshening the compound before molding may improve part yield.

# Extrusion

Fluorosilicone rubber compounds can be extruded to fabricate a number of products, including gaskets, tubing, wire insulation and various profiled seals. Although the process is similar to organic elastomer extrusion, there are significant differences. In general, fluorosilicone compounds should be extruded at room temperature due to their relatively low viscosity. Spot temperatures above 50°C during extrusion may produce scorching in the extruder, resulting in different profile measurements (due to higher viscosity in the extruder) and may also result in a less complete cure from partial loss of the curing agent due to volatilization. Most fluorosilicone compounds are cured via hot air vulcanization (HAV) immediately following extrusion.

Extrusion Techniques and Tips:

- The screw used for extruding a fluorosilicone compound should be one designed specifically for fluorosilicone or VMQ silicone. Extruder manufacturers can recommend the best design for the type of tubing or profiles planned.
- A breaker plate to hold screens (60 200 mesh) may be necessary to maintain a high, even back pressure, and provide a consistent profile cross-section. This technique can also aid in trapped air removal from the compound.
- Extruder barrel cooling is recommended to maintain cool compound temperatures.
- Some highly-filled, light-colored extrusions can produce an extrudate with dark streaks, typically caused by metal wear particles due to the hard, abrasive nature of some extending fillers. In some cases, modifications can be made to the barrel to minimize this occurrence.
- When manufacturing thin-walled tubing, low-pressure air is normally introduced into the inside of the tube while in the extruder to prevent collapse of the profile.
- As with fluorosilicone molding compounds, most extrusion grade fluorosilicone rubber formulations will benefit from mill freshening prior to fabrication. This process can further remove any trapped air and provide a consistent viscosity to reduce start-up waste. Without a refreshening step, older inventory may require different extruder set-up conditions than fresh supplies of the same compound.
- Hot air curing ovens should have an air exhaust system to remove volatiles generated from the fluorosilicone and peroxide by-products.
- The use of roller feeds (particularly when using strip coils) ensures a more consistent fill of the extruder, resulting in constant backpressure and a more uniform extrusion profile.

# Calendering

Either a 3- or 4- roll calender may be used for calendering fluorosilicone

rubber compounds. In most cases, the 3-roll calender is a vertical stack design. A 4-roll calender may also be a vertical stack, but inverted 'L' or inclined 'Z' configurations can be used, as well. The end result of the calendering process is a solid sheet of fluorosilicone, either unsupported, impregnated into a carrier fabric, or laminated onto a film. The main advantage of the calendering process is to produce long, continuous sheets of uniform thickness. A variable speed main drive is recommended, and the ratio of the take-off rolls should normally be 1:1. In some extremely stiff fluorosilicone compounds, a slight ratio change between the rolls at the take-off nip may bring an improvement by making use of friction at the nip. Fluorosilicone rubber compounds are generally calendered at room temperature, however, some heating capacity may be helpful in specific compounds and may improve tack to fabric or carrier sheets (to assist in take-off).

Calendering Techniques and Tips:

- Most fluorosilicone rubber compounds will benefit from mill freshening before processing on a calender.
- It is recommended that an unsupported fluorosilicone sheet be calendered onto a release liner that will be stripped off after curing.
- When using a release liner, strip the sheet while warm (whenever possible). If allowed to cool and the liner tears or sticks, re-warm the roll before attempting to strip the liner from the sheet.
- If transfer to fabric is poor or intermittent, dip coating the fabric in a solution (10-20%) of the compound (then drying and curing) prior to the calender step will add tack to the fabric.

# **Fabric Coating**

Bases and compounds can be dispersed in appropriate solvents to be coated onto fabrics or other substrates. Heat cure follows solvent removal.

# FEATURES AND PROPERTIES

Typical property ranges for commercially available fluorosilicone bases are listed in Table 2.

ASTM Test Description	Property Range*
Durometer Hardness, Shore A, Pts.	20 - 80
Tensile Strength, MPa	7.5 – 12.0
Elongation at Break, %	150 – 690
Tear Strength, Die B, kN/m	17.5 – 46
Compression Set, Plied Disks, 22 hrs. @ 177°C, %	10 – 20
Volume Swell, Fuel B, 24 hrs. @ 23°C, %	15 – 23
Service Temperature, °C	-60 - +280

 Table 2: Typical Property Ranges for Fluorosilicone Bases

* All combinations are not typical for a single base

Fluorosilicone elastomers are resistant to many non-polar fluids, which include hydrocarbon fuels, oils and solvents. Fluorosilicone compounds are not, however, the best choices for service environments that include polar solvents (e.g., ketones, esters).

The resistance of fluorosilicone to select reference oils, fuels, solvents, and steam is illustrated Table 3.

Fluid	Immersion Condition	Hardness Change, Pts.	Tensile Change, %	Elongation Change, %	Volume Change, %
IRM 903 oil*	70 hrs. @ 150°C	-4	-8	+4	+2
Fuel A*	168 hrs. @ 24°C	-5	-40	-30	+15
Fuel B*	168 hrs. @ 24°C	-5	-40	-30	+20
Fuel C*	168 hrs. @ 24°C	-14	-20	-19	+19
JP-8**	168 hrs. @ 24°C	-9	-13	-6	+4.6
Toluene	168 hrs. @ 24°C	-10	-50	-35	+20
Heptane	168 hrs. @ 60°C	-10	-30	-30	+25
Steam	24 hrs. @ 100 psi	-5	-20	+15	nil

Table 3: Fluid Resistance of Fluorosilicone Elastomers

*ASTM Reference Fluids

** Jet Engine Fuel

From a functional standpoint, fluorosilicone elastomers exhibit a stable performance response over a wide temperature range. For applications such as seals, grommets, connectors, and diaphragms, the tensile modulus is a good indicator of flexibility. The tensile modulus response can be thought of as the resistance to stretch. The following chart illustrates the typical tensile modulus response from room temperature (23°C) to 200°C using two commercial fluorosilicone bases.



Figure 2: Modulus Response to Temperature for Fluorosilicone Elastomers

# DESIGN OPPORTUNITIES USING FLUOROSILICONE

# Blends with VMQ

Unique solutions can be derived beyond adding curing agents to bases or using custom formulated, ready to use high consistency compounds. Other compounding options include blending with VMQ silicone rubber bases to improve processing and part economies (if the loss in fuel and solvent resistance is acceptable);

# **Liquid Polymers**

In addition to the millable type of fluorosilicone compounds, fluorosilicone elastomers are also available in other forms. FVMQ/VMQ liquid copolymers are available and designed for automated injection molding systems, and 100% liquid fluorosilicones for improved fuel resistance (compared to liquid copolymers). The 100% fluorosilicone liquid systems can open design possibilities that are ideal when fabricating small, intricate parts utilizing fast cycle times, high yields, and the potential for flashless parts and automated molding processes. The lower viscosity (compared to millable compounds) also has the additional potential for process and economic improvements. These might include reduced injection pressure, faster fill speed, and the possibility of an increased number of cavities in the mold.

# **Translucent Polymers**

Unlike many organic elastomers that develop dynamic performance characteristics from reinforcing carbon black, fluorosilicone bases are typically translucent or light colored. This feature can be used to easily pigment the compound to color match other components in an assembly, or be used for easy identification of finished parts.

# **APPLICATIONS**

At first view, fluorosilicones' wide service temperature range and fuel and solvent resistance lend itself to automotive fuel line and aerospace fuel contact applications. Automotive underhood applications where hot oil or potential fuel splash locations exist, fluorosilicone parts are specified for electrical connector inserts and grommets. Fluorosilicone compounds can be designed for low compression set which can make it the material of choice for a variety of sealing applications. Examples of some of these applications include:

- · Fuel line quick connect seals
- · EGR and other fuel and gas diaphragms
- · Hydraulic and electrical clamp blocks
- · Automotive vapor recovery management system seals
- · Automotive, in tank, in line fuel check valve seals
- · Fuel system "duck bill" valves
- Turbocharger hose liners





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Photos courtesy of Dow Corning Corporation

#### FLUOROCARBON ELASTOMERS

#### by R. D. Stevens and P. A. Ferrandez

DuPont Performance Elastomers, L. L. C. Wilmington, DE

Commercially produced fluoroelastomers, which were developed and introduced in the mid-1950s, provide extraordinary levels of resistance to chemicals, oil and heat, and a useful service life above 200°C (392°F). The high stability and excellent oil resistance of these materials are due to the high ratio of fluorine to hydrogen, the strength of the carbon-fluorine bond and the absence of unsaturation in the polymer chain. Fluoroelastomers are referred to generically as FKM polymers according to the nomenclature in ASTM D 1418.

#### FKM History and Background

The first useful fluoroelastomer was a chlorotrifluoroethylene (CTFE)/ vinylidene fluoride (VF₂) dipolymer (KEL-F, M. W. Kellogg Co.); however, substitution of hexafluoropropylene (HFP) for CTFE yielded a considerably more stable and more processable elastomer. Viton[®] A fluoroelastomer, introduced by the DuPont Company in 1957, and Fluorel[®] brand fluoroelastomer, marketed by the 3M Company in the early 1960s, are prime examples.

To provide even greater thermal stability and solvent resistance, tetrafluoroethylene-containing (TFE) terpolymers were introduced by DuPont in 1959. Montecatini-Edison introduced 1-hydro-pentafluoropropylene-based dipolymers and terpolymers in the 1960s. These materials lacked the thermal stability of the corresponding HFP polymers, and as the patent protection expired for the basic VF₂/HFP and VF₂/HFP/TFE compositions, Montecatini-Edison and its successors began producing HFP-based fluoroelastomers.

In the mid-1970s, DuPont introduced fluoroelastomers containing perfluoro (methyl vinyl) ether (PMVE). These polymers, which offer substantially improved low-temperature performance, are VF₂/PMVE/TFE compositions that incorporate a bromine-containing cure site monomer that renders the polymers curable by peroxides. At the same time, DuPont also introduced methanol-resistant, peroxide-curable VF₂/HFP/TFE polymers with a very low VF₂ content. Recently, both Daikin and Ausimont have also introduced VF₂-based, peroxide-curable fluoroelastomers.

A perfluoroelastomer, based on TFE and PMVE, was developed by DuPont in the early 1970s. This elastomer provides thermo-oxidative stability and resistance to aggressive chemicals and solvents approaching that of polytetrafluoroethylene (PTFE). Perfluorocarbon elastomer parts made from variants of this polymer are sold by DuPont under the Kalrez[®] trademark.

In the 1990's FKM suppliers went through some restructuring, with major producers entering into mergers and joint ventures. DuPont combined with Dow Chemical to form DuPont Dow Elastomers, L.L.C. which strengthened its position as the leading supplier of specialty elastomers. 3M and Hoechst formed

Dyneon L.L.C. to broaden their base as fluoroproducts suppliers. Montedison, after a few years with EniChem, consolidated a fluoroproducts enterprise and became Ausimont. Ausimont was later acquired by Solvay and renamed Solvay Solexis S.p.A.

In 1997, DuPont Dow Elastomers introduced Viton Extreme[™] ETP. These fluoroelastomers have extended fluids resistance to strong bases, ketones and mixed solvents, while retaining the aromatic hydrocarbon resistance normally associated with FKM elastomers.

In the 2000's FKM suppliers continued their restructuring. The DuPont Dow Elastomers joint venture dissolved and DuPont Performance Elastomers was formed. AGC Chemicals Americas, Inc. was formed in January 2004, as the result of a merger between sister companies Asahi Glass Fluoropolymers USA and AGA Chemicals.

Today the major producers of fluorocarbon elastomers are DuPont Performance Elastomers (Viton fluoroelastomer and Kalrez perfluoroelastomer parts), Dyneon (Dyneon[®] brand fluoroelastomer), Solvay Solexis (Tecnoflon[®] fluoroelastomer), Daikin (Dai-El[®] fluoroelastomer) and AGC Asahi Glass (Aflas[®] fluoroelastomers).

## **End-Use Applications**

Fluoroelastomers are used in a wide variety of high-performance applications because they provide premium performance and long-term reliability even in harsh environments. Their exceptional resistance to heat aging and a broad range of fuels, solvents and chemicals makes them ideal for many demanding aerospace, automotive and industrial applications. Since fluoroelastomers maintain their excellent balance of properties even after brief excursions to temperatures above their upper service limit, they can significantly extend the service life of a component. Current end-use applications for fluoroelastomers are shown in Table 1.

Aerospace	Automotive	Industrial
O-ring seals in fuels, lubricants, and hydraulic systems	Shaft seals Valve stem seals	Hydraulic O-ring seals Check valve balls
Manifold gaskets	Fuel Injector O-rings	Military flare binders
Fuel tank bladders	Fuel hoses	Diaphragms
Firewall seals	In tank and quick connect fuel system seals	Electrical connectors
Engine lube siphon hose	Gaskets (valve & manifold)	Flue duct exp. joints
Clips for jet engines	Balls for check valves	Valve liners
Tire valve seals	Lathe cut gaskets	Roll covers - Sheet stock/cut gaskets

#### Table 1: Current End-Use Applications for Fluoroelastomers

#### Fluoroelastomer Types

Fluoroelastomers are generally classified into two different groups: Standard types and Specialty types. The Standard types comprise A, B and F families that have increasing fluid resistance derived from increasing fluorine levels (66 percent, 68 percent and 70 percent, respectively). A-types are copolymers of hexafluoropropylene (HFP) and vinylidene fluoride (VF₂) while B and F-types are copolymers of HFP and VF₂ with tetrafluoroethylene (TFE) incorporated at different levels. Group extensions of these polymers are the AL and BL types, which are, respectively, A and B families with slightly better low temperature flexibility. Polymers in the Specialty group possess unique properties, such as improved low-temperature flexibility or base resistance.

Polymers within a group possess similar heat and fluid resistance. Because of comparable fluorine levels, polymers within a group also feature similar low-temperature properties. In general, molecular weight distribution and viscosity are the only differences between polymers within a group. However, these differences are very important because they result in varying degrees of extrudability and mold flow.

Available fluoroelastomers, divided into standard, peroxide cured, low temperature specialty and base-resistant types are listed in Table 2, including fluorine content.

Families	Types		DuPont Performance Elastomers	Dyneon	Solvay Solexis	Daikin	Asahi Glass
Trade Name			Viton	Dyneon	Tecnoflon	Dai-El	Aflas
Standard Types (normally bisphenol cured)	A AL B BL F	(66%F) (66%F) (68%F) (67%F) (70%F)	X X X X X X	X X X X	X X X X X	x x x	
Peroxide Cured Standard Types	GA GAL GBL GF	(66%F) (66%F) (67%F) (70%F)	X X X	x x	X X	x x	
Low Temperature "Specialty" types	glt gblt gflt ltfe	(65%F) (66%F) (67%F) (67%F)	X X X	х	X X X X	х	
Base Resistant "FEPM" types	TFE/P TFE/P/VF ₂ TFE/P/csm TFE/VF ₂ /HI PMVE/E	(57%F) * (60%F) FP/	x x	X X	Х		X X
	ETP	(67%F)	Х				

#### **Table 2: Suppliers and Types of Fluoroelastomers**

*csm = cure-site monomer

Standard polymers are usually available in gums or precompounds in which cure chemicals are already incorporated. Peroxide and Specialty fluoroelastomers are usually provided in gum form only.

#### Fluids resistance differences between types of FKM

Since one of the primary attributes of a fluoroelastomer is its fluids resistance, it is helpful to define the capability of each type of fluoroelastomer in various environments so that the correct type of polymer can be selected for any application. Data for some Viton fluoroelastomers are shown in Table 3.

	Family & Type Of Viton Fluoroelastomer							
	Α	В	F	GB-S	GF-S	GLT-S	GFLT-S	ETP-S
				Cure s	ystem			
	Bisphenol Peroxide							
Aliphatic hydrocarbons, process fluids, chemicals	1	1	1	1	1	1	1	1
Aromatic hydrocarbons (toluene, etc.), process fluids, chemicals	2	1	1	1	1	2	1	1
Automotive & aviation fuels (pure hydrocarbons - no alcohol)	1	1	1	1	1	1	1	1
Automotive fuels containing legal levels (5-15%) of alcohols & ethers (methanol, ethanol, MTBE, TAME)	2	1	1	1	1	2	1	1
Automotive / methanol fuels blends up to 100% methanol (flex fuels)	NR	2	1	2	1	NR	1	1
Engine lubricating oils (SE-SF grades)	2	1	1	1	1	1	1	1
Engine lubricating oils (SG-SH grades)	3	2	2	1	1	1	1	1
Acid (H ₂ SO ₄ , HNO ₃ ), hot water, and steam	3	2	2	1	1	1	1	1
Strong base, high pH, caustic, amines	NR	NR	NR	NR	NR	NR	NR	1-2
Low molecular weight carbonyls — 100% concentration (MTBE, MEK, MIBK, etc.)	NR	NR	NR	NR	NR	NR	NR	1-2
Low temperature flexibility TR-10 test results, °C	-17	-14	-7	-15	-6	-30	-24	-11

Table 3: Fluids Resistance & Low Temperature vs. Types of Viton

1 = Excellent, minimal volume swell; 2 = Very Good, small volume swell; 3 = Good, moderate volume swell; NR = Not Recommended, excessive volume swell or change in physical properties

Since all fluoroelastomers have outstanding heat and oil resistance, it is preferable to focus on properties that highlight their differences. Such properties include low temperature flexibility, swell in oxygenated fuels, and resistance to base and base additives (corrosion inhibitors).

Two plots are used to differentiate fluoroelastomers. Figure 1 shows the major fluoroelastomers for fuel systems. Low temperature flexibility and swell in oxygenated fuels are major properties sought after by the automotive industry. Improving fuel resistance is achieved through higher fluorine contents, but a higher fluorine content negatively impacts low temperature flexibility. Compression set and processability are affected only to a minor extent.





Figure 2 shows the major fluoroelastomers for base additive resistance applications. ASTM oil 105, a 10W/30 test fluid with an aggressive additive package, is positioned on the "Y axis" and is contrasted to oil / volume swell resistance with IRM 103 oil on the "X axis".



Figure 2: Comparison of FKM & FEPM Families for Powertrain Base-Resistant Applications

## **New FKM Polymer Development**

Advanced Polymer Architecture technology

In the fall of 2002, DuPont Dow Elastomers launched a new line of specialty, improved processing Viton fluoroelastomers made with Advanced Polymer Architecture (APA) technology. These APA types are produced in a plant in Dordrecht, Netherlands. Specialty fluoroelastomers such as peroxide-cured types, low temperature types, and base-resistant types are the fastest growing FKM segment, but are difficult to process and lacking in some end-use properties. Using the new Advanced Polymer Architecture technology, which includes enhanced curesite chemistry and finely tuned molecular weight distribution, research chemists were able to convert these difficult to process materials into robust fluoroelastomers that exhibit improved processing (improved mold flow and mold release) and improved properties (better fluids and compression set resistance).

The range of these products is set out in the Table 4. The new APA products carry an "S" suffix after the commercial name so that they can be easily distinguished from older types of Viton.

Class	Product Name	Mooney [@] 121°C	Fluorine %	Low temp. Tg
Peroxide_	GF-600S	65	70	-6°C
(Standard types)	GF-200S	25	70	-6°C
	GBL-600S	65	68	-15°C
	GBL-200S	25	68	-15°C
	GAL-200S	25	66	-20°C
Peroxide - LT	GLT-600S	65	64	-30°C
(Low temperature types)	GLT-200S	25	64	-30°C
	GBLT-600S	65	66	-27°C
	GFLT-600S	65	67	-24°C
	GFLT-200S	25	67	-24°C
Extreme ETP-S	ETP-600S	65	66	-11°C
Extreme TFE-P type (base resistant)	VTR-8804	60	60	-2°C

Table 4: APA Technology Types of Viton Fluoroelastomer

- APA technology peroxide polymers have:
  - o Good tensile properties, both the 25 & 65 Mooney products
  - o Improved mold release characteristics
  - o Improved compression set resistance with little or no-postcure
  - o Good fluids resistance equivalent to old technology grades
    - APA technology polymers can be cured without a metal oxide – improves water and acid resistance
  - o Better long term sealing force retention
  - Moderate improvement in low temperature sealing performance (LT types)
- Base resistant VTR-8804 & ETP-600S
  - VTR-8804 is a bisphenol cure included TFE/P/csm precompound
  - ETP-600S is a peroxide cured FEPM formulate it like other APA technology peroxide cured polymers

Evidence of the improved mold release characteristics of peroxide cured G-type APA technology polymers can be seen in Figure 3. In this test small O-rings were compression molded and removed by blowing air across the mold once. O-rings that would not blow out were recorded as "sticking" in the chart. The data show that APA technology GLT-600S exhibited very little mold sticking as compared to original GLT. The same mold release improvement seen here with GLT-600S has been confirmed with GFLT-600S, GF-600S, and GBL-600S.



Figure 3: APA Polymers De-mold Easily in Compression Molding

Another APA technology polymer, Viton Extreme ETP-600S, has a unique profile of low volume swell in a diverse set of fluids as can be seen in Figure 4. In this test common FKMA-401C, high fluorine content GF-600S, and base resistant TFE/P are compared to ETP-600S in gear lube @ 150°C, wheel bearing lube @ 150°C, aromatic hydrocarbon toluene @ 40°C, methyl-t-butyl ether (MTBE) @ 40°C, solvent methyl ethyl ketone (MEK) @ 23°C, and a mixed solvent of 50% methyl ethyl ketone with 50% toluene. ETP-600S exhibits low volume swell in the gear lubes and aromatic solvent like FKMs A-401C and GF-600S, and improved ketone and MTBE resistance vs. TFE/P. ETP-600S is the only polymer in the test matrix that exhibits low volume swell over the whole range of fluids tested including the demanding mixed MEK/toluene solvent blend.



Figure 4: ETP-600S Has Broad Resistance to a Diverse Set of Fluids

#### Compounding FKM

A typical fluoroelastomer formulation contains the following components:

- Polymer
- Cure System
- Acid Acceptor System
- Filler(s)
- Processing Aid(s)

Depending on the application, a specific type (or blend of types) of polymer, in the appropriate cure system, acid acceptor system, filler and processing aid must then be chosen.

Table 5 illustrates the general structure of a typical diamine, bisphenol, and peroxide cured FKM compound recipe. Different levels of metal oxides, fillers, and process aids can be used to obtain compounds from 55 to 95 durometer depending on the cure system used in the recipe.

#### Table 5: Typical Formulations for Fluoroelastomer Compounds

Ingredients	<u>Diamines</u>	<u>Bisp</u>	<u>henol</u>	Peroxides**		
Fluoroelastomer	100	100	100*	100		
Magnesium oxide	15	3	3	-		
Calcium hydroxide	-	6	6	-		
Zinc oxide	-	-	-	0-3		
Filler(s)	5-50	5-60	5-60	5-60		
Process Aid(s)	1-4	0-2	0.5-2	0.5-1.5		
Diamine Curative	1-3	-	-	-		
Bisphenol Curatives	-	3-8	*	-		
Coagents(s)	-	-	-	1-4		
Peroxide	-	-	-	1.25-3		
* Bisphenol curatives incorporated into fluoroelastomer						
** APA peroxide G - types like GF-S, GBL-S, GLT-S & GFLT-S						

# Cure Systems

Diamine, bisphenol and peroxide cure systems for fluoroelastomers are available, but the bisphenol cure system is predominately used. The diamine cure system was used until 1970, when the bisphenol cure system was introduced with Viton E-60C. The bisphenol cure system provided significant advances in cure behavior and compression set resistance. Peroxide curing of fluoroelastomers, which offers improved resistance in aqueous media, began in 1976 with the introduction of Viton GF and Viton GLT. Fluoroelastomers containing a specific cure site are required for peroxide curing.

The relative performance of these three cure systems, with regard to a variety of processing and physical property characteristics, is shown in Table 6. Some characteristics of a compound, such as demolding-tear, are much more dependent on the amount, rather than the type, of curative used.

Processing and Physical Property Characteristics	Diamine Cure (Diak™ No. 1, 3 & 4)	Bisphenol Cure (Viton Curatives 20, 30 & 50)	Peroxide Cure (VAROX [®] DBPH-50)
Scorch Safety	Poor to Fair	Good to Excellent	Good to Excellent
Balance of Fast Cure and Good Scorch Safety	Poor	Excellent	Excellent
Mold Release	Good	Excellent	Good-Excellent
Ability to Single- Pass Banbury Mix	#1 No; #3 Risky; #4 Okay	Yes	Yes
Adhesion to metal	Excellent	Good	Good
Tensile Strength	Good to Excellent	Fair to Excellent	Good to Excellent
Compression Set	Fair	Excellent	Good
Water, Steam, Acid	Fair	Good	Excellent

 Table 6: Relative Performance of Various FKM Cure Systems

#### Acid Acceptor Systems

Acid acceptors are used in compounds of fluoroelastomers. They participate in bisphenol cure reactions and enhance high-temperature performance. Table 7 lists the various acid acceptor systems commonly used for fluoroelastomers, and summarizes the use and caution information associated with each system.

Table 7: Summar	ry of Common Acid Acceptors for Fluoroelastome	rs
-----------------	------------------------------------------------	----

Acid Acceptor	Recommended Use	Caution Information
Magnesium Oxide (MgO), low activity	General-purpose diamine cures.	Sensitive to water and acid.
Magnesium Oxide (MgO), high activity plus Calcium Hydroxide (CaOH ₂ )	General-purpose bisphenol cures.	Sensitive to water and acid.
Zinc Oxide (ZnO)	To improve heat aging, tear resistance and processing safety for peroxide cures.	Results in a lower rate and state of cure, as well as reduced water and acid resistance.
Calcium Oxide (CaO)	To minimize fissuring, improve adhesion and reduce mold shrinkage.	Difficult to disperse. Hygroscopic. Causes slow cures.
No metal oxide (APA peroxide cured Viton)	To improve water, steam and acid resistance and replace old lead oxide recipes	Lack of metal oxide reduces heat resistance above 200°C

#### Fillers

A variety of carbon black and mineral fillers can be used when compounding fluoroelastomers. In general, increased amounts of filler result in higher compound viscosity, lower vulcanizate elongation and higher vulcanizate hardness, modulus and tensile strength. A summary of fillers commonly used for fluoroelastomers is given in Table 8.

Filler	Description
N990 MT Carbon Black	Best general-purpose filler. Provides excellent compression set resistance.
Austin Black ^{®*} (Coal Fines)	Black filler that provides improved high temperature compression set resistance when used in combination with MT Black. Has poorer extrudate quality and lower tensile strength and elongation than MT Black.
N762 SRF Carbon Black	Black filler that is well-suited for high strength, high modulus compounds. Can moderately aggravate mold sticking. Compression set not quite as good.
Blanc Fixe (Barium Sulfate)	Neutral filler that is well-suited for colored compounds and offers the best compression set resistance among non-black fillers. Provides poorer tensile strength than MT black.
VANSIL [®] W-40 (Calcium Metasilicate)	Good, general-purpose non-black filler that features a tensile strength comparable to that of MT Black. This neutral filler is well-suited for colored stocks. Calcium metasilicate with a coupling agent like an aminosilane can increase tensile strength.
Ti-Pure [®] R-960 (Titanium Dioxide)	Good filler for light colored compounds. Provides good tensile strength but features poorer heat aging than other fillers.
Red Iron Oxide	Substance used with neutral mineral fillers, at levels of 5 phr to 10 phr, to make red-brown compounds.
Graphite powder, Zonyl [®] PTFE powder	Substances that can be combined with other fillers, at levels of 10 phr to 15 phr, to improve wear resistance.
Celite [®] 350 (Diatomaceous Silica)	General-purpose, neutral filler that provides good tensile strength.
Multifex [®] MM (fine particle size, precipitated Calcium Carbonate)	Good, general-purpose mineral filler that exhibits the least amount of change in physical properties due to ambient moisture.

 Table 8: Summary of Common Fillers for Fluoroelastomers

* Proper postcure oven loading and ventilation must be used when working with Austin Black (coal fines) to prevent an oven fire.

#### Plasticizers

Commercial plasticizers are not compatible with fluoroelastomers and should normally not be used. Only low levels (<5 phr) of ester plasticizers may be used to ease extrusion, and only if heat stability is not a major requirement.

#### Processing Aids

A variety of processing aids for fluoroelastomers are currently available. These processing aids are used to improve release from molds and calenders; to improve flow during molding and extrusion; and to smooth extrudates. They are generally added at levels of 0.5 phr to 2 phr. It is important to use the proper amount of processing aid in a formulation because an excess will result in problems ranging from excessive mill release to poor knit in molded parts. Some processing aids commonly used for fluoroelastomers are compared in Table 9.

Process Aids	Mold Release	Mill & Calender Release	Extrusion Smoothness	Compression Set Resistance
Carnauba wax	++	++	++	-
VPA No. 1	0/+	+	0/+	0/-
VPA No. 2	++	++	++	-
Low MW PE wax	0	+	+	-
Struktol® WS280	+	+	+	0/-
Struktol HT290 (for peroxide cured FKM)	++	+	+	-
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Table 9: Comparison of Common Processing Aids for Fluoroelastomers

Key: ++ very positive effect; + positive effect; 0 no effect; - negative effect

## Processing

#### Storage and Handling

To maintain properties at optimum levels, fluoroelastomers should be stored in a dry environment at 18.3°C (65°F). In addition, fluoroelastomers should be kept in original shipping containers to prevent possible contamination.

Mixed stocks should also be stored at  $18.3^{\circ}C$  ( $65^{\circ}F$ ). Before further processing, the stock should be removed from the refrigerated storage area and allowed to warm to room temperature in the processing area (for approximately four hours). Condensation should be removed to prevent blisters and other processing problems.

# Mixing

Most fluoroelastomers can be mixed easily on a conventional two-roll rubber mill or in an internal mixer, such as a Banbury mixer.

If mill mixing is used, a cold mill  $(25 \pm 5^{\circ}C [77 \pm 9^{\circ}F])$  is recommended to ensure good dispersion and minimal scorch. To optimize dispersion and speed the mixing process, all dry ingredients should be pre-blended for simultaneous addition to the banded polymer.

A "one-pass" mix in an internal mixer for three to four minutes generally yields good results. Ample cooling water, preferably refrigerated water, is required for this process. The load factor, determined by the compound type and mixer size, plays an important role in preventing scorch.

After mixing, stocks should be cooled as rapidly as possible. This can be accomplished in a water dip or by a spray combined with forced air drying. Stearates should not be used in the dip or spray.

# Molding

Fluoroelastomers can be compression, transfer or injection molded. Modern

polymers, such as Viton A-206C for injection molding and Viton 401C and A-601C for compression molding, are specially formulated to provide exceptional performance in critical molding applications. Typically, mold temperatures between 175°C and 205°C (350°F and 400°F) are used. Clean, chrome-plated steel molds are recommended. In addition, the compound should contain an internal release agent, such as carnauba wax or VPA No. 2. If an external mold release agent / spray is required, the most basic system is a dilute solution of a polyethylene emulsion, such as Lubrex® PE-40 and Poly-EM® 40. New mold sprays that are more permanent in nature and do not require use during each heat cycle have been developed. These include Stoner A353 & A373, and DuPont's TraSys® 9825 semi-permanent release for peroxide cured FKM.

#### Postcuring

After molding, parts should be placed in a circulating air oven for a postcure at 204°C to 260°C (400°F and 500°F). The time of this postcure can vary between 5 to 24 hours, depending on the part thickness and the state of cure desired. This postcuring step enhances the mechanical strength and compression set resistance of the molded part, as shown in Figure 5.



Figure 5: Effect of Time on Compression Set in 232°C Oven Postcure Extrusion

Extrusion is another processing method commonly used with fluoroelastomers. Medium to low viscosity FKMs tend to be best for profile extrusions. Cold feeding of the stock to a relatively cool extruder barrel and screw provides uniform conveyance and prevents air entrapment. For critical fuel and filler neck extrusion applications, where the veneer is often thin and stretched, 69% fluorine Viton B-303C (formerly VTR-9209) and Viton B-204C (formerly VTR-9217) are recommended.

Extrudate smoothness depends upon the FKM polymer used, the extrusion process aid in the compound, and the stock temperature. Carnauba wax or VPA

No.2 at a level of 1.0 phr or more can aid extrusion smoothness. A front extruder zone and head temperature of 85-95°C will help insure that the process aid melts, lubricates the die, and provides a smooth extrusion.

Extrudates can be vulcanized by steam curing for 0.5 to 1.5 hours at a steam pressure of 550 kPa to 690 kPa (80 psi to 100 psi).

#### Calendering

Calendering fluoroelastomer compounds can produce air-free sheets with good surface integrity. Polymers such as Viton A-331C and B-601C are recommended for use in this process. The feed stock must be uniform in viscosity, temperature and flow volume. In addition, a uniform rolling bank must be maintained.

After calendering, the wrapped stock should remain in the liner for approximately 24 hours to ensure stress relaxation. The calendered sheet can then be cured in steam or hot air. Curing conditions vary depending on the number of wraps on the curing drum and the insulating effect of the liner material.

Calendered sheets can be postcured by festooning in an oven. To allow for proper air circulation, a distance of 10 cm (4 in.) between the festoons is recommended.

#### **Physical Properties**

Typical physical properties of commonly used fluoroelastomers, representing the A, B and F groups (both bisphenol and peroxide cure systems), are presented in Table 10.

Polymer	Viton A-401C*	Viton B-601C*	Viton F-605C*	Viton GBL-600S**
Group	А	В	F	В
Fluorine, %	66	68	70	67
Cure System	Bisphenol	Bisphenol	Bisphenol	Peroxide
Original Physicals				
Hardness, Shore A	78	78	80	70
100% Modulus, MPa	6.9	5.6	7.0	4.4
Tensile, MPa	13.4	13.2	13.9	20.4
Elongation, %	175	230	200	325
Compression Set, Method B (	O-rings)			
70 hrs. @ 200°C, %	14	31	36	26
Temperature Retraction,				
TR-10, °C	-17	-14	-6	-15
Fluid Resistance, Volume Swell, %				
Fuel C, 7 days @ 23°C	8	5	3	5
Methanol, 7 days @ 23°C	70	22	4	55
Concentrated Sulfuric Acid,				
7 days/149°C (300°F)	Dissolved	28		10

#### **Table 10: Typical Physical Properties of Fluoroelastomers**

* Compound formulation: 100 Polymer / 30 N990 Black / 6 Calcium Hydroxide / 3 Maglite® D

** Compound formulation: 100 Polymer / 30 N990 Black / 3 Zinc Oxide / 3 Diak No.7 / 3 VAROX DBPH-50

#### Safety and Environmental Considerations

Fluoroelastomers, which are processed and used worldwide, present no unusual risk or hazard compared to many polymeric materials. However, as in the compounding and processing of other elastomeric compositions, care and safe practices are required to avoid personal injury and environmental damage.

The specific safety recommendations and handling precautions provided by fluoroelastomer producers should be followed when using these polymers. Bulletin VTE-H71129-00-E1105, "Handling Precautions for Viton and Related Chemicals", printed by DuPont Performance Elastomers, is recommended as general reading.

#### by Tom Jablonowski and Jim Ahnemiller

TSE Industries, Inc. Clearwater, FL

In this chapter on polyurethane elastomers we will briefly cover cast polyurethane prepolymers and thermoplastic polyurethane (TPU), but will emphasize millable (thermoset) polyurethane rubber.

Professor Otto Bayer invented the first polyurethane elastomer in 1937. Millable polyurethane elastomers were among the first synthetic elastomers developed in the 1950's. Developments of thermoplastic polyurethane and liquid cast prepolymers followed soon after.

Polyurethane elastomers have excellent abrasion resistance, toughness, tear resistance and load-bearing ability. Polyurethanes can be cost effective despite their relatively high cost, by reducing downtime in many processing operations such as mining and paper mill operations. In these markets, urethanes are selected because they can outperform other materials by a large margin, justifying the higher raw material cost because the urethane part will last two, four or six times longer than other materials.

Polyurethane elastomers do not perform well at elevated temperatures because they have a degree of thermoplasticity, and their properties tend to deteriorate under heavy loads at temperatures around 120°C. Polyurethane also has poor resistance to moisture in hot, humid environments. Polyether urethanes have better performance than polyester urethanes in these conditions because polyesters are subject to hydrolysis. Another limitation of polyurethane is its poor resistance to strong acids and bases, as well as solvents like toluene, methyl-ethyl ketone and esters like ethyl acetate. However, there are many conditions in which urethane performs very well when exposed to water at low temperature and when exposed to certain solvents, fuels and oils.

All polyurethanes, including millable polyurethane rubber, are based on the three main ingredients: *polyol, isocyanate,* and *chain extender*. The basic reaction to produce polyurethane is described in Figure 1:

 $\begin{array}{cccc} H & O \\ & & \parallel \\ R-N=C-O & + & R'-O-H & \rightarrow & R-N-C-O-R' \\ \mbox{isocyanate} & polyol & polyure thane \\ \mbox{Figure 1: The Basic Polyure thane Reaction} \end{array}$ 

Polyols are polyethers like Polytetramethylene Ether Glycols (PTMEG), or polypropylene glycols (PPG), or polyester adipates. Recent high performance polyurethanes have been made from caprolactone and polycarbonate polyols. The polyester adipates are made from various glycols reacted with adipic acid. These glycols include ethylene glycol, propylene glycol, butylene glycol

(1,4-butanediol), neopentyl glycol, and hexanediol. Typically, combinations of these glycols are used for specific properties. Some of the polyol chemical structures are shown in Figure 2.

Poly(Ethylene Adipate)

-(O-(CH₂)5

Polycaprolactone

# HO(CH₂CH₂CH₂-O-)_nH

PTMEG (Polytetramethylene Ether Glycol)

## **Polyol Examples**

#### Figure 2: Commonly Used Polyols

On the isocyanate side, aromatics like 4,4'-methylenediisocyanate (MDI) or toluene diisocyanate (TDI) or aliphatic isocyanates like methylene bis-(4-cyclohexylisocyanate) ( $H_{12}$ MDI) are used. Specialty diisocyanates like p-phenylene diisocyanate (PPDI), naphthalene-1,5-diisocyanate (NDI) and 1,4-cyclohexyl diisocyanate (CHDI) have found high temperature and other niche applications. The chemical structures of the most commonly used isocyanates are shown in Figure 2.



## Isocyanate Examples Figure 3: Commonly Used Isocyanates

Chain extenders can be diols like ethylene glycol, 1,4-butanediol, resorcinol based HQEE (hydroquinone di-(beta-hydroxyethyl)ether) and HER (hydroquinone di-(beta-hydroxyethyl) ether) and 2-methyl-1,3-propane diol (MP diol). Common

diamine chain extenders are used with TDI based prepolymers are methylene bis-ortho-chloroaniline (MBOCA), Ethacure 300-dimethylthiotoluenediamine (DMTDA), or 4,4'-methylene-bis-(3-chloro-2,6-diethylaniline (MCDEA). For millable polyurethane, glycerol-monoallylether and trimethylolpropanemonoallylether are used for sulfur vulcanization through the allylic unsaturation pendant to the main chain. The chemical structures of some of the widely used chain extenders are shown in Figure 4.



HO-CH₂CH₂-OH Ethylene Glycol

MBOCA Methylene Bis(Orthdaniline)

HO-CH₂CH(OH)CH₂OCH₂CH=CH₂ GAE Glycerol Allyl Ether

# **Chain Extender Examples**

# Figure 4: Widely Used Chain Extenders

*Millable polyurethane* rubbers are usually produced with a final stoichiometric excess of hydroxyl groups. This is defined as "under indexed". "Index" is the ratio of the amount of isocyanate (NCO) to reactive hydroxyl (OH) groups. Millable polyurethanes are on the "OH" side and are processed like conventional rubbers.

*Cast polyurethane* pre-polymer systems are made by reacting polyol with a surplus of isocyanate in order to be liquid during processing. During final processing, the liquid prepolymer is mixed with chain extenders, poured into a mold and oven cured to make the final part.

Thermoplastic polyurethanes are mostly produced in one step with a slight excess of isocyanate (NCO) versus the combined OH number of polyol and chain extender. By definition, thermoplastic polyurethane is melt processed by means of extrusion, injection molding, calendering and thermoforming.

Millable polyurethane is produced with a final stoichiometric deficiency of isocyanates in order to obtain a stable Mooney viscosity. Polyurethane rubber is therefore in need of further crosslinking or vulcanization by using sulfur or peroxide as vulcanizing agents to form strong, covalent chemical bonds between the polymer chains. These curatives are mixed into millable polyurethane rubber using a two-roll mill.

# Millable Polyurethane Rubber Produced with a stoichiometric deficiency of diisocyanate Castable Polyurethane Prepolymer Produced with a high excess of diisocyanate Thermoplastic Polyurethane (TPU) Produced with a slight excess of diisocyanate

#### Table 1: Comparison of Polyurethane Rubber to Other Polyurethane

#### Liquid Cast Polyurethane Prepolymers

Urethane prepolymers allow the fabricator to produce polyurethane parts by liquid casting technique. A heated prepolymer (80°C to 100°C) is mixed with a curative in a certain stoichiometric proportion, poured into a mold and allowed to cure in an oven. Parts are then de-molded and often postcured to achieve maximum physical properties. Liquid prepolymer systems require less labor, energy and equipment than conventional rubber fabricating processes. These polyurethanes have excellent physical properties and are considered engineering materials.

Polyurethanes are noted for abrasion resistance, toughness, tear strength and load bearing ability. The cast prepolymer systems have lower tooling costs and equipment costs for small production runs.

Liquid cast polyurethane prepolymers contain terminal isocyanate groups (NCO) which react chemically with hydroxyl or amine chain extenders (called curatives) to form polyurethane elastomers. Prepolymers are made of polyethers and polyesters and various diisocyanates. MDI prepolymers generally use diols (1, 4-butanediol, 1, 6-hexanediol) and triols (trimethylolpropane, triisopropanolamine) or combinations of the two as curatives. TDI prepolymers use mostly diamine curatives like MBOCA.

It is very important to keep all components of the cast recipe dry. Isocyanate reacts with water to form carbon dioxide bubbles which can be trapped in the casting resulting in a rejected part. Exposing the prepolymer to excessive heat will cause the isocyanate groups to react with one another. This reaction results in high viscosity which makes processing difficult.

Most cast urethane parts are made using hand casting of small batches. Care must be taken to ensure good mixing and long enough pot life. Large rollers and high volume production parts are typically processed using casting machines which meter the prepolymer and curative continuously. Commercially available prepolymers and curatives are listed in Table 2. Each system provides a unique level of price, performance and processing.

Recent improvements include prepolymers with very low free TDI content, and polyether backbones with a more regular configuration and tighter molecular weight distribution. These improvements enhance processing, worker safety and performance. The casting process starts with heating to the prepolymer to a temperature of 70°C to 90°C. A vacuum is placed on the heated prepolymer to remove dissolved gases. The curing agent (diol or diamine) is heated separately. The two components are mixed with vigorous agitation and poured into a preheated mold. Degassing may again be used to remove air bubbles

from the mixture in the mold. The part is cured in the mold for five minutes to one hour at 93°C to 149°C. The time and temperature are determined by the development of sufficient "green strength" to allow removal from the mold without distortion. An optional post cure may be used, commonly 4 to 24 hours at elevated temperature (typically 100°C), or 1 to 4 weeks at room temperature.

Manufacturers of cast urethane show many examples of applications on their web sites. Cast polyurethane applications include: industrial wheels, roll coverings, metal-forming dies, snowplow blades, valve linings, silk screen wipers, tank treads, snow blowers, instrument protection, cogs, star wheels, sprockets, gears, flexible couplings, bowling balls, mining applications, springs, log pushers, filter press leaves, amusement ride wheels, firefighting water buckets, oil field specialties, roller skates, in-line skates and skateboard wheels.

	Trade Names		
Supplier	Prepolymers	Curatives	
Air Products	Airthane [®] Versathane [®]	Versalink [®] Lonzacure [®] MCDEA	
Albemarle Corporation		Ethacure®	
Anderson Development	Andur®	Curene®, MBOCA	
Baule SAS/Bayer Material Science	Baytec [®] Vulkollan [®]		
BASF		1,4-BDO	
Chemtura	Adiprene [®] , Vibrathane [®] Royalcast [®]	Caytur [®] Vibracure [®] A133	
Conap	Conathane®		
Freeman Chemical	ISP, Interpol®		
ISP (GAF Corp.)		1,4-BDO	
ITWC		Xthane	
Omni Specialty Corporation		MBOCA	
Polaris Corp.	PF Prepolymers		
Polyurethane Corp. of America	PCA Prepolymers		

#### Table 2: Suppliers of Urethane Prepolymers and Curatives (USA)

#### **Thermoplastic Polyurethane**

Thermoplastic polyurethane (TPU) is a block copolymer composed of short polyurethane hard segments, and long polyurethane chains known as soft segments. The soft segments provide flexibility while the hard segments provide the rigid structure resulting in the elastomeric properties of the TPU.

The hard segment can be either aromatic or aliphatic. Aromatic TPU's are based on isocyanates such as MDI, while aliphatic TPU's are based on isocyanates like H₁₂ MDI. When these isocyanates are combined with short-chain diols like 1,4- butanediol, they become the hard block. Most TPU elastomers are made

from aromatic diisocyanates, but when maintaining color when exposed to sunlight is important, aliphatic diisocyanates are employed.

The soft segment can be polyether, polyester, or caprolactone polyols. When the application requires hydrolytic stability then a polyether polyol is used to make the TPU. If oil or fuel resistance is needed, a polyester-based TPU is selected. Caprolactone TPU combine some of the features of both ether and ester polyols. For even greater range of physical properties, the molecular weight, ratio and chemical type of the hard and soft segments can be varied.

Like all thermoplastics TPU's are melt-processable. TPU's are processed on extrusion, injection, calendering, blow and compression molding equipment. Other processes such as vacuum-formed or solution-coated are also employed. Various compound ingredients can be added to TPU. Hydrolytic stabilizers, antioxidants, light stabilizers and colors can enhance the use of TPU for a variety of applications.

Processing TPU for injection molding requires drying in a dehumidifying hopper dryer for 2 hours, with air flow temperature at 85°C to 105°C. If a hot air oven is used, spread the TPU pellets evenly on a tray 2 cm to 4 cm thick and heat 1 to 4 hours at 93°C to 104°C, depending on the type of TPU, prior to molding. Injection pressures range from 10 MPa to 86 MPa at temperatures ranging from 170°C to 225°C. Melt processing temperatures can be 180°C to 230°C with mold temperatures generally at 29°C to 50°C.

TPU is processed on unvented single screw extruders with very good temperature control. TPU must be properly dried prior to entering the feed zone of the extruder. TPU in its melt state has a relatively narrow process temperature range, and as a non-Newtonian material exhibits melt flow behavior where melt viscosity changes rapidly from high to low viscosity. A typical temperature profile for extrusion of TPU is: 180°C feed zone; increasing to 190°C transition zone; die temperature at 195°C and a melt temperature of 205°C. The preferable L/D ratio for the extruder is 24:1 to 30:1 to ensure a uniform melt. A single screw design of 24:1 L/D and a compression ratio of 3:1 are desirable.

TPU resins offer exceptional properties for a broad range of applications. Recent developments in soft TPU in hardness of 80 Shore A provides a soft touch to molded articles. TPU can be made to comply with FDA food contact regulations. Typical applications for TPU are automotive instrument panels, caster wheels, handles for power tools, extruded film and sheet. Many medical devices and sporting goods are molded from TPU.

Supplier	Trade Name	Туре
A. Schulman Inc.	Polypur [®] TPU	Unspecified
Arkadia Plastics	ARK [®] TPU	Polyester
BASF Corporation	Elastollan® TPU	Polyester, polyether
Bayer Material Science	Desmopan [®] TPU	Polyester, polyether
Bayer Material Science	Texin [®] TPU	Polyester, polyether
COIM S.p.A	Laripur [®] TPU	Polyester, polyether, caprolactone
Eastman Chemical	Neostar® TPU	Polyether
Huntsman Corporation	Irocoat [®]	Caprolactone, polyester, polyether, polycarbonate
Lubrizol Advanced Materials	Estane [®] , Estaloc [®] , Tecoplast [®] , Tecothane [®] TPU	Caprolactone, polyester, polyether

Table 3: Suppliers of Thermoplastic Polyurethane (USA)

# Millable Polyurethane Rubber

Millable (and other) urethanes come in two general types: polyether urethanes and polyester urethanes. Within these categories, the properties can vary depending on the polymer composition, but general comparisons of the properties achieved by the two types are in Table 4 below.

Property	Polyether	Polyester
Abrasion Resistance	E	E
Coefficient of Friction	High	Medium
Wet Traction	F	G
Dry Traction	E	F
Water Resistance	VG	P-VG**
Oil Resistance	G	E
Fuel Resistance	F	G
Solvent Resistance	F	VG
Heat Resistance	G	VG
Compression Set	F-G	G-E
Low Durometer	G	E
Bonding to Metal	E	G
Rebound	High	Low-High

Table 4: Comparison Polyether and Polyester Properties*

*F = Fair, G = Good, VG = Very Good, E = Excellent

**Very Good, non-permanent, hydrolysis resistance with hydrolysis stabilizers
Commercial grades of millable polyurethanes are shown in Table 5.

Trade Names	Supplier	Vulcanization	Characteristics					
Polyether Urethanes								
Millathane® CM	TSE Industries	Sulfur, Peroxide	Hydrolysis resistance, Dynamic and very good low temperature properties					
Millathane E34	TSE Industries	Sulfur, Peroxide	Excellent hydrolysis resistance, easy processing					
Millathane 26	TSE Industries	Peroxide	Food handling (FDA) application like belting, rollers					
Millathane 97	TSE Industries	Peroxide	Transparent, excellent abrasion resistance					
Urepan [®] 50EL- 06G	Rhein Chemie	Sulfur, Peroxide	High resilience, hydrolysis resistance					
Millathane E40	TSE Industries	Sulfur, Peroxide	Excellent low temperature properties, easy processing					
Polyester Urethanes								
Millathane 66	TSE Industries	Peroxide	Good heat resistance, compression set and good low temperature properties					
Millathane 5004	TSE Industries	Peroxide	High tear strength oil and solvent resistance					
Millathane 76	TSE Industries	Sulfur, Peroxide	Superior oil and fuel resistance, best for low hardness compounds					
Millathane HT	TSE Industries	Sulfur, Peroxide	Good low temperature properties and frictional characteristics					
Urepan 600	Rhein Chemie	Isocyanate	Excellent strength properties at high hardness					
Urepan 640G	Rhein Chemie	Peroxide	Good oil and fuel resistance, good impermeability to gases					
Urepan 641G	Rhein Chemie	Peroxide	Good oil and fuel resistance, good hydrolysis resistance					
Urepan 643G	Rhein Chemie	Peroxide	Good oil and fuel resistance, good low temperature properties					

# Table 5: Millable Polyurethane Grades

# Compounding

Millable polyurethane is compounded similar to other conventional thermoset rubber materials and is processed on typical rubber equipment.

# Curatives

Millable urethanes can be vulcanized with *sulfur*, *peroxides* and *isocyanates*, although different grades may be specific to one cure method or another.

*Sulfur* - For sulfur curability, a reactant with double bonds, such as GAE (glycerol allyl ether) is introduced into the polymer chain at a low level, typically from (1 to 10%). Since the double bonds are not in the backbone of the polymer chain but pendant to the chain, the polymer has very good/excellent resistance to oxygen and ozone attack.

The original sulfur cure system was produced by DuPont when they developed Adiprene C (similar to Millathane CM), and a variation of that cure system is still the primary sulfur cure system used today. It contains a combination of ALTAX[®] (MBTS), CAPTAX[®] (MBT), Thanecure[®] ZM (a zinc chloride-MBTS complex) and sulfur. Zinc stearate is included as an activator for the cure system, and it also functions as a process aid. A comparison of the "classic" cure system vs. the "standard" sulfur cure system is show in Table 6.

Ingredients	<u>Classic</u> phr	<u>Standard</u> phr
Millathane CM	100.00	100.0
Zinc Stearate	0.50	0.5
N330 Carbon Black	25.00	25.0
DBEEA (TP-95)	5.00	5.0
ALTAX (MBTS) Accelerator	4.00	4.0
CAPTAX (MBT) Accelerator	1.00	2.0
Thanecure ZM	0.37	1.0
Sulfur		1.5
Totals	136.62	139.0
Original Physical Properties, Press Cured @ 160°C		
Cure Time, mins.	19	8
Tensile, MPa	29	33
Physical Properties After Heat Aging in Hot Air, 70 hrs. @ 100°C		
Tensile, % Change	-2	-38
Elongation, % Change	-26	-53
DIN Abrasion Loss, mm ³	76	55
Compression Set, Method B, 22 hrs. @ 70°C		
%	52	43

Table 6	: The	Classic	and	Standard	Sulfur	Cure S	vstems
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As seen in Table 6, the standard sulfur cure system provides, vs. the "Classic" cure system:

- Shorter cure times
- Higher tensile strength
- Better abrasion resistance
- Lower compression set
- · Poorer retention of properties after heat aging

*Peroxide* cures can be used for all the millable urethanes, with the differences in properties between sulfur and peroxide cures as seen in the Table 7 below.

Property	Sulfur	Peroxide
Tensile Strength	+	-
Tear Strength	+	-
Compression Set	-	++
Heat Aging	-	++
Reversion Resistance	-	++
Flex Resistance	+	-
Lower Heat Build-up	+	-
Abrasion Resistance	++	-
Solvent and Oil Resistance	+	++

Table 7: Comparison of Properties for Sulfur vs. Peroxide Cures

Typical peroxides used in millable urethanes include VAROX[®] DCP, VAROX DBPH and VAROX 231. The specific type of peroxide to be used is dependent on the curing temperature. The optimum level of peroxide used will vary depending on the specific grade of millable urethane, ranging from about 0.5 phr for Millathane HT and Millathane 97, to 2-4 phr for Millathane 66 and Millathane 5004.

Varying the peroxide level from 4 to 8 parts of VAROX DBPH-50 in the millable polyester urethane Millathane 66, as the data in Table 8 demonstrates, when the peroxide level is increased there is a:

- Significant increase in tensile stress (modulus)
- Moderate decrease in elongation
- Slight increase in hardness
- · Slight reduction in tensile and tear strength
- Improvement (reduction) in compression set

Ingredients	phr	phr	phr	phr
Millathane 66	100.0	100.0	100.0	100.0
Stearic Acid	0.2	0.2	0.2	0.2
Ultrasil [®] VN3	25.0	25.0	25.0	25.0
Silquest [®] A-172	0.5	0.5	0.5	0.5
TP-95	2.0	2.0	2.0	2.0
Millstab [™] P	2.0	2.0	2.0	2.0
Struktol® WB222	1.0	1.0	1.0	1.0
SR-350	2.0	2.0	2.0	2.0
VAROX DBPH-50	4.0	5.0	6.0	8.0
Totals	136.7	137.7	138.7	140.7
Original Physical Properties				
Hardness, Shore A	73	75	75	75
100% Modulus, MPa	2.7	3.3	3.5	4.4
300% Modulus, MPa	11.0	15.4	15.6	22.7
Tensile, MPa	34.6	29.8	31.9	27.6
Elongation, %	535	425	435	335
Tear, Die C, kN/m	46.0	42.9	42.1	36.6
DIN Abrasion Loss, mm ³	75	69	76	88

Table 8: Results of Varying Peroxide Levels in Millathane 66

#### Compression Set per ASTM D 395 Method B



Peroxide (VARoX DBPH-50), phr

Figure 5: Compression Set vs. Levels of Peroxide

Coagents are very often used in peroxide cures to modify processing and properties. The most commonly used coagents are the difunctional and trifunctional liquid methacrylates (i.e. DEGDMA and TMPTMA, respectively), with

the high vinyl butadiene resins and cyanurates (TAC) used to a lesser extent. TMPTMA is very effective in raising hardness while reducing compound viscosity, although high levels can produce "brittle" compounds, with low elongation and low tear strength. Blends of difunctional with trifunctional methacrylates will give improved tear and elongation, so high hardness compounds with good flexibility can be achieved.

A comparison of sulfur and peroxide curing of a polyester millable urethane is shown in Table 9. As this data shows, the sulfur cure provides better tensile properties, while the peroxide cure has improved heat aging and compression set properties. Polyether millable urethanes react similarly to peroxide and sulfur cures, although they are more sensitive to peroxide curing because of the tendency of the peroxide to cleave the ether linkage in the polymer chain.

	<u>Sulfur</u>	<u>Peroxide</u>
Ingredients	phr	phr
Millathane 76	100.0	100.0
Zinc Stearate	0.5	
Stearic Acid		0.5
N220 Carbon Black	20.0	20.0
ALTAX (MBTS)	4.0	
CAPTAX (MBT)	2.0	
Thanecure ZM	1.0	
Sulfur	1.5	
VAROX DCP-40C		3.0
Totals	129.0	123.5
Original Physical Properties, Press Cured 15 min. @ 155°C		
Hardness, Shore A	65	65
300% Modulus, MPa	12.0	22.0
Tensile, MPa	34.9	29.0
Elongation, %	570	360
Tear C, kN/m	64.8	38.5
Physical Properties After Aging in Air, 70 hrs. @ 100°C		
Hardness, Pts. Change	+10	0
Tensile, % Change	-18	+2
Elongation, % Change	-39	-10
Compression Set, Method B, 22 hrs. @ 100°C		
%	65	17

### Table 9: Sulfur vs. Peroxide Cures in Polyester Millable Urethane

Certain grades of millable urethanes are designed for isocyanate curing only. Compounds of these polymers tend to give very good mechanical properties at high hardnesses, but compression set values increase with increasing hardness. Compounds using the isocyanate cure system are very fast curing, have extremely short shelf lives, and typically must be cured at temperatures below 140°C. Examples of isocyanate-cured millable urethane are shown in Table 10.

Ingredients	phr	phr	phr
Urepan 600	100.0	100.0	100.0
Stearic Acid	0.5	0.5	0.5
Crosslinker 30/10		7.0	10.0
Desmodur [®] TT/G	8.0	20.0	27.0
Rheongran® AUI-70	0.5	0.5	0.5
Totals	109.0	128.0	138.0
Original Physical Properties			
Hardness, Shore A (Shore D)	70	90	95 (50)
300% Modulus, MPa	7.6	10.1	11.2
Tensile, MPa	24	28	33
Elongation, %	680	600	560
Tear, Die C, kN/m	30	47	53
DIN Abrasion Loss, mm ³	20	30	32
Compression Set, Method B, 24 hrs. @ 70°C			
%	35	45	65

Table 10: Isocyanate-Cured Millable Urethane

# Fillers

The same types of fillers that are used in other rubbers are also used in millable urethanes, although typically at more moderate levels (10-50 phr). Highly reinforcing carbon blacks such as N330 (HAF) give good reinforcement, as do precipitated and fumed silicas. Less reinforcing fillers, such as larger particle size blacks (i.e. N550, N774) and mineral fillers, such as clays and talcs, can be used to extend the rubber for lower cost and processing improvement, at some sacrifice in physical properties. Compounds that have significant amounts of silicas or clays can benefit from the addition of silane coupling agents, which generally increase tensile stress (modulus), tear strength and abrasion resistance. Mercapto- and sulfur-silanes are commonly used with sulfur cures, while vinyl-silanes are typically used with peroxide cures.

# Plasticizers

Many of the plasticizers used in polar rubbers, like NBR, can also be used in millable urethanes for reducing compound viscosity, improving flow and modifying cured hardness. Typical plasticizers include DBEEA (TP-95), DBEEF (TP-90B), Di-propylene Glycol Di-benzoate (Benzoflex[®] 9-88), and the coumarone indene resins (for sulfur cures only).

#### Process aids

Millable urethane compound will typically contain one or more process aids to help processing, reduce sticking to metal surfaces during mixing and molding, and to improve mold flow. Zinc stearate is an effective process aid and is also used as an activator in sulfur cures. Peroxide cures will typically contain a small amount of stearic acid (~0.25 phr), as high levels tend to bloom and promote hydrolysis of polyester urethanes. Other process aids such as Struktol WB222, VANFRE® AP-2 and low melting polyethylene (AC® 617A) can also be used as

process aids, typically at 0.5-3 phr.

# Other additives

As polyester urethanes will undergo hydrolysis when exposed to water, carbodiimide hydrolysis stabilizers can be added to improve hydrolysis resistance. The polymeric carbodiimides (i.e. Millstab P and Stabaxol[®] P) have improved performance compared to the monomeric and oligomeric grades, and should be used at 1-5 phr levels, depending on the application and the end part's expected environment. Some grades of millable urethane have an hydrolysis stabilizer incorporated into them for better polymer and cured part life.

Transparent grades of millable urethane require the inclusion of small amounts of antioxidant and ultraviolet light stabilizers for good UV light and yellowing resistance. The combination of Songnox[®] 1010, Songsorb[®] 3280 and Songlight[®] 2920 at 0.25 phr each, has been found to be effective.

# Processing

Millable urethanes can be mixed on two-roll mills or internal mixers, with similar mixing procedures as other rubbers. Millable urethanes tend to build up significant heat during mixing and tend to stick to the metal surfaces of mixers, especially when the metal is warm or hot, so it's important to keep the stock and mixer cool. For mills and internal mixers, cooling water should be on full throughout the mix and dump temperatures should be <130°C without curatives, and <100°C with curatives. Also, process aids should be added at the beginning of the mix cycle and blended well, before other ingredients are added.

A typical mill mixing procedure is:

- 1. Band rubber, add process aids, blend well.
- 2. Add ¹/₂ of the filler, colorants and other solid additives, blend well.
- 3. Add 1/2 of the filler plus the plasticizer, blend well.
- 4. Add other additives, blend well.
- 5. If batch is not too hot, curatives can be added, blend well, slab off.

A typical internal mixer mixing procedure is:

- 1. Add rubber and process aids, ram down, clock to zero.
- 2. 1' Add ½ of the filler, colorants and other solid additives, ram down.
- 3. 2-4' Sweep, add 1/2 of the filler and the plasticizer, ram down.
- 4. 3-6' Sweep, add other additives, ram down.
- 5. 4-7' Dump (100° 130°C).
- 6. Add curatives on cool mill or in a second internal mixer pass.

# Applications

Millable urethanes are used in many applications that require the good combination of properties that urethanes are known for, among them high abrasion resistance, excellent tensile and tear strength, and excellent oil resistance. Typical applications include rubber covered rollers for printing and

paper handling, belting, seals and diaphragms and footwear. Starting-point formulations are shown in Tables 11, 12 and 13.

Ingredients	phr
Millathane E34	100.0
Struktol WB222	1.0
Zinc Stearate	0.5
Ultrasil VN3	30.0
TP-95	5.0
Si 69	1.0
ALTAX (MBTS)	4.0
CAPTAX (MBT)	2.0
Thanecure ZM	1.0
Sulfur	2.0
Total	146.5
Mooney Viscosity, ML 1+4 (100°C)	62
Original Physical Properties, Press Cured 17 min. @ 155°C	
Hardness, Shore A	70
100% Modulus, MPa	2.6
200% Modulus, MPa	5.1
300% Modulus, MPa	9.0
Flongation %	575
Tear Die C kN/m	48.8
Tear Die B, kN/m	67.4
DIN Abrasion Loss, mm ³	54

Table 11: Rubber Covered Roller for Extrusion Building/Autoclave Curing

Ingredients	phr
Millathane 97	100.0
Stearic Acid	0.20
Wacker HDK N20 fumed silica	20.00
Silquest A-172	0.50
Songnox 1010	0.25
Songsorb 3280	0.25
Songlight 2920	0.25
DEGDMA	3.00
VAROX 231	0.50
Total	124.95
Mooney Viscosity, ML 1+4 (100°C)	75
Original Physical Properties, Press Cured 3 min. @ 155°C	
Hardness, Shore A	65
100% Modulus, MPa	1.9
200% Modulus, MPa	3.2
300% Modulus, MPa	5.0 26.1
Flongation %	20.1
Liongalion, 70 Tear Die C. kN/m	31.5
Tear Die B, kN/m	55.5
DIN Abrasion Loss, mm ³	62

Table 12: Transparent Shoe Sole and Molded Applications

# Table 13: Belting for Food Handling Applications*

Ingredients	phr
Millathane 26	100.0
Stearic Acid	0.3
Ultrasil VN3	25.0
TP-95	2.0
Struktol WB222	2.0
Liquid Polybutadiene Resin	10.0
VAROX DCP-40C	5.0
Total	144.3
Mooney Viscosity, ML 1+4 (100°C)	44
Original Physical Properties, Press Cured 10 min. @ 160 C	
Hardness, Shore A	62
100% Modulus, MPa	1.7
200% Modulus, MPa	3.3
300% Modulus, MPa	6.9
Tensile, MPa	23.1
Elongation, %	490
Tear Die C, kN/m	25.4
DIN Abrasion Loss, mm ³	88

* Ingredients are compliant with FDA regulation 21CFR177.2600

# Summary

Millable urethanes are specialty polymers that have found use in applications that require the unique combination of properties that urethanes offer: excellent abrasion resistance, tensile and tear strength, oil resistance, low temperature flexibility and ozone resistance not found in traditional rubbers like natural rubber, EPDM, NBR or Neoprene.

Isocyanate-cured polyurethane rubber has high hardness, abrasion resistance and toughness that match the properties of TPU and cast elastomers. A newly developed millable polymer filled a gap in the range of commercial polymers by qualifying for FDA wet food handling requirements. This development expanded the range of applications for millable urethanes, making them more competitive with cast urethanes and thermoplastic polyurethanes.

High-hardness TPU and cast polyurethane elastomers bridge the gap between plastics and rubber. These elastomers have outstanding toughness, durability and process ease. Processing TPU by injection molding has been made easier through the development of lower viscosity materials. Low hardness TPU and clear TPU have opened up new applications such as shoe soling, handles and flexible tubing.

Unlike TPU and millable polyurethane rubber, cast urethane prepolymers are liquids which are easily mixed and dispensed into molds at low pressure. Consequently, tooling is much less expensive and rapid prototyping can be quickly accomplished. Tooling does not need to withstand thousands of pounds of pressure to make polyurethane parts, so parts can be molded to almost any shape, thickness or size. Cast polyurethane has an advantage over TPU's and millables in having a broader hardness range and so it is suitable for low-, medium- and high-hardness applications.

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#### SPECIALTY SYNTHETIC RUBBERS

### by Daniel L. Hertz, Jr.

# Seals Eastern, Inc. Red Bank, NJ

Specialty synthetic rubbers are usually expensive, but are economically justified by having one or more unique properties required for some specific demanding service. They account for less than 0.5% of the synthetic rubber volume, but are indispensable in many critical markets. This chapter will highlight some of these properties, probably in more detail than one might initially care to absorb, but far less than is required for many specific applications. Rubber is an engineering material, and many applications place unique mechanical demands on the end product. The external influences will be outlined in more detail later in this chapter.

# **Rubber and Materials Science**

The first chapter of this book notes that most of the precursor monomers are gases, so that rubbers are in effect supercondensed gases. The typical rubber density is about 1000 times greater (10³) than that of its gaseous monomers, and the viscosity about 10¹¹ times higher than that of the gas. It is not surprising that the ideal gas equation PV=nRT, and modifications thereof, are recurrent in more detailed discussions of the elasticity, permeability and swelling of rubber.

This chapter will focus on the elemental consideration that n (number of molecules) and R (gas constant) are fixed in any rubber component. Thus if T (temperature) increases so does V (volume), and the molecules have more space to move about, making the rubber more "lively". Remember that heat also is the mobile energy of atoms. Conversely, if the pressure increases (due to mechanical loading), V decreases, causing an increase in hardness and modulus.

### Structure - Property Relationships

The specialty elastomers discussed in this chapter have unique properties which are best understood by considering their structure-property relationships. By "structure" is meant both chemical and physical characteristics, and how they interact in a system. Chapter 1 notes the importance of molecular weight to mechanical properties. This can be expanded to include fatigue life, fracture resistance and better retention of physical strength at higher temperatures.

Historically, molecular weight has been an indicator of physical properties. Increasing molecular weight is usually indicated by increasing Mooney viscosity. The higher viscosity elastomers typically have higher tensile strength and elongation and better compression set resistance.

For hydrocarbon resistance, polarity must be incorporated into the molecular structure. Polarity is achieved by the substitution of very light hydrogen (atomic number 1) by heavier atoms such as nitrogen (7), oxygen (8), fluorine (9) and chlorine (17). The polar group of each elastomer is listed in Table 1. Molecular

weight comparisons become less significant with these substitutions. A better understanding is achieved by considering the monomer as a constitutional repeating unit (CRU), i.e. -[C-C]- indicating one CRU. The long-chain molecule perspective is reformed; typically a low Mooney might be 500-1000 CRUs, a medium Mooney 1200-2000 CRUs and a high Mooney 2000-5000 CRUs. Higher CRU values are more difficult to process, with actual shearing of the elastomer chains occurring during routine factory processing.

The effect of side chains or branching is also a major component of molecular structure. Table 1 outlines branch structures based on the effect of their physical size, since they contribute to some unique mechanical properties in addition to making the polymer rubbery.

#### Viscoelasticity

Rubbers are unique as engineering materials. Their ability to simultaneously store and dissipate energy through their characteristic large strain behavior having time dependence is called viscoelasticity. Using the spring and dashpot combinations as a model it is simple to illustrate the elastic component (spring) and the viscous, time dependent component (dashpot). A molecular approach uses rotational energy barriers to model the elastic component and monomeric friction coefficients in order to describe the viscous or time dependency response. It is this viscoelastic property we are specifically interested in for these specialty synthetic rubbers and it will be described by reviewing their dynamic mechanical properties. It is important to remember that creep, stress-relaxation, dynamic loss tangent, hysteresis and heat generation are interrelated due to the viscoelastic nature of rubber.

#### Dynamic Mechanical Properties

When this term is used we instinctively think of tires, motor mounts or shock absorbers. This list can be expanded to include shaft seals, static and dynamic o-ring applications, lip seals and many other products.

Most engineering applications of rubber are under some degree of deformation or load. Basic to this discussion is that the dynamic mechanical properties of rubber, within reasonable deformations (<25%), are *independent* of the magnitude of deformation. Conversely, they are strongly dependent on the rubber's molecular architecture, temperature, time (frequency) and, to some extent, compounding.

Dynamic mechanical property data are developed by mechanically displacing the rubber specimen in shear or torsion, by applying a sinusoidal deformation at a series of fixed frequencies. The test instrument applies the principle that when a force is applied to rubber, the rubber does not instantaneously take the appropriate strain level or displacement. The strain *always* lags the stress (the internal resistance to the applied force), with the actual resulting stress displaced in a negative direction along the angular displacement axis. Rubber, when tested in shear exhibits a linear relationship of stress versus strain, and the resulting value is shear modulus G. The typical test instrument applies a measured mechanical displacement to the rubber sample with a measured load. The resulting output – a vector force, having both magnitude and direction (the phase angle difference between input and output), is solved trigonometrically. The output value, called complex shear modulus G*, is the result of two imaginary values:

- a. The elastic component (Hooke's Law), in phase with the strain is called the "shear storage modulus G'"
- b. The viscous component (time/temperature dependent), is 90° out of phase since it is unrecoverable energy (heat) and is called the *"shear loss modulus G"* "

As illustrated below, the two components are now resolved by solving a right triangle where the hypotenuse (magnitude of the instrument output – stress) and phase angle difference (tangent of the phase angle or tan  $\delta$ ) are the known values developed by the test instrument.



In engineering terms we are moving a force through a distance, thus performing actual work. The shear storage modulus G' is recoverable energy. Shear loss modulus G'' is unrecoverable and is the source of dynamic heat build-up. Thus a small tan  $\delta$  is preferred in applications of an elastomeric component subject to continuous cyclic loading. Conversely, a high tan  $\delta$  value is preferred for intermittent or random loading of an elastomeric component. Actual elastic recovery time intervals can be calculated from dynamic mechanical data. These recovery times can be matched to the disturbing frequency whose time interval is determined by the equation:

Time interval =  $\frac{1}{2} \pi Hz$  (Hz - cycles per second)

The technique can be used to determine the sealing integrity of any seal subject to external cyclic or non-cyclic disturbances in service. Logically, if the elastomeric recovery time (determined by dynamic testing) is shorter than the time disturbance interval, leakage can occur.

Rubber is essentially an isotropic material, so Young's modulus E is equivalent to 3 times shear modulus G. Table 2 reports the data in Young's modulus E since seals are typically loaded in compression, and provides a better understanding and comparison of the dynamic mechanical properties of the specialty synthetic rubbers discussed in this chapter.

Name	Polyacrylate	Vamac®	Aflas®	Epichloro- hydrin	Fluoro- silicone	Perfluoro- elastomer
ASTM D 1418 Designation	ACM	EEA	FEPM	CO/ECO	FVMQ	FFKM
Backbone Structure	-[C-C]-	-[C-C]-	-[C-C]-	-[C-C-O]-	-[Si-O]-	-[C-C]-
Branch Structure (Side Chains)	-COR	-COC	$-CH_3$	-CH ₂ CI	-C-C-C-	$-OCF_3$
Polar Group(s)	CO₂R	$-CO_2CH_3$	-CF ₂	-CH ₂ CI	$-CF_2, -CF_3$	-OCF ₃ ,CF ₂
Bond Energy, Backbone (kj/mole)	83	83	83	93	106	83
Aged in ASTM IRM 903, 70	hrs. @125°C					
Volume Swell, %	20-60	50	<10	10-20	10	<2
Aged in Toluene (Fuel), 22h	nrs. @ 20°C					
Volume Swell, %	425	310	40	150	20	<2
Density, Mg/m ³	1.1-1.15	1.04	1.55	1.36/1.27	1.4	2.01
Type/Class SAE J2000/ ASTM D 2000 Material	DF,DH	EE,EF	ΗK	CH,CE	FK	KK
Durometer, Shore A, Range	40-90	40-90	65-95	40-90	40-80	70-95
Tensile, MPa (max)	16	15	20	18/17	10	15
Elongation, % (max)	400	500	300	350/400	400	400
Glass Transition Temp, °C	-54/24	-32	-3	-52/-22	-80	-19

Table 1: Basic Properties of Specialty Synthetic Rubbers

# Table 2: Dynamic Mechanical Properties at 10Hz (63 radians per second)

				Epic	hloro-	Fluoro-	Perfluoro-
Name	Polyacrylate ¹	Vamac	Aflas	hy	drin ²	silicone ³	elastomer⁴
Hardness, Shore A	67	68	70	73	74	50	75
				CO	ECO		
Glass Transition Temp	., T _g (°C) as mea	sured by:					
Loss Modulus, E" (m	ax) -32	-18	+11	-14	-32	-60	+1/+7
Tangent $\delta$ , (max)	-25	-12	+18	-1	-27,-20	-50	+15/+21
Tangent $\delta$ ,							
@ Max.	0.75	0.60	1.49	0.40	0.19	0.41	0.89/1.29
@ 20°C	0.17	0.20	1.34	0.22	0.11	0.20	0.87/1.26
@ 100°C	0.05	0.20	0.15	0.06	0.09	0.11	0.06/0.67
@ Max. + 60°C	0.12	0.20	0.13	0.09	0.09	0.21	0.01/0.84
Complex Dynamic Tensile Modulus, E*							
@ 20°C	21.0	16.0	45.4	30.7	54.3	9.2	30.0/75.0
@ 100°C	8.2	5.8	8.4	135	25.6	5.0	4.1/9.0
Change 20°C vs. 100°	C -61%	64-%	-81%	-56%	-53%	-46%	-94/-81%

¹HyTemp[®] ²Hydrin[®] (CO), Hydrin CM (ECO) ³Silastic[®]LS2332

⁴Range of five (5) FFKM's

#### **Polyacrylate Rubbers**

Polyacrylate rubbers, or more accurately acrylic-based elastomers, were an outgrowth of early synthetic rubber development in Germany prior to World War I. The rubbery nature of poly(n-alkyl) acrylates was identified in the mid 1930's. The first commercial acrylic rubber was introduced by B. F. Goodrich in 1947. Parallel work was done by the U. S. Department of Agriculture, which was trying to develop a commercial product from whey, a cheese by-product. Although the acrylate structure had potential crosslink sites, it was found to be easier to copolymerize with a second monomer having specific, readily used crosslink sites.

# Supplier

Zeon Chemicals markets polyacrylates in North America under the trade name HyTemp.

# Applications

Acrylic rubbers afford superior resistance to heat, ozone, and ultraviolet light because they do not have any unsaturation in their backbone. The very polar acrylate group not only develops oil resistance, but is also resistant to crosslinking by sulfur-bearing lubricants. Sulfur compounds are increasingly used in the extreme pressure (EP) lubricants necessary for high performance automotive applications. Sulfur, of course, is a typical vulcanizing agent for unsaturated elastomers.

# Dynamic Properties

With regard to the dynamic mechanical properties presented in Table 2, the physical changes in terms of Tg and tan  $\delta$  would track those of a typical nitrile rubber with an equivalent glass transition temperature. At 100°C the viscous component, as represented by the tan  $\delta$ , has almost disappeared, which indicates high resilience. The values of complex dynamic tensile modulus E* over a 20 to 100°C temperature range are unusual, indicating high internal viscosity. When E* values of HyTemp are compared with those of Aflas, which is far more typical of a normal elastomer, the "stiffening" effect of the longer R branch is apparent.

# Nomenclature and Basic Properties

The basic properties of polyacrylate rubbers are outlined in Table 1. The ASTM name is alkylacrylate copolymer. The IUPAC approved trivial name is poly(alkyl acrylate), while the IUPAC structure-based name is poly[(I-alkoxy carbonyl) ethylene]

# Characteristics of Polyacrylate Rubbers

The basic structure of most early acrylic rubbers was the ethylene group with a carbalkoxy ( $CO_2R$ ) branch structure:

By varying the R group from C₁ (methyl) to C₈ (octyl), the brittlepoint can be shifted by as much as 60°C (see T_g entry in Table 1). Oil resistance decreases as the R group length increases, due to the increasing hydrocarbon nature of the acrylic rubber. Other commonly used acrylic monomers are ethyl, n-butyl, 2-methoxyethyl and 2-ethyoxyethyl acrylates.

# Curesite Monomers

The more tractable cure mechanism offered by the curesite monomer has enabled the wider use of polyacrylates. The current practice heavily favors a reactive halogen, specifically one having the activity of an allylic chlorine group. Allylic chlorines are particularly easy to displace, so they allow the use of a wide range of curing systems. One major exception is acrylic rubbers used for high pressure hose, where an epoxide curesite monomer is preferred. Polymerization of the monomers is done in an emulsion or suspension phase typically initiated by a free radical source. The "poor water resistance" is due in part to ionic polymerization residues such as the sulfonate and sulfate surfactants left in the rubber after polymerization.

#### Heat Resistance and Thermal Stability

The absence of double bonds in the acrylic backbone allows the elastomer to be used in higher temperature applications than standard nitrile (NBR) rubbers. Typical formulations for automotive applications include 1000 hour testing at 150°C. The basic heat resistance increases or decreases as a function of the R (acrylate branch) group. The ethoxy groups offer the maximum potential. The thermal stability is not much greater than the heat resistance, with backbone chain scission dominating in an aggressive environment. The eventual breakdown products are gases, unlike the nitrile rubbers that leave a high percentage of "char".

# Crosslinking (Vulcanization)

The ease of displacement of the allylic chlorine allows a wide variety of crosslinking systems to be used, i.e.:

ammonium adipate ammonium benzoate blocked diamines (hexamethylenediamine carbamate) (Diak[™] No.1) ethylene thiourea m-phenylene-bis-maleimide (VANAX[®] MBM) polyamines (triethylamine tetramine) quaternary ammonium or phosphonium salts/bisphenol-A soap-sulfur

Halogens (e.g., chlorine) are normally displaced with each crosslink, so an acid acceptor should be considered for maximum heat stability.

# Compound Technology

Suppliers' bulletins provide information about polyacrylates and the most recent material developments. Mixing is done in both open mill and internal mixers. The thermoplastic nature of the ethylene backbone usually causes sticking.

# Process Aids

Process aids are critical for mill release. An incorrect selection can interfere with cure rate or promote rapid aging. VANFRE® AP-2 is very effective in many compounds. VANFRE M is less effective but will not detract from the corrosion ratings of seals. Consult the elastomer supplier for the latest recommendation based on the type of elastomer, cure system, and service requirements.

#### Fillers

As is common with other amorphous elastomers, acrylic rubbers require reinforcing fillers such as the high structure carbon blacks for high strength and resistance to tear and abrasion. The reinforcement of light-colored compounds is best achieved using fine particle silane-modified silicate fillers.

#### Plasticizers

Plasticizers are generally ineffective due to their lack of permanence. Hydrocarbon process oils are not used due to thermodynamic incompatibility. The efficiency of a plasticizer is a function of the molecular weight; the lower the value, the higher the efficiency in improving low temperature flexibility. This is also true of the plasticizer's volatility: increasing molecular weight yields decreasing volatility. The required 175°C temperature tends to volatilize most plasticizers during the postcure process.

#### Blends

The polar nature of acrylic rubbers not only allows them to be reasonably miscible with other halogen containing elastomers, but also allows them to use the same cure system.

#### Ethylene/Acrylic Rubbers

Vamac ethylene acrylic rubber, introduced in 1975, was originally offered as an oil-resistant elastomer suitable for 175°C service. This temperature rating proved too optimistic for long-term service; 150°C is a more realistic limit with a six months time to embrittlement. Vamac has unique dynamic mechanical properties, and the automotive market is probably its strongest growth area.

#### Supplier

DuPont Performance Elastomers is the only supplier of this class of elastomers.

#### Applications

Vamac's basic fluid resistance somewhat limits its utility in petroleumbased engine lubricants. Being an ethylene-type elastomer, it has similar low temperature characteristics, i.e. a brittlepoint lower than the glass transition temperature Tg (-60° vs. -32°C). A tenfold increase in torsional stiffness from an original 70 duro occurs at -26°C, which translates to about 98 duro.

Vamac's low brittlepoint made it the logical replacement for polyacrylate rubber, which was often subject to seal fracture at lower temperatures, although improved polyacrylate elastomers have recaptured much of this market. Vamac's potential applications are rocker covers and oil-pan gaskets, due to its damping characteristics and lower swelling in alcohol-contaminated lubricating oils.

### Dynamic Properties

Dynamic data (Table 2) indicate that the glass transition temperature is in the range of low temperature grade nitrile. The complex dynamic modulus E^{*} is equivalent to polyphosphazene elastomers (no longer produced), and tan  $\delta$  values indicate consistent inherent damping capabilities. These same data indicate that shaft seals operating at high RPMs have a strong potential for leakage.

#### Nomenclature and Basic Properties

Vamac's basic properties are outlined in Table 1. ASTM refers to Vamac as ethylene-acrylic acid copolymer. The IUPAC approved trivial name is poly (ethylene-acrylic acid), whereas the IUPAC structure-based name is poly[ethylene-co-(I -methoxy carbonyl ethylene)].

Characteristics of Vamac

The basic structures creating Vamac are:

Ethylene  $CH_2 = CH_2$ 

Methyl acrylate O $CH_2 = CH-C-O-CH_3$ 

Carboxyl curesite monomer

0 ∥ R − C − OH

Vamac is categorized as a terpolymer with an ethylene-methyl acrylate ratio of about 2:1. The curesite monomer is probably less than 5%. Oil resistance is imparted by the carboalkoxy  $(-CO_2 - CH_3)$  group.

# Heat Resistance and Thermal Stability

The saturated backbone does not offer a site for oxidative attack. Assuming the application is dynamic, DuPont data show that properly compounded Vamac has a +20% change in shear storage modulus G' after six months at 121°C. At 150°C, the same formulation has a 20% increase after one month.

# Crosslinking

Cure systems for low compression set are typically developed using a guanidine (DPG or DOTG) to activate a diamine. This reaction occurs at the

carboxyl group, creating an amide crosslink. Two moles of water are typically created. If a carbamate curative is used, a mole of  $CO_2$  is also generated. Thick sections tend to fissure during postcure, so that a secondary amine activator is recommended. The amine supplier's latest offerings should be reviewed.

# Compounding Technology

The polymers are sold as both black and non-black master batches, including filler, stabilizer and process aids. The uncompounded gum elastomer is available, with only the stabilizers added. Dynamic data from Table 2 illustrate the effect of temperature on viscosity, again characteristic of ethylene-type elastomers. The physical property response to both black and non-black fillers is characteristic of most elastomers. The Vamac Product Book contains an extensive compound formulary that addresses a variety of property requirements.

# Process Aids

Vamac has a pronounced tendency to stick to mill rolls, so that process aids are a necessity. Alkyl acid phosphates such as VANFRE UN or VANFRE VAM (at 2 phr) are often used in addition to the basic ingredients: 2 phr stearic acid and 0.5 phr octadecyl amine (Armeen[®] 18D).

# Plasticizers

Monomeric ester plasticizers such as dioctyl sebacate (DOS) improve low temperature flexibility, but they are readily extractible by hot oils, and are volatile in dry heat. Polyester plasticizers are more stable but not as efficient. As with polyacrylate rubbers, caution is required in demanding mechanical applications where plasticizers are used at temperatures greater than 100°C.

# Blends

Vamac is not normally blended with other elastomers, but can be blended with Elvax[®] (ethylene/vinyl acetate) to improve processing and reduce compound costs.

# **Tetrafluoroethylene-Propylene Elastomers**

Asahi Glass Co. introduced tetrafluoroethylene-propylene rubber to the US market in 1976 under the trade name Aflas. Although it is essentially a "half-fluorinated EPDM", its thermal stability at 200°C is outstanding. Unlike the fluoroelastomers containing vinylidene fluoride (VF₂), it is very stable in the presence of bases (alkalis). This resistance to bases has resulted in its acceptance in oilfield applications where amine inhibitors are used. The relatively high glass transition temperature has prevented its widespread acceptance.

# Supplier

Asahi Glass Company, Ltd. is the sole manufacturer and distributor of this product.

# Applications

The resistance of Aflas to acids, alkalis and oxidizing agents is far superior to that of conventional  $VF_2$ -containing fluoroelastomers. Its higher hydrogen

content, compared to that of typical fluoroelastomers, leads to higher swelling in media such as ASTM Fuel B (60%), although swell in 100% aromatics (toluene) is lower (40%), as shown in Table 1. This deficiency is offset by its unique compatibility with the complete range of common hydraulic fluids, i.e. esters (di & poly), phosphate, silicate, polyglycols and hydrocarbon-based oils. Its inherent resistance to dehydrofluorination (unlike VF₂-containing fluoroelastomers) gives it access to critical markets such as downhole oilfield service. Other potential applications are seals and gaskets for high temperature engine lubricants (typically stabilized with oil-soluble amines), and engine coolants (aqueous electrolytes), which are also typically modified to an alkaline pH using amine-type inhibitors or organic acids to minimize corrosion.

Aflas has a volume resistivity equivalent to that of EPDM. When correctly compounded, it is alone among elastomers in having steam resistance at up to 200°C.

# Dynamic Properties

Table 2 indicates that the high glass transition temperature of Aflas is apparent (-3°C or 270°K). As in any dynamic testing, the Tg shift effect is more obvious (+11 or +18) using E" max or tan  $\delta$  max. The Tan  $\delta$  at 20°C, 10 Hz, for a 70 durometer formulation indicates a strongly damping elastomer with an apparent hardness of 80 Shore A. The high tan  $\delta$  at 100°C (0.15) indicates inherently strong damping capabilities, exceeded only by Vamac (0.20).

# Nomenclature and Basic Properties

The basic properties are outlined in Table 1. The ASTM D 1418 designation is FEPM. The FKM designation *should not* be used to classify this elastomer. IUPAC uses poly(tetrafluoroethylene-propylene) as the approved trivial name, or poly(difluoromethylene-co-propylene) as the structure-based name.

# Characteristics of Tetrafluoroethylene-Propylene Rubber

The basic structures creating the Aflas FA 1XX series are:

Tetrafluoroethylene	$CF_2 = CF_2$	
Propylene	$CH_2 = CH - CH_3$	

Heat Resistance and Thermal Stability

The alternating monomer relationship develops unique high temperature resistance. Based on 50% retention of tensile strength after aging, the elastomer is suitable for 10 years at 180°C. Tensile and elongation show little change after aging 60 days at 200°C.

# Crosslinking

The basic copolymer (not commercially available) is white and difficult to crosslink. Modification by an apparent thermal process (leaving the elastomer brown to black) causes dehydrofluorination, leaving backbone unsaturation available for a crosslink site. The most effective crosslinking combination is Diak No.7 (TAIC, triallylisocyanurate) and VAROX[®] 802 peroxide.

# Compounding Technology

The basic elastomer is available in molecular weights ranging from 40,000 to 135,000. The higher molecular weight products (FA100H, FA100S) are normally used for mechanically demanding applications. Lower molecular weight polymers (FA150 P, E & L) are used for calendered and extruded products where resistance to chemical attack is the primary requirement. The latest suppliers' bulletins should be reviewed for compounding guidelines, since a great deal of filler studies have been conducted.

	Low Set Formulation (phr)	General Purpose Formulation (phr)		
Aflas FA 100S	100.0			
Aflas FA 150P		100.0		
N990 Carbon Black	15.0	35.0		
Austin Black	15.0			
Diak No. 7	5.0	4.0		
VAROX 802-40KE	4.0	3.0		
Carnauba Wax	1.0	1.0		
Span [®] 60 (Sorbitan Monostearate)	1.0	1.0		
Original Physicals, Press Cured 10 min. @ 350°F/Oven Postcured 4 hrs. @ 400°F				
Hardness, Shore A	75	75		
100% Modulus, MPa (psi)	6.8	4.1		
Tensile, MPa (psi)	14.9	13.9		
Elongation, %	235	280		
Compression Set, Measured on .139 Inch Cross-Section O-Rings.				
70 hrs. @ 200°C,%	28	45		

# **Table 3: Aflas Formulations**

# Process Aids

Aflas, together with the TAIC triazine curative, has a pronounced tendency to adhere to molds. Typical supplier literature indicates 1-2 phr of sodium stearate as a process aid. This ingredient can cause swelling of about 12-15% for each part of sodium stearate present when tested in steam or superheated water at 200°C. Any process aid should be tested in the proposed application; giving preference to hydrophobic agents should be considered.

# Plasticizers

The typically high temperature and aggressive media environments encountered by Aflas preclude successful use of plasticizers because of volatility and/or extraction. Avoid phosphate esters entirely if plasticizers are used. If phosphate esters are ignited or pyrolized, the development of very dangerous, toxic by-products is possible (this is true for any fluoroelastomer).

#### Blends

Hydrocarbon-type elastomers are readily blended in small quantities to improve moldability and mold release. EPDM, including low viscosity-high diene types, along with Vestenamer[®] polyoctenylene, are commonly used. The blends

retain both the chemical and thermal resistance of the primary elastomer.

# **Epichlorohydrin Elastomers**

In 1983, E. J. Vandenberg described the development of epichlorohydrin elastomers during the process of developing crystalline polymers from polar monomers. Vandenberg noted that a particular catalyst polymerized epichlorohydrin to a rubbery, predominantly amorphous polymer. The amorphous polyepichlorohydrin was categorized as a homopolymer. Subsequent work resulted in the development of a 1/1 copolymer of epichlorohydrin and ethylene oxide that was also primarily amorphous, with only a small amount of crystallinity. The moderate cost and good oil and gasoline resistance of these two products, coupled with their excellent low temperature flexibility, made them particularly attractive to the automotive industry. Hercules licensed the technology to B. F. Goodrich in the early 1960s. Zeon Chemicals, having purchased B. F. Goodrich's polymer business, is now the only domestic supplier.

# Applications

The combination of fuel resistance, air-aging characteristics, broad temperature range and cost has ensured epichlorohydrin a large market in the automobile industry. Hose, tubing, seals, gaskets and coated fabrics are major applications. Rubber-covered rolls, oilfield specialties, and industrial products are also substantial markets. Epichlorohydrin's very good low temperature properties have led to special military applications such as oxygen mask hose and large gaskets for fuel-transfer systems.

# Dynamic Properties

The dynamic mechanical data values shown in Table 2 indicate excellent low temperature properties, minimum heat build-up and stable complex dynamic modulus E* over a temperature range of 20°C to 100°C.

# Nomenclature and Basic Properties

The basic properties are summarized in Table 1; ASTM uses CO to designate epichlorohydrin polymer and ECO to designate the copolymer with ethylene oxide. The IUPAC structure-based name is poly[oxy(chloromethyl)ethylene] for the homopolymer; -co-oxyethylene is added to designate the copolymer.

# Characteristics of Epichlorohydrin Elastomers

Epichlorohydrin elastomers are available as both the CO homopolymer and the ECO copolymer. There is also a terpolymer, essentially a copolymer with a curesite monomer, which allows greater freedom in crosslinking chemistry. Within the various classes, there is a range of molecular weights (Mooney values) available for specific compounding.

# Monomers for Polymerization

Monomers employed in epichlorohydrin elastomer production are characterized as cyclic ethers. Three examples are on the following page:

Epichlorohydrin (chloromethyl oxirane)

0 / \ CH₂-CH-CH₂CI

Ethylene oxide (oxirane)



Ally glycidyl ether (curesite monomer)

/ \ CH₂-CH-CH₂-O-CH₂-CH=CH₂

The CO homopolymer is saturated polyether with the polar aspect created by the chloromethyl side group. The 38% chlorine content provides fuel resistance and promotes flame retardancy. The ECO copolymer has a lower chlorine content (about 26%). It has improved low temperature flexibility, contributed by the ethylene oxide monomer, and higher fuel swell resulting from the lower chlorine content. The terpolymer curesite monomer allows the application of a variety of peroxide, peroxide/coagent and sulfur cure mechanisms.

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# Heat Resistance and Thermal Stability

The very polar chloromethyl group common to CO and ECO elastomers not only creates basic oil resistance, but is also the crosslinking site. The displacement of chlorine by a nucleophile and heat is the cure mechanism. During the crosslinking process it is assumed that there is one crosslink for every 130-200 constitutional repeating units (CRU). This leaves the bulk of the chlorine atoms on the chloromethyl groups vulnerable to dehalogenation. During the early years of polymer development it was assumed that dehalogenation and the subsequent formation of HCI caused the rapid degradation of formulations.

Yamada, et al (1973) and Nakamura, et al (1974) proved conclusively that aging occurs in two steps:

- 1. Oxidative degradation initiating at a beta hydrogen following the thermal decomposition mechanism for alkylene oxides.
- 2. Subsequent formation of a hydroperoxide, creating a chloroketone structure that decomposes, yielding HCI.

Providing long-term heat stability dictates both an antioxidant (step 1) and an HCI acceptor (step 2). Typical antioxidants are metal dithiocarbamates such as VANOX[®] NDBC. A combination of the antioxidants METHYL NICLATE[®] and ISOBUTYL NICLATE is used for maximum extraction resistance.

An environmentally safe HCl acceptor is magnesium oxide (albeit with diminished water resistance). Zinc oxide and zinc stearate should be avoided, because they become strong Lewis acids and promote rapid elastomer breakdown.

Low temperature properties of the ECO copolymer are particularly good. The ether linkage in the backbone is highly mobile – much like the siloxy linkage in the silicone rubber backbone.

Long-term aging characteristics are a function of operating temperature. The antioxidant and HCl acceptor ingredients are essentially sacrificial. Once these agents are depleted, there is typically a reversion to lower molecular weight materials.

Fluid resistance values with regard to automotive service are available from the supplier, whose literature demonstrates the long-term service capabilities of CO and ECO elastomers. Sour (peroxidized) gasoline continues to be a major problem, causing degradation similar to that described above as step 2 of the aging process. Specific compounding can minimize sour gasoline attack, but cannot completely stop it. Aqueous and nonaqueous electrolytes should be avoided, since they promote nucleophilic attack on the chloromethyl group, causing rapid breakdown.

# Crosslinking

The crosslinking of CO and ECO elastomers can proceed by several mechanisms, each using nucleophilic displacement of the chlorine from the chloromethyl group by one of the following cure systems:

- 1. Ethylene thiourea (nucleophile and crosslinker) Magnesium oxide (acid acceptor)
- Amine accelerator (nucleophile, VANAX 808) Thiadiazole complex (crosslinker) Barium carbonate (acid acceptor) Magnesium oxide (acid acceptor)
- Biphenyl guanidine (nucleophile, DPG) 2,4,6-Trimercapto-s-triazine (crosslinker, Zisnet[®] F) Magnesium oxide (acid acceptor)

The terpolymer can be crosslinked through the reactive double bond that is pendant to the backbone by the following cure systems:

- 1. Peroxide/coagent, peroxide (VAROX DBPH)
- 2. Sulfur and organic accelerators
- 3. 2,4,6-Trimercapto-s-triazine and organic accelerators

# Compounding Technology

Some typical CO and ECO formulations using the different cure mechanisms follow:

Nucleophile Cure	phr
Homopolymer (CO)	100.0
Process aid	1.0
Magnesium oxide (MgO ₂ )	5.0
Filler	40.0
Ethylene thiourea	1.2
VANOX NDBC	1.0

Ті	iazine Cure phr
Copolymer (ECO)	100.0
Process aid	2.0
Calcium carbonate (shelf-life improver	) 5.0
Filler	40.0
Zisnet F-PT (2,4,6-Trimercapto-s-triazi	ne) 0.9
VANTARD [®] PVI Retarder	1.0
VANOX NDBC	1.0

Peroxide Cure	phr
Terpolymer (ECO)	100.0
Process aid	2.0
Magnesium oxide	3.0
Calcium carbonate	5.0
Filler	40.0
VAROX DBPH	2.0
Sartomer® SR350 (Trimethylolpropane Trimethacrylate)	

Mixing can be carried out on both open mill and internal mixers. The high Mooney elastomers have rapid heat build-up tendencies and should be treated accordingly.

# Processing Aids

Process aids are critical for mill release. An incorrect selection can interfere with cure rate or promote rapid aging. The elastomer supplier should be consulted for the latest recommendation, based on the type of elastomer, cure system, and service requirements.

# Fillers

Fillers are typically furnace-type blacks with the predictable reinforcing effects. N500 types are used in plasticizer-free formulations. N700 types are used to offset the softening effects of plasticizers, while maintaining tensile strength and

hardness. Non-black fillers, specifically hydrated silicas, give improved dry-heat aging properties.

### Plasticizers

Plasticizers are typically diesters and ethers, similar to those that are used in NBR compounding for low-temperature improvement. The supplier should be consulted for current technology.

# Epichlorohydrin Elastomer Blends

Blends with other elastomers can now be found in the literature. Typically, these are polar elastomers that might use a compatible curing system.

# Fluorosilicone Elastomers

The addition of fluorine to the alkyl groups of silicone elastomers creates elastomers with a high degree of solvent resistance and excellent low temperature capabilities. There are currently three major suppliers: Dow Corning Corporation, Momentive Performance Materials, and Shinetsu Chemical Company.

#### Applications

The original market for fluorosilicone, primarily o-ring seals, has expanded greatly. Current high volume applications also include shaft seals and gaskets, molded goods, duct hose, and covers. Other applications include wire and cable, insulation, electrical connector inserts, and North Slope oilfield service.

The dynamic mechanical data values shown in Table 2 indicate fluorosilicone's excellent low temperature properties. These properties, together with the low swell in hydrocarbon lubricants and fuels, makes fluorosilicone a good seal elastomer.

# Dynamic Properties

The relatively high value for the tan  $\delta$  (at a temperature of  $T_g$  + 60°C) indicates strong inherent damping by branch structures (side groups). This indicates a slow elastic recovery rate, which could be a problem under high-rate cyclic loading conditions at lower temperatures. The 46% decrease in E* between 20°C and 100°C is quite modest compared to the carbon backbone type rubbers.

#### Nomenclature and Basic Properties

The basic properties of fluorosilicone elastomers are summarized in Table 1. The ASTM name is fluorovinyl polysiloxane. The IUPAC trivial name is poly(methyltrifluoropropylsiloxane), while the structure-based name is poly (oxymethyl-3,3,3-trifluoropropyl silylene).

# Characteristics of Fluorosilicone Elastomers

Fluorosilicone elastomers, as specified by MIL-R-25988, are available as three types: general-purpose, high strength general-purpose, and high modulus increased temperature resistant. Typically, fluorosilicone elastomers are a copolymer of 90 mol % trifluoropropylsiloxy and 10 mol % dimethylsiloxy monomers.

#### Monomers and Polymerization

Monomers currently used in commercial fluorosilicone elastomer production are:

- cyclic alkyl trifluoropropyl trisiloxane (CF₃CH₂CH₂SiCH₃O)₃, and
- cyclic dimethyl trisiloxane ( CH₃SiCH₃O )₃ plus curesite monomers

A specific curesite is created by incorporating 0.2 mol % of methylvinyl siloxane. The highly reactive vinyl site allows a wide latitude in the selection of the peroxide crosslinker. The basic hydrocarbon resistance is imparted by the polar trifluoro ( $-CF_3$ ) group.

The fluorosilicone content of the copolymer can range from 40 to 90 mol %. Cost and service (swelling) considerations dictate the copolymer ratios. The basic copolymers appear to polymerize with little or no branching, as evidenced by low gel content. A range of molecular weights (as measured by Mooney viscosity) are typically available as part of the supplier's product specifications. A better molecular weight/viscosity relationship can be determined by considering the average number of CRUs or monomer segments in the particular fluorosilicone. In terms of IUPAC nomenclature, the basic CRUs for fluorosilicone elastomers are the (SiO) structure. The degree of polymerization of 6000 indicates that the fluorosilicones are typically high molecular weight elastomers.

# Heat Resistance and Thermal Stability

These terms, often used interchangeably, are defined as follows for this discussion: heat resistance is the maximum temperature at which a given elastomer is capable of operating for an extended period of time while still maintaining usable properties; thermal stability is the maximum temperature an elastomer can withstand before a chemical change occurs.

In terms of heat resistance, the fluorosilicone elastomers are capable of thousands of hours of service life at 175°C. At 200°C, about half of the tensile strength is reported lost after 26 weeks. Useful service life is often strongly influenced by design and application. In terms of physical properties, the high molecular weight and minimum attraction between adjacent atoms contribute substantially to both the room temperature and elevated temperature strength of fluorosilicones. A typical fluoroelastomer loses 70% of its tensile strength at 100°C, while fluorosilicone elastomers lose only 50%.

Thermal stability varies according to compounding technique. Degradation is accompanied by crosslink scission and depolymerization.

#### Low Temperature Properties

The (SiO) structure offers a high degree of backbone mobility as evidenced by the very good low temperature properties of fluorosilicone elastomers.

#### Aging Characteristics

Long-term aging characteristics are outstanding for all fluorosilicone elastomers, with no age control considerations necessary for seals and molded components. After installation, age controls may be incorporated to monitor stress-strain relaxation effects in seals, hoses, and gaskets.

# Fluid Resistance

Fluid resistance should be considered in terms of nonelectrolytes (nonpolar fluids) and aqueous/nonaqueous electrolytes (polar fluids).

Nonelectrolytes are typically hydrocarbons ranging from gases to liquids to solids. Lower molecular weight aliphatic hydrocarbons have moderate interactions with all fluorosilicones. Aromatic hydrocarbons (benzene, toluene, xylene, etc.) interact to a greater extent.

Aqueous and nonaqueous electrolytes such as aldehydes, ketones, and esters generally have varying degrees of interaction with fluorosilicone elastomers. For applications requiring immersion in these fluids, long-term testing should be done to determine suitability. Most suppliers have detailed fluid resistance guides, which can assist in elastomer selection.

# Crosslinking Fluorosilicone Elastomers

Fluorosilicone elastomers can be crosslinked by any of the basic classes of peroxides:

Class	Typical Peroxide		Free Radical Produced
Dialkyl	Dicumyl peroxide	(VAROX DCP)	Cumyloxy, Methyl
Dialkyl	2,5-dimethyl-2,5- di(t-butylperoxy) hexane	(VAROX DBPH)	t-Butoxy, Methyl
Diacyl	Benzoyl peroxide	(VAROX ANS)	Benzyloxy
Peroxyester	t-Butyl perbenzoate	(VAROX TBPB)	Benzyloxy, t-Butoxy

The reason for using each class of peroxides is briefly outlined below.

Dialkyl peroxides are specifically reactive to vinyl crosslinking sites. Their half-life temperatures are higher and allow greater processing safety at higher curing temperatures.

Diacyl peroxides are not only reactive to vinyl crosslinking sites but also create additional crosslink sites. Half life temperatures are far lower and allow hot air vulcanization (HAV) cures.

Peroxyester peroxides are reactive at temperatures intermediate between those of dialkyl and diacyl peroxides. The free radicals produced are reactive at both the specific vinyl crosslinking site and at non specific sites. They are suitable for HAV cures.

Each of the peroxide groups has possible disadvantages. Dialkyl radicals react with oxygen and cause elastomer chain scission, while benzyloxy radicals leave acidic by-products, causing poor aging in confined applications.

# Compound Technology

Formulations are available that meet specific requirements and specifications for commercial applications. Base compounds of 40 and 80 durometer hardness

are available. Blending various ratios of bases allows the compounder to develop compounds with specific hardness. Reinforced gum stocks are also available for in-house specification compounding.

Blending and curative addition can be done on both open mill and internal mixers. Baker Perkin mixers are typically used by suppliers to make original formulations.

# Process Aids

Process aids are typically proprietary. Their functions range from blocking filler surface activity to serving as flow improvers.

# Fillers

Reinforcing fillers are typically silicas (silicon dioxide) because of their stability and their compatibility with the elastomeric silicon-oxygen backbone. These silica fillers cover the entire range: naturally-occurring, or obtained by silicon tetrachloride hydrolysis, arc furnace, or precipitation. Surface area ranges from 0.54 to 400 m²/g, with the average particle size ranging from 100 to 6 nm. This broad range of particle size and surface area gives the compounder substantial flexibility in developing or controlling properties such as modulus, abrasion resistance, tear resistance, and processability.

Lutz, et al (1985) provide an excellent three part review of the performance of wet process (precipitated) silicas in silicone and fluorosilicone elastomers. Siloxane and silazane coupling agents are also discussed in these articles. Other commonly used fillers are calcium carbonate, iron oxide, titanium oxide, and zinc oxide. Conventional dimethylsilicone oils and gums have been used in small percentages to aid in mill release and mold release.

# Plasticizers

Plasticizers are generally fluorosilicone oils of various viscosities for optimum thermodynamic compatibility. The efficiency of a plasticizer is a function of the molecular weight – the lower the value, the higher the efficiency. This is also true of the plasticizer's volatility: increasing molecular weight, decreasing volatility. Postcuring tends to volatilize some low molecular weight plasticizers.

#### Fluorosilicone Elastomer Blends

Blends with other silicone elastomers should be assumed to have possible phase incompatibility with the polar/nonpolar nature of the components.

### Perfluorocarbon Elastomers

The widely used vinylidene fluoride-containing fluoroelastomers contain a large percentage of hydrogen on a molar basis. The goal of a totally fluorinated elastomer (one having the heat and solvent resistance of polytetrafluoroethylene) was achieved by DuPont in the early 1970's. Despite the very significant cost of the elastomer, sold under the trade named Kalrez[®], some applications have been developed.

# Suppliers

DuPont Performance Elastomers, Daikin Industries Ltd. (1990), and Solvay-Solexis (1995) are current sources. DuPont Performance Elastomers sells molded parts only; Daikin and Solvay Solexis sell the basic elastomer to a specific and limited number of molders.

# Characteristics of Perfluoroelastomers

The presence of hydrogen makes a fluoroelastomer vulnerable to attack by aqueous and non-aqueous electrolytes such as coolants and highly stabilized lubricants. Totally fluorinated elastomer, "perfluoroelastomer", offers the user a rubbery fluoropolymer with outstanding long-term resistance to heat, solvents and chemicals.

# Compounding

There is little significant information available for compounding guidelines.

# Crosslinking Chemistry

A copolymer of tetrafluoroethylene (TFE) and perfluorovinylmethylether (PMVE) in a specific ratio is "rubbery" but not capable of being crosslinked. The curesite is developed by incorporating a third monomer, which could be a perfluorophenoxy moiety, a diolefin moiety, a triazinic/cyano moiety, or an iodine/ bromine substituted moiety. The perfluorophenoxy crosslinking chemistry uses the bisphenol (dihydroxy) complex as a crosslinker. The reaction is ionic. The triazinic/cyano system offers the highest heat resistance. The other monomers can be crosslinked using a polyfunctional compound (triazines, etc.), with the site activated by a peroxide. This crosslink is developed by a free radical mechanism (as opposed to the ionic mechanism) and is more stable in the high temperature aqueous and non-aqueous electrolyte (high pH) environments.

# Application

The perfluoroelastomer's inherent hydrocarbon and mixed solvent resistance originally found application in the aerospace, military and petrochemicals markets. The outstanding heat resistance (greater than 225°C) made this class of elastomers a problem solver in high temperature applications such as jet engines.

# Dynamic Properties

As indicated in Table 2, all FFKM elastomers have strong damping (high tan delta) at 20°C. At 100°C, the damping characteristic is a function of the specific crosslink structure, ranging from 0.06 to 0.67. The complex dynamic modulus E* at 20°C is quite typical, with the exception of the diolefin crosslink. This is due to the difunctional crosslink structure, as opposed to the trifunctional (triazine) and other more complex crosslinkers.

# Nomenclature and Basic Properties

The basic properties are summarized in Table 1. The ASTM class designation is FFKM and the ASTM D 2000 material category is Type KK.

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# by C. P. Rader, PhD

Consultant to the Rubber Industry Akron, OH

Thermoplastic elastomers (TPEs) are "a diverse family of rubberlike materials that, unlike conventional vulcanized rubbers, can be processed and recycled like thermoplastic materials." Thus they are materials with the properties and performance of rubber, yet are fabricated with the same equipment and techniques as thermoplastics. The performance properties of TPEs are similar to those of conventional thermosets such as natural rubber, SBR, EPDM or neoprene. However, TPEs are converted to end products by thermoplastic injection molding, extrusion and blow molding – the same systems used for processing polypropylene, polyethylene or polyvinyl chloride.

The unique properties of TPEs are based on their morphology. TPEs commonly consist of two or more intermingled polymer systems, each with its own phase and softening temperature ( $T_s$ ). In the useful temperature range of a TPE, the soft or elastomeric phase will be above its  $T_s$ , while the hard phase will be below its  $T_s$ . The hard phase thus anchors or restricts the polymer chain movement of the soft phase, in much the same way that carbon black and chemical crosslinks restrict the motion of thermoset elastomer chains.

When a TPE is heated above the  $T_s$  of its hard phase, the polymer chain movement of the soft phase if no longer restricted and the material behaves like a viscous liquid. On cooling, the hard phase resolidifies and the TPE again becomes rubberlike in its performance properties. This melting/solidification cycle is reversible and can be repeated many times, since it involves the breaking and remaking of relatively weak physical bonds.

# The Growth of TPEs

The following are the major classes of TPEs which have been developed over the past five decades in response to the needs of specific market segments.

Thermoplastic polyurethane rubbers first appeared in 1959. Styrenic block copolymers came on stream throughout the 1960's. During the 1970's, copolyesters and polyolefinic blends were introduced and gained rapid acceptance. Thermoplastic vulcanizates (TPVs) were introduced in 1981. Polyamides, the top of the line in performance and price, were introduced in 1982. The recent past has witnessed the development of elastomeric polyolefins prepared with metallocene catalysts.

TPEs have firmly established themselves as a major elastomer group in the Rubber Industry, with an estimated 16-18 percent of the industrial rubber (non-tire) market in 2007. This penetration is expected to approach 23 percent by 2012.

As with most materials, an improvement in the performance properties of TPEs increases their cost. The major classes of TPEs can thus be ranked according to



their relative cost and performance, as shown in Figure 1.

# Figure 1: Relative Ranking of Major Classes of TPEs and Thermoset Rubbers by Performance and Cost

# Advantages and Disadvantages of TPEs

TPEs provide advantages and disadvantages as compared to thermoset rubbers. The desirability of each depends on the requirements of the specific product application.

The advantages of TPEs include:

- 1. *Little or no compounding required,* since most TPEs are fully formulated and can be used as received.
- 2. *Simplified processing,* with fewer fabrication steps. No batch compounding or vulcanization is needed for TPEs.
- 3. Shorter processing cycle times, with molding cycles for TPEs usually measured in seconds, as opposed to minutes for thermoset rubber.
- 4. *Recycling of clean scrap (regrind),* since a reprocessed TPE retains its properties.
- 5. *Reduced energy consumption,* a direct result of simplified processing and shorter cycle times.
- 6. *Better quality control (QC),* both in processing, and in finished part tolerance, with QC costs actually lower. This is a result of TPEs' greater compositional consistency and thermoplastic processing.
- 7. Lower density than comparable thermoset rubbers. Materials are

purchased on a weight basis, but used on a volume basis. Thus more parts can be fabricated from a given weight of material.

- 8. Use of thermoplastic processing methods unavailable with thermoset rubbers, including blow molding, thermoforming and heat welding.
- 9. Use of automated high-speed fabrication and assembly methods, a result of tighter dimensional tolerances.
- 10. *Greater design flexibility,* enabling the use of sophisticated methods such as finite element analysis.

The disadvantages of TPEs, compared to thermoset rubbers, include:

- 1. Novel technology, unfamiliar to most rubber processors.
- 2. *Different processing equipment,* unfamiliar to most rubber processors and fabricators.
- 3. *Material drying is often required prior to processing,* a step not needed in thermoset rubber fabrication.
- 4. *High volume production* is needed for good processing economies.
- 5. *Melting occurs at elevated temperatures*, an inherent property of TPEs This prevents their use in applications requiring brief exposures to temperatures at or above their melting point.

# Classes of TPEs

Virtually all TPEs fall into one of three overall categories:

- 1. Block copolymers of two or more monomers, such as styrenics, polyurethanes, copolyesters and polyamides,
- 2. Simple blends of thermoplastics, such as the polyolefinics, and rubbery polymers, or
- 3. TPVs with a discontinuous crosslinked rubberlike phase and a continuous thermoplastic phase.

The hardness range of the different classes of commercial TPEs are given in Figure 2, and compared to the range of conventional thermoset rubbers and hard thermoplastics.



Figure 2: Hardness Range of Generic Classes of TPEs

Figure 3 compares the dry heat service temperature and the oil resistance of these TPE classes to that of thermoset rubbers, employing the widely used ASTM D 2000 scheme for classifying rubbers.



Figure 3: Classification of TPEs and Thermoset Rubbers According to ASTM D 2000/SAE J200 System

#### Styrenic Block Copolymers

Chemistry – Styrenic TPEs are block copolymers of styrene and a diene such as butadiene, isoprene, or an olefin pair such as ethylene-butylene. Their properties are markedly different from those of a random copolymer of styrene and butadiene (SBR rubber). In styrenic block copolymers, the hard phase is an aggregate of polystyrene blocks, and the soft phase an aggregate of rubberlike polydiene or olefin pair blocks. The two phases are bonded to each other by covalent chemical bonds.

*Properties* – While styrenic TPEs are low cost, their overall performance is only modest. On the other hand, there are many applications calling for a rubberlike material with modest performance. Specific gravities of styrenic TPEs range from 0.9 to 1.1. Hardness ranges from 10 Shore A to 60 Shore D. Ultimate tensile strength varies from 3.5 to 27.6 MPa (500 to 4000 psi). Useful service temperature runs from a low of -57°C (-70°F) to a high of 93 to 104°C (200 to 220°F).

The diene segment backbone unsaturation is subject to degrading attack by oxygen, ozone and UV radiation – the three principal environmental threats to the longevity of an elastomer. When styrenic TPEs are made with olefin pair soft blocks, they are much more resistant to weathering and solvent attack, due to the saturation of these soft blocks.

Styrenic TPEs are resistant to polar fluids, particularly water and its solutions. They are especially susceptible to oils, fuels, organic solvents and surfactants.

*Typical Applications* – The largest fabricated application for styrenic TPEs is shoe soles, particularly for shoes with cloth uppers. This application exploits the resistance of styrenic TPEs to abrasion and fatigue, as well as their traction on walking surfaces.

Styrenic TPEs are extruded into film, sheeting, tubing, reinforced hose, and insulation and jackets for electrical wire and cable. Injection molded and blow molded articles include parts for automotive, electrical applications and appliances. Additionally, styrenic TPEs are widely used as asphalt modifiers and in the preparation of sealants, coatings, caulking and adhesives. They are often used to add impact resistance, toughness and flexibility to polyolefins. The styrenic block copolymers are commonly used as compounding ingredients in the preparation of a wide spectrum of rubber and plastic compositions.

*Brands, Producers* – Shell Chemical Company originally developed styrenic TPEs, and marketed them under the trade name Kraton[®]. The Kraton products are now marketed by Kraton Polymers, LLC. Other styrenic TPE suppliers in Europe and/or the Americas include GLS Corporation (Dynaflex[®]), Multibase (Multiflex[®]), Teknor Apex (Monprene[®] from its QST subsidiary, Elexar[®] and Tekron[®]) and Alpha Gary (Evoprene[™]).

#### **Polyolefin Blends**

Chemistry – This class of TPEs (thermoplastic elastomeric olefins, TEOs)
consists of two-polymer systems – thermoplastics such as polypropylene or polyethylene mechanically blended with unvulcanized elastomers such as EPDM, natural rubber, SBR, etc. The most common materials are polypropylene for the hard phase and EPDM for the soft phase. There is little or no crosslinking of the elastomer phase.

The continuous phase is usually the polymer, which makes up the greater part of the blend, which is likely to be the thermoplastic (due to its lower melt viscosity). The fine dispersion of the discontinuous phase provides sufficient interphase surface contact for the attractive forces between the two phases to be relatively strong.

*Properties* – TEOs (called thermoplastic polyolefins, TPOs, in earlier literature) have low specific gravities of 0.9 to 1.0, with hardness ranging from 60 Shore A to 65 Shore D. Ultimate tensile strengths run from 3.4 to 20.7 MPa (500 to 3000 psi), with strength generally increasing as hardness goes up. Service temperatures range from -40 to 100°C (-40 to 212°F).

TEOs' resistance to polar fluids is rated as very good. However, non-polar hydrocarbon or halocarbon fluids readily attack TEOs, particularly at higher temperatures. While properties such as stress-strain, tear strength and compression set are good at ambient temperatures, these properties fall off rapidly at elevated temperatures.

*Typical Applications* – TEO blends have found wide use in the automotive market, particularly for exterior applications such as rub strips, fascias, air dams, bumper covers, moldings and trim. These TPEs are used in electrical applications, wire and cable insulation and jacketing. Roofing membranes for larger buildings are currently a rapidly growing market. Ease of processing makes TEOs well-suited for extruded tubing, hose and sheeting, as well as a broad range of injection molded articles for mechanical goods applications.

Brands, Producers – Uniroyal Chemical Company originally developed TEOs under the brand name of TPR, which is no longer used. Other U.S. brands and producers include Telcar[®] from Teknor Apex, Polytrope[®] from A. Schulman Company, Sarlink[®] from DSM and Vistaflex[®] from ExxonMobil Chemical. European brands include Dutral[®] from Polimeri Europa.

# **Thermoplastic Vulcanizates**

*Chemistry* – Described as elastomeric alloys in earlier literature, the term TPV is now sanctioned by both ASTM and ISO standards. These TPEs frequently contain the same polymers as a TEO. They differ in having been dynamically vulcanized to crosslink the rubbery polymer. The result is material characteristics and performance properties often superior to those of a TEO.

TPVs have a polyolefin matrix as the hard phase, and a highly vulcanized elastomer such as EPDM, nitrile rubber or butyl rubber as the soft phase. The soft phase is finely divided and evenly dispersed throughout the polyolefin matrix. Fineness of dispersion and degree of vulcanization give the TPV its superior properties.

*Properties* – TPVs range in hardness from 35 Shore A to 55 Shore D, with ultimate tensile strength running from 2.0 to 27.6 MPa (290 to 4000 psi). Specific gravity ranges from 0.9 to 1.0. Resistance to polar fluids is rated as excellent. Resistance to oils and hydrocarbon fluids is fair to good, depending on the nature of the soft phase. Maximum continuous service temperature is 125 to 135°C (257 to 275°F), based on 1000 hour air agings.

The crosslinking of the soft phase offers superior resistance to compression and tension set, excellent retention of properties at elevated temperatures, outstanding fatigue resistance and superior resistance to oils.

Applications – TPVs find many applications in the automotive market for underthe-hood components such as hose jacketing, air ducts, convoluted boots, seals, grommets and O-rings. Their electrical insulating properties have opened up a range of wire insulation and jacketing uses.

Mechanical rubber goods are a major application area for TPVs, where flexible parts are components in the other assemblies or devices. These TPEs are used to make gaskets, bushings, seals, tubing, boots, housings, vibration dampers, architectural glazing seals, etc. Special grades have been developed to meet individual requirements, such as flame retardance, FDA regulations, vibration damping and ultraviolet resistance.

*Brands, Producers* – TPVs are marketed worldwide by Exxon Mobil Chemical under the brand names of Santoprene[®], Geolast[®], Trefsin[®] and Vyram[®]. DSM Thermoplastic Elastomers markets TPVs under the trade name Sarlink[®]. Advanced Polymer Alloys markets them under the trade name Alcryn[®], and Teknor Apex markets them under the name Uniprene[®].

#### **Thermoplastic Polyurethanes**

*Chemistry* – Thermoplastic polyurethanes (TPUs) are block copolymers with urethane backbone linkages. They have soft and hard blocks, similar to those of styrenic TPEs. The hard phase consists of diisocyanate and short-chain diol polymer blocks. The soft phase consists of oligomeric diol blocks. The hardness and modulus of the finished material is determined by the ratio of hard to soft phases. The greater the ratio, the harder and stiffer the material.

Non-polar fluids and solvents usually have little effect on TPUs. These materials are relatively stable in water and aqueous solutions, with a pH near neutral (7  $\pm$  2). However, acids and bases can cause hydrolysis of the urethane and ester linkages, resulting in chain scissions and a pronounced, immediate loss of physical properties.

*Properties* – The hardness of TPUs ranges from 70 Shore A to 70 Shore D. As hardness increases, several material properties improve, including tensile strength, modulus, tear strength, specific gravity, flexural modulus and resistance to environmental attack. Ultimate tensile strength runs from 13.7 to 48.3 MPa (2000 to 7000 psi), and can be improved with postcuring. Specific gravity varies from 1.1 to 1.3.

Service temperatures range from -57 to 125°C (-70 to 257°F). However, at elevated temperatures, key properties may degrade due to changes in morphology as well as chemical degradation.

Applications – No other TPE can equal TPUs in their resistance to abrasion and surface wear. They are outstanding in uses where a low coefficient of friction is required. On the other hand, a low coefficient of friction precludes uses that demand good rubber-surface traction, such as tire treads.

TPUs are widely used for shoe soles and heels, caster wheels, drive belts and hose jacketing, due to their outstanding flexibility, light weight and abrasion resistance.

The toughness, abrasion resistance and flexibility of TPUs justify their cost in automotive applications. These include painted exterior parts, as well as under-the-hood components such as seals, gaskets, bushings and stabilizer housings.

Biomedical uses abound for TPUs, taking advantage of their toughness, resistance to fatigue, hemocompatibility and low toxicity. Special grades have been developed for applications like temporary and permanent artificial heart devices, cardiac pacemakers, and diagnostic and therapeutic catheters.

*Brands, Producers* – U.S. brands of TPUs include Texin[®] from Bayer, Pellethane[®] from Dow and Estane[®] from Lubrizol. European TPUs include Desmopan[®] from Bayer and Elastollan[®] from BASF.

#### Copolyesters

*Chemistry* – Copolyester thermoplastic elastomers (TEEEs) consist of block copolymers of alternating hard and soft phases, connected by ester and ether linkages. The hard phase is poly-1,4-butanediol terephthalate. The soft phase is long-chain polyalkylene ether terephthalate. In contrast to the A-B-A structure of styrene block copolymers, TEEEs have an A-B-A-B- structure. However, the morphological basis of their TPE properties is analogous to that of styrenic TPEs.

*Properties* – While the material cost of TEEEs is higher than that of most other TPEs, they offer an unusual combination of performance properties. Their specific gravity ranges from 1.1 to 1.3. Hardness ranges from 35 Shore D to 70 Shore D, slightly above that of conventional thermoset rubbers. Modulus can be as high as 50 percent above that of thermoset rubbers of equivalent hardness. The combination of all these properties often means that a manufacturer can replace thermoset rubber or a thermoplastic with a TEEE by redesigning the part to reduce its volume by 50 to 85 percent – with no decrease in strength or other mechanical properties. The resultant cost savings can significantly offset the higher material cost of TEEEs.

The service temperature range of TEEEs extends from -65 to 130°C (-85 to 266°F). Resistance to organic fluids is rated as very good, except for that of halogenated solvents. These TPEs function well in aqueous solutions, except

at the extremes of pH. Both acids and bases attack the ester linkages of these materials, degrading the polymer.

Below their elastic limits, TEEEs offer a unique combination of strength and elasticity. Tensile strengths range from 21 to 55 MPa (3000 to 8000 psi); however, TEEEs are elastic only at low strain levels (up to 25 percent). Above these levels, they are irreversibly deformed. Within this elastic limit, their resilience and resistance to creep and fatigue are very good. Flexural modulus ranges from a low of 55 MPa (8000 psi) for softer grades to a high of 620 MPa (90,000 psi) for the hardest grades, an indication of significant load bearing capabilities. Impact resistance is rated as outstanding.

TEEEs are unusual in that, in contrast to most other TPEs, they contain no plasticizer. They therefore provide unmatched purity in the fabrication of articles for medical and food contact applications.

Applications – TEEEs are well-suited for applications demanding high strength and flexibility. Since they possess between two and fifteen times the strength of conventional thermoset rubbers, the thickness of parts made of TEEEs need only be 15 to 20 percent that of the original rubber part. In other words, unreinforced TEEEs can replace reinforced thermoset rubber.

Most applications for TEEEs fall into the automotive and mechanical rubber goods categories, where premium quality and high performance are needed. Fuel tanks, exterior automotive body parts, gear wheels, protective convoluted boots, drive belts, hose jacketing, pipe clamp dampers, ski boots, flexible couplings and diaphragms are among the more popular uses. TEEEs have also been selected for a number of medical and food contact applications. TEEEs have replaced metals, thermoplastics, leather and rubber in a broad range of applications, often with reductions in finished part costs.

*Brands, Producers* – In the U.S., Hytrel[®] is offered by E.I. DuPont, Riteflex[®] by Ticona and Ecdel[®] by Eastman Chemical Company. In Europe, Arnitel[®] is produced by DSM.

# Polyamides

*Chemistry* – Polyamide TPEs are block copolymers of hard and soft phases connected by amide linkages. There are two types, one a polyether block polyamide, the other a polyester block polyamide. The hard phases are polyamides and the soft phases are either an aliphatic polyether or polyester. The hard segments determine the polymer melting point and maximum service temperature, as well as the material's properties at elevated temperatures. The soft segments determine fluid resistance and low temperature flexibility. Polyester soft segments usually have better oxidation stability and non-polar fluid resistance. Polyether soft segments generally have better hydrolytic stability and better functional properties at low temperature.

*Properties* – Polyamide TPEs offer the highest performance (and highest cost) of all the generic classes of TPEs. They can give rubberlike performance

at temperatures as low as -40°C (-40°F) and as high as 170°C (340°F). Their specific gravity ranges from 1.0 to 1.2, with hardness ranging from 60 Shore A to 65 Shore D. Tensile strength ranges from 21 to 41 MPa (3000 to 6000 psi), with a very high percentage of tensile strength retained at elevated temperatures. At 100°C (212°F), both ultimate tensile and modulus are retained above 50 percent of their ambient temperature values. Both tear strength and fatigue resistance are rated as very good. Abrasion resistance is very high, being second only to urethane TPEs.

The greater strength of polyamide TPEs often allows a sizable decrease in part thickness and material use, with no decrease in strength or performance.

When subjected to dry air aging, polyamide TPEs retain their essential properties at temperatures up to 170°C (338°F). However, in humid air, polyesterbased polyamide TPEs are susceptible to hydrolysis, thus limiting their maximum service temperature. Polyether-based materials are much less sensitive to the effects of moisture.

Polyamide TPEs' fluid resistance is generally quite good, as is their resistance to oils, greases and polar organics. Aqueous media will not attack polyamide TPEs unless their pH is very acid or very basic and the temperature is elevated. Under these conditions, hydrolytic cleavage of the polymer backbone occurs. Again, polyester-based materials are more susceptible to this hydrolysis than polyether-based materials.

Applications – Commercial applications of polyamide TPEs are progressively emerging. Promising uses include heavy-duty hose, tubing and electrical jacketing, where elastomeric performance is demanded at elevated temperatures and/or in hostile fluid media. Automotive applications include bellows and protective boots for under-the-hood uses. Also, applications are developing in household appliances and industrial environments, such as seals and gasketing requiring a high level of oil and/or chemical resistance.

*Brands, Producers* – In the U.S., Pebax[®] is marketed by Arkema, and Grilamid[®] by EMS-Chemie. In Europe, Vestamid[®] is produced by Evonik Industries.

#### Processing of TPEs

Most of the advantages of using the TPEs mentioned above are related to their ability to be fabricated into finished parts using standard thermoplastic processing methods and equipment. However, several factors must be taken into consideration.

*Drying* – Most TPEs should be dried immediately prior to processing, to ensure moisture levels low enough to preclude processing problems. Drying temperatures should range from 70 to 110°C (170 to 230°F), and drying times from two to six hours, depending on the specific TPE. Desiccant dryers should be used, with moisture removed from the air prior to recirculation.

*Rheology* – The rheology of TPEs is both unusual and complex, and quite unlike that of uncrosslinked thermoset rubber. The viscosities of molten TPEs

are extremely non-Newtonian and highly sensitive to shear. Processors working with TPEs should be thoroughly familiar with their shear sensitivity, and use it to their advantage in article fabrication.

*Processing* – Thermoplastic processing equipment should be used to fabricate TPEs into parts. This equipment offers the best, most reliable processing "window." While some TPEs can be fabricated with rubber processing equipment, practical experience has shown that rubber equipment offers a narrower processing window and a much smaller margin for error, resulting in unusable, out-of-spec parts.

*Extrusion* is widely used to produce tubing, sheet and many cross-section profiles. Crosshead extrusion is used for the continuous insulation and jacketing of wire and cable, and the production of reinforced hose. Co-extrusion uses two or more extruders feeding one die to produce dual-durometer articles.

Extruders for TPEs commonly have a length to diameter ratio of 24:1 or greater, to develop the required heat history in the molten material (melt). A single-stage feed screw with a compression ratio of 3:1 (depth of feed zone to depth of metering zone) can provide the required amount of work to produce a homogeneous melt. This equipment is commonly used for thermoplastics such as polyethylene, polypropylene or polyvinyl chloride.

Extrusion melt temperatures for TPEs are almost always greater than 160°C (320°F), and often in the 190 to 220°C (375 to 430°F) range. On the other hand, thermoset rubbers are usually extruded at 120 to 140°C (250 to 285°F). It is now commercially feasible to extrude foamed TPEs to produce articles with extremely low specific gravities. The foaming of TPEs is usually achieved using chemical blowing agents such as azodicarbonamide, or physical blowing agents such as water, pentane, or a combination of the two.

Injection molding employs the inherent rheological properties of TPEs to produce flash-free articles. Standard thermoplastics machines should be used, with a clamping force of 40 to 70 MPa (3 to 5 tons per square inch of projected shot area). Relatively small nozzles, sprues, runners and gates should be used. It is also possible to do hot-runner molding. Moderately high injection pressures and fast injection rates should be used. Molded parts are normally flash-free.

Cycle times of 15 to 40 seconds are common for parts up to 6mm (0.25") thick. The high shear rate of injection molding takes advantage of the shear rate sensitivity of the rheological properties (viscosity) of many TPEs. Mold shrinkage generally runs from one to three percent, depending on the TPE and the degree of mold packing.

Many injection molding operations produce sizable amounts of scrap because of the mold's sprues and runners. This scrap often rivals or exceeds the weight of the molded parts. Unlike thermoset rubber, clean TPE scrap can be recycled and remolded as regrind, after drying and blending it with virgin material.

Blow molding, a process to manufacture hollow parts, has long been used by

thermoplastic processors. Most TPEs are suitable for either extrusion or injection blow molding. In blow molding, a tube of molten material (parison) is extruded or injection molded, then clamped into a mold shaped like the finished article. Air blown into the hot molten parison inflates it against the cold mold walls to form the article.

In general, TPE parisons retain their shape and integrity quite well prior to mold closure and blowing. In a broad range of applications, blow molding of TPEs has resulted in major cost savings in the manufacture of hollow, flexible rubber parts.

*Calendering* is a feasible process for making TPE sheeting, although the higher processing temperatures of TPEs usually make sheet extrusion preferable to calendering. Other factors influencing this choice include the simpler fabrication of TPEs, and the speed of extrusion as compared to calendering.

*Compression and transfer molding* are almost never used for TPEs. The longer cycle time (usually several minutes) and greater labor input make them far less competitive than injection molding.

Post-Processing Operations – The thermoplastic nature of TPEs opens up a number of post-processing fabrication methods. Thermoforming of TPE sheet (both by positive pressure and by vacuum) can be done to form large articles. Heat welding can be used to form large or complicated TPE gaskets and seals, without having to insert-injection mold. With heat welding, a TPE can be bonded to itself or to a compatible thermoplastic material.

# Summary

TPEs are a well-established, rapidly growing segment of both the rubber and plastics industries. As new TPEs are introduced, and as new uses are found for existing TPEs, their prospects for future growth are good. This situation will probably continue through the second decade of the twenty-first century.

Worldwide TPE use in 2007 was approximately 2400 metric kilotons, with a projected cumulative annual growth rate of five to six percent. Worldwide TPE use should therefore exceed 3100 metric kilotons by 2012. There is ample reason to believe that this massive growth will continue in both the industrialized and developing nations until at least 2015.

The growth of TPEs is expected to come from: 1) the replacement of existing uses of conventional thermoset rubbers, 2) new uses for a material with the properties and functionality of rubber, and 3) the substitution in existing uses of soft thermoplastics.

The importance of TPEs is likely to increase for some time, particularly when one considers the 10 to 11 million metric tons of rubber that are used annually (as of 2007) in the non-tire rubber market. TPEs have failed to find significant use in the pneumatic tire segment of the rubber products market.

Generally speaking, TPEs have replaced thermoset rubbers in applications

where they have demonstrated improved part performance and/or reduced part cost. Though they will not totally displace thermoset rubber in non-tire uses, TPEs will provide formidable competition for many years to come, especially in new applications. The future progress of TPEs will be most interesting to watch.

# Acknowledgement

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# Compounding Materials and Uses

# by Carrie Burr and Joseph E. DeMello*

R.T. Vanderbilt Company, Inc. *Retired

There are a large number of ingredients and variations of ingredients that can be used in the successful compounding of natural and synthetic rubber (elastomers). The specific ingredients chosen for a compound will be dictated by the ultimate physical properties of the finished product, the processing characteristics required by the manufacturing process, and the costs acceptable to the user of the finished product. Compounding ingredients may be classified as follows:

- Elastomer (natural or synthetic rubber)
- Vulcanizing agents (sulfur, sulfur bearing accelerators, organic peroxides, and special purpose crosslinking agents)
- Accelerators
- · Accelerator activators and retarders
- Antidegradents (antioxidants and antiozonants)
- Processing aides (plasticizers, softeners, tackifiers, etc.)
- · Reinforcing fillers (carbon black, silica, mineral fillers) and resins
- · Inert fillers and diluents
- Special purpose materials (abrasives, blowing agents, colors, reodorants, etc.)

Elastomers have been extensively discussed in previous chapters. The following sections of this chapter discuss R.T. Vanderbilt Company, Inc. compounding materials and their major uses. For the most up-to-date product information, including specifications and material safety data sheets, please visit the Vanderbilt website at www.rtvanderbilt.com.

# **Vulcanizing Agents**

The word *vulcanizing* is derived from Vulcan, the Roman god of fire, and implies the use of heat. In 1839 Charles Goodyear discovered that by mixing sulfur with natural rubber and subjecting the mixture to heat, a plastic substance was transformed into an elastic substance. Vulcanization was the name originally given to the process, and the name continues to be used today. Later, it was learned that the sulfur actually crosslinks the chains of the rubber molecules. Over time chemicals other than sulfur were used to crosslink elastomers. This has caused the term *crosslinking* to become synonymous with *vulcanization*.

Vulcanization is normally achieved with time and temperature activation of specific chemicals that react with polymeric materials, producing a crosslinked network of molecular chains with visco-elastic properties. The terms *cure*, *cured*, and *curing* are also commonly used to describe the vulcanization process.

## Sulfur

The discovery of vulcanization with sulfur marked the founding of the present rubber industry. Today sulfur continues to be the most widely used chemical for crosslinking natural and synthetic rubber.

With natural rubber, two main types of vulcanizates may be obtained depending on the quality of sulfur present in the formulation: 1) soft rubber vulcanizates contain 3% or less sulfur, and 2) hard rubber vulcanizates (ebonite) contain 25% or more sulfur. Sulfur for vulcanization may be used in either or its elemental forms: the finely ground rhombic crystals (rubbermaker's grade) or the polymeric material (insoluble sulfur), which is converted to the rhombic form after heating.

### Sulfur-bearing Accelerators

METHYL TUADS[®], ETHYL TUADS[®], MORFAX[®], and SULFADS[®] are examples of sulfur-bearing ultra accelerators. These materials, which actually donate elemental sulfur, are used in compounding for heat resistance. Added in quantities of 2-4%, these products produce vulcanizates that retain good physical properties in elevated temperature service without the use of any elemental sulfur. In order to speed up the curing rates of these accelerators, small quantities of sulfur (1% or less) can be used in both natural and synthetic rubber formulations.

#### **Organic Peroxides**

Organic peroxides extract hydrogen atoms from the polymer units thereby establishing reaction sites for carbon to carbon bonds between the polymer units. These carbon-carbon bonds are more thermally stable than the sulfurcarbon or sulfur-sulfur bonds that are produced during sulfur vulcanization. Because carbon to carbon bonds are more stable, polymers crosslinked with organic peroxides have higher heat resistance and better heat resistant related properties.

When selecting a peroxide, consideration must be given to the crosslinking efficiency at a specific time and temperature (this determines the half-life of the peroxide), the polymer in which it is being used, and the processing conditions to which it will be subjected. Dialkyl peroxides are the most efficient polymer crosslinkers and generally have the longest half-lives. Peroxyketals, although less efficient than dialkyl peroxides, have shorter half-lives and will effectively crosslink elastomers at lower temperatures. Peroxyketals are also effective in curing polymers that have higher levels of unsaturation. The VAROX[®] peroxide product line supplied by R.T. Vanderbilt Company, Inc. is listed below:

VAROX ANS, 56.6% active benzoyl peroxide in paste form, crosslinks silicone molded parts and extrusions.

VAROX A-75, 76.5% active benzoyl peroxide in powder form, crosslinks most elastomers and polyolefins such as EPDM, EPM, EVA, and PE.

VAROX DBPH, 92% active 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, is used for crosslinking silicone, diene-type elastomers, G-type Viton[®], and polyolefins.

This product is especially effective when good crosslinking efficiency and minimum odor are required. VAROX DBPH-50 (50% active on a free flowing inert carrier) provides an easily handled solid form of the peroxide. VAROX DBPH-50-EZD (50% active on a silica carrier for easier dispersion) provides very translucent cross-sections in unpigmented silicone rubber. VAROX DBPH-50HP is a scorch retardant form of VAROX DBPH-50. VAROX DBPH-P20 (19.5% active in polypropylene) is specifically designed for modifying polypropylene. Dosage should be adjusted according to the percent activity of each product.

VAROX DCBP-50 Paste, 50% active 2,4-dichlorobenzoyl peroxide in a silicone paste, is specifically designed for the crosslinking of silicone rubber.

VAROX DCP, 98% active dicumyl peroxide, is the most efficient peroxide for crosslinking polymers. However, it does require a higher curing temperature than sulfur vulcanizates and is accompanied by a sweet odor. VAROX DCP-40KE (40% active on kaolin clay) is an easier to use form of VAROX DCP that should be used where a minimum of water absorption is desired. VAROX DCP-40C (40% active on calcium carbonate) is also a more easily handled form of this peroxide. VAROX DCP-40C-SP2 (40% active on calcium carbonate) is the same as VAROX DCP-40C, but with improved scorch protection for quicker mixing cycles. Dosage for all of these products should be adjusted according to the assay. This peroxide is a non-sulfur curing agent for NR, IR, SBR, BR, NBR, PE, EPDM, EPM, Silicone, EVA, and VAE.

VAROX TBPB, 98% active t-butyl perbenzoate in liquid form, is a crosslinking agent for silicone and other elastomers. It is effective in the service temperature range of 132° to 173°C (265° to 345°F). VAROX TBPB-50 (50% active on inert filler) provides an easily handled solid form of the peroxide.

VAROX VC-R, 96% active  $\alpha, \alpha'$  (bis(t-butylperoxy)-diisopropylbenzene, is a non-sulfur curing agent for NR and SR. It is a crosslinking agent for PE, CPE, EPDM, EPM, silicone, EVA, and VAE. VAROX 802-40C (40% active on calcium carbonate) and VAROX 802-40KE (40% active on kaolin clay) are easier to use forms of VAROX VC-R, which provide excellent compression set resistance. VAROX 802-40C but with improved scorch protection for quicker mixing cycles, enhanced mold flow, and quicker molding cycles. VAROX 802 SP-40MB Pellets (40% active extended grade masterbatch of EPM and calcium carbonate) also offers additional scorch protection. In a standard EPDM compound, scorch time measured at 125°C is 3 times longer than with VAROX 802-40C.

VAROX 130-XL, 45-48% active 2,5-dimethyl-2,5-di(t-butylperoxy)-hexyne-3 on an inert filler, is a peroxyketal vulcanizing agent for EPDM, EPM, and CPE. It is also a crosslinking agent for PE and EVA.

VAROX 230-XL, 40% active n-butyl-4,4'-bis(t-butylperoxy)valerate on an inert filler, is a peroxyketal crosslinking agent for elastomers such as polybutadiene, CPE, and EPDM. This peroxide provides faster action times at given temperatures than dialkyl peroxides. VAROX 230 XL-SP, 40% active on an inert filler, is the

same as VAROX 230-XL but with improved scorch protection.

VAROX 231, 92% active 1,1'bis(t-butylperoxy)-3,3,5 trimethylcyclohexane, is a peroxyketal vulcanizing agent for SBR, NBR, EPDM, EPM, CPE, and silicone, and it is a crosslinking agent for PE and EVA. The recommended curing temperature is 135° to 175°C (275° to 350°F). VAROX 231-XL (40% active on an inert carrier) provides an easily handled solid form of the peroxide. VAROX 231 XL-SP (40% active on an inert carrier) a more scorch resistant version of VAROX 231 XL.

### Special Purpose Curatives

DIAK[™] No. 1, hexamethylenediamine carbamate, is a diamine curing curative for FKM polymers, especially for applications requiring adhesion to metals. This product provides a high degree of physical properties including: hot tensile, low compression set, and excellent aging. Recommended usage of 1.0 - 1.5 phr provides better physical properties than DIAK No. 3 and a faster rate of cure than DIAK No. 4.

DIAK No. 3, N,N'-dicinnamylidene-1,6-hexanediamine, is a low cost diamine curative. It is recommended at levels of 2.0-3.5 phr especially for use in Viton A and Viton B-type compounds. This product is less scorchy than DIAK No. 1. The use of this product may contribute to overall mold fouling.

DIAK No. 4, 4,4'methylenebis(cyclohexylamine) carbamate, is a curing agent for fluoroelastomers. It is particularly useful in Viton B-type polymers for relatively safe processing and fast cures. This product is listed in 21 CFR Part 177.2600, Rubber Articles for Repeated Use (in Contact with Food).

DIAK No. 7, triallyl isocyanurate, is one of the most active coagents when used in combination with peroxides especially in FKM stocks. Generally 2.5 - 4.0 phr of DIAK No. 7 with 1.0 phr of a peroxide such as VAROX DBPH-50 is recommended. This product also works well in APA polymers.

DIAK No. 8, trimethallyl isocyanurate, is considered less active than DIAK No. 7. This may allow for better mold fill and a higher state of cure, with a lower compression set. This product should not be used with APA polymers.

VANAX[®] 829, a substituted 1,3,4-thiadiazole, is a crosslinking agent for polyacrylate elastomers. It provides better initial elongation than trifunctional triazines without sacrificing resistance to compression set.

VANAX MBM, M-phenylenedimalemide, is a coagent in peroxide-cured polymers. It can also be used as an accelerator in chlorosulfonated polyethylene (CSM) in conjunction with SULFADS and VANOX® NDBC. It minimizes reversion in sulfur-cured elastomers. It is a very effective coagent for EPDM at lower levels than Trimethylolpropane Trimethacrylate (TMPTMA), but doesn't lower compound viscosity.

VANAX PY, 23% poly-p-dinitrosobenzene in wax, is a chemical conditioner for butyl (IIR). It decreases cold flow while increasing uncured and cured modulus.

Processing safety, resilience, electrical properties, and the "leg strength" in cements are improved with the use of this product. Physical properties of butyl elastomers are significantly improved by heat treating the polymer in a Banbury for 10 minutes at 154°C (310°F) with 1.5 phr VANAX PY.

Viton Curative VC-20 Pellets is a bisphenol accelerator system masterbatch, which contains 33% of an organophosphonium salt in a Viton polymer. This product is generally used in pre-compounded Viton polymers ("C" at the end of the polymer grade designates that the polymer has the cure included). It offers a balance of conditions, i.e., controlling scorch, physical properties, and rate and state of cure.

Viton Curative VC-30 Pellets is a bisphenol accelerator system masterbatch, which contains 50% of a dihydroxy aromatic compound in a Viton polymer. Like other masterbatch cure systems, recommended levels of addition to FKM compounds are designed to maximize processability and physical properties in most commercial applications.

Viton Curative VC-50 Pastilles is a bisphenol cure system masterbatch blend, which reacts like a eutectic mix. Potential improvements offered by the blend include reduced mold fouling and an increased cure rate without a significant increase in scorch rate. The key to obtaining these improvements is to insure that this product is melted (approximately 116°C), which allows for optimum dispersion. Please note that under these processing conditions, there may be a decrease in metal adhesion.

#### Accelerators

Suitable accelerators for compounding may be selected from a large number of organic compounds, which contain nitrogen, sulfur, or both. The type and amount used depends upon the elastomer to be cured, the specified processing requirements, and the desired rate of cure. The following accelerators are just some of the choices available today to rubber compounders:

# Thiazoles

ALTAX[®] (MBTS), 2,2'-Dibenzothiazyl disulfide, was originally developed for the safe processing of rubber compounds cured at or above 142°C. This product continues to be widely used in compounds of all types for many major commercial applications. Its activity and scorch properties can be controlled over a wide range of temperatures by using it alone and in combination with CAPTAX[®] and ultra accelerators. When developing or modifying compounds, especially mineral-filled compounds where acidic clays may produce scorchy stocks, ALTAX is an ideal component.

CAPTAX (MBT), 2-mercaptobenzothiazole, was the first thiazole to be used commercially in the rubber industry. It is used effectively in applications requiring a high degree of curing activity at temperatures below 142°C. It can also be used in slower curing synthetic rubbers. Compounds cured with CAPTAX attain and maintain an optimum state of cure. Combinations of CAPTAX with ultra accelerators can be used where faster curing is needed and an increase in scorch can be tolerated i.e., curing systems designed for continuous curing in hot air or hot liquids at 232°C or higher, including salt baths.

ZETAX[®] (ZMBT), zinc 2-mercaptobenzothiazole, is a thiazole with a scorch rate and cure activity between CAPTAX and ALTAX. It also attains and maintains the optimum curing properties obtained with CAPTAX. Generally ZETAX is the preferred thiazole for latex curing systems.

# Sulfenamides

AMAX[®], N-oxydiethylenebenzothiazole-2-sulfenamide, is a delayed action accelerator preferred by many compounders for natural or synthetic rubber compounds. This product is particularly effective in compounds requiring maximum processing safety and a high state of cure. The overall properties of natural and synthetic compounds cured with AMAX generally have a higher state of cure than those obtained with thiazoles.

CURE-RITE[®] 18, N-oxydiethylenethiocarbamyl-N'-oxydiethylene sulfenamide, is a very efficient delayed action accelerator. Compounds made from combinations of CURE-RITE 18 with other sulfenamides have high modulus with good aging profiles, due to the efficient use of sulfur.

DURAX[®] (CBS), N-cyclohexyl-2-benzothiazolesulfenamide, is used in natural and synthetic rubber. It is faster curing than AMAX, and while it develops a higher state of cure, it can also be scorchy. DURAX (0.25 phr) in combination with a thiourea will act as a retarder in Neoprene, thereby increasing scorch safety.

MORFAX, 4-morpholinyl-2-benzothiazole disulfide, is a delayed action accelerator which is faster curing in natural and synthetic rubber than other sulfenamides. Its sulfur donating capability imparts good heat aging and stable dynamic properties. MORFAX is desirable for obtaining uniform cures in thick parts and for fast curing of scorchy synthetic compounds that are otherwise difficult to process. This is particularly evident when MORFAX is used in combination with ETHYL CADMATE® or CURE-RITE 18, especially in natural rubber compounds, which produces a minimum reversion pattern. Ideally MORFAX can be added late in a masterbatch, which is free of accelerators, in an internal mixer where it will melt rapidly at 116°C (240°F), providing a homogenous dispersion. After the second pass, compounds exhibit outstanding storage stability and workability (138°C). Rapid cure rates develop at about 154°C with a high rheological plateau.

VANAX NS, N-tert-butyl-2-benzothiazolesulfenamide, is one of the more common sulfenamide accelerators. It is less scorchy and faster curing than DURAX in natural and synthetic rubber compounds. In many compounds the dosage can be reduced by up to 10% when compared with similar accelerators. VANAX NS is the sulfenamide of choice in many tire applications.

#### **Ultra Accelerators**

The designation "ultra" is applied to accelerators that have the greatest impact on the rate of vulcanization. Generally, not only are smaller quantities of elemental sulfur required in ultra accelerated compounds, but also optimum physical properties can be obtained in a shorter curing time than with other classes of accelerators, such as thiazoles or sulfenamides. The three classes of ultra accelerators are: dithiocarbamates, thiurams, and xanthates.

## Dithiocarbamates

BISMATE[®] Powder, bismuth dimethyldithiocarbamate, is particularly effective in compounds vulcanized at temperatures greater than 160°C. This product is often used with ALTAX for low scorch rate at processing temperatures and for maintaining an optimum state of cure in articles with thick and thin sections. Wire insulations can be cured in open steam using BISMATE in combination with other accelerators. BISMATE is considered a very fast accelerator.

BUTYL EIGHT[®], activated dithiocarbamate, was developed for low and room temperature vulcanization of cements and proofing compounds. This product can be accelerated with dibutylamine, or retarded with CAPTAX.

ETHYL CADMATE Dustless, cadmium diethyldithiocarbamate, is used in combination with other accelerators to provide heat resistant compounds based on IIR, EPDM, and NBR elastomers. It can also be used in EV (Efficient Vulcanization) systems, especially with MORFAX in reversion resistant NR compounds.

METHYL CUMATE[®], copper dimethyldithiocarbamate, is recommended for SBR, EPDM, and IIR, and it is a powerful secondary accelerator. The use of METHYL CUMATE with ALTAX increases cure rate while maintaining or decreasing the scorch rate in some compounds. Its use results in high modulus and tensile and low compression-set SBR compounds. This product also shows a distinct advantage in curing thick items. Compounds designed with METHYL CUMATE should contain VANOX ZMTI blends to obtain maximum aging, especially in mineral filled stocks. Please note: Copper is a pro-oxidant for natural rubber; therefore, the use of this product is not recommended for use in polyisoprene compounds.

AMYL LEDATE[®], lead diamyldithiocarbamate, is a liquid dithiocarbamate that improves dynamic properties in NR and IR. It is often used in combination with OCTOATE[®] Z and BUTYL TUADS in soluble cure systems for carbon black filled compounds. It can also provide exceptionally low compression set values. Like all lead containing products, the future use of this product may be limited.

METHYL LEDATE Dustless, lead dimethyldithiocarbamate, is a low scorch ultra accelerator with excellent activity under both normal and elevated temperature curing conditions. It is especially useful in injection molding compounds. This product is effective in sulfur-curing systems, particularly in polymer blends. In halobutyl, the use of METHYL LEDATE with ALTAX provides good compression set. This product should not be used in light colored compounds because of discoloration with heat. Like all lead containing products, the future use of this product may be limited.

METHYL SELENAC[®], selenium dimethyldithiocarbamate, is an ultra accelerator that is primarily used in sulfur-free or low sulfur cures. It may be used for heat resistance in insulating rubber parts, molded goods, steam hose, and conveyor belts for hot material service. METHYL SELENAC can also be used to avoid sulfur staining of rubber parts when in contact with copper staining material.

ETHYL TELLURAC[®], tellurium diethyldithiocarbamate, is a fast curing accelerator for EPDM and IIR vulcanization. ETHYL TELLURAC, METHYL TUADS combinations with CAPTAX are used extensively in IIR compounds requiring rapid cures.

VANAX 552, piperidinium pentamethylenedithiocarbamate, is an accelerator that is used primarily in cements and latexes. It is an ultra-fast accelerator for low temperature cure and acts as a chemical peptizer for sulfur modified (G-type) Neoprenes.

AMYL ZIMATE[®], zinc diamyldithiocarbamate, is a liquid dithiocarbamate recommended for improved dynamic properties in NR and synthetic polymers. It can be used in mineral filled, soluble cure systems.

BUTYL ZIMATE, zinc dibutyldithiocarbamate, is an ultra-fast accelerator for EPDM, as well as natural and synthetic latexes. In EPDM compounds, combinations with other accelerators provide low compression set and good heat aging with minimal bloom. Additionally, this product functions as a stabilizer and nondiscoloring antioxidant in uncured stocks. BUTYL ZIMATE is also available in a water-based dispersion and a dustless powder.

ETHYL ZIMATE, zinc diethyldithiocarbamate, is generally used as a primary accelerator in NR and SBR. For safer processing and a wider cure range, the use of a thiazole modifier is recommended. This product is generally nondiscoloring in light colored stocks. Finally, it acts as a stabilizer in thermoplastic rubbers and hot melts. This product can be used in place of METHYL ZIMATE; quantities should be increased by approximately 10% in order to obtain comparable results.

METHYL ZIMATE, zinc dimethyldithiocarbamate, is used extensively in dry rubber compounding for high temperature, continuous vulcanization (CV curing) of wire insulation. METHYL ZIMATE with CAPTAX provides good curing activity in EPDM formulations. It is generally non-discoloring in light colored compounds.

# Thiurams

SULFADS, dipentamethylenethiuram hexasulfide, is a sulfur bearing ultraaccelerator and sulfur donor for NR and synthetic polymers. It has 35.7% available sulfur for vulcanization as compared to 13.3% and 10.5% respectively for METHYL TUADS and ETHYL TUADS. This product can be used to compound heat resistant NR and SBR, as an accelerator for CSM vulcanization, and in curing systems for IIR and EPDM. In latex, SULFADS is an excellent sulfurdonor. BUTYL TUADS, tetrabutylthiuram disulfide, is a liquid thiuram for soluble cure systems in natural and synthetic polyisoprene cure systems. For EPDM compounds, this product works well in conjunction with AMYL LEDATE.

ETHYL TUADS, tetraethylthiuram disulfide, is an ultra accelerator and sulfur donor for NR and synthetic rubbers. This product can also be used as a cure modifier for Neoprene (retards G types, accelerates W types), and is nondiscoloring in light stocks. Product recommendations and commercial applications are the same as for METHYL TUADS, except that quantities used should be increased by approximately 10% to obtain comparable results.

METHYL TUADS, tetramethylthiuram disulfide, is an ultra accelerator and sulfur donor for NR and synthetic rubbers that is particularly effective in IIR and CR. This product can also be used as a cure modifier for Neoprene (retards G Types, accelerates vulcanization of W Types). It is nondiscoloring in light stocks. METHYL TUADS is used extensively in heat resistant compounds, designed for sulfurless and semi-efficient low sulfur cures. It can also be used to activate thiazoles and sulfenamides. A blend of 60% METHYL TUADS and 40% ETHYL TUADS can be used to reduce bloom on the finished product.

UNADS[®], tetramethylthiuram monosulfide, unlike other thiurams, contains no available elemental sulfur. This product can be used in conjunction with sulfur to provide good curing activity. It also has a lower scorch rate than ETHYL TUADS and METHYL TUADS.

# **Other Accelerators**

PROPYL ZITHATE[®], zinc isopropyl xanthate, is a low temperature, nondiscoloring accelerator that is generally used in NR and synthetic cement stocks to prevent copper staining. Curing temperatures are usually below 120°C when using this product.

VANAX 196 Liquid, 100% active Alkyl dithiophosphate, is an accelerator and sulfur-donor for sulfur-based cure systems. This product will not generate nitrosamines, and it imparts excellent reversion resistance in NR. VANAX 196 Solid, a 70% active form on an inert carrier, provides an easily handled powdered form of the accelerator.

VANAX 808 HP, an 85% active 3,5-diethyl-1,2-dihydro-1-phenyl-2propylpyridine, is an activator for acidic accelerators. It provides excellent cures for reclaims and hard rubber. When used as a latex accelerator, vulcanizates age well. Finally, it can be used as a secondary accelerator for chlorinated polyethylene (CPE). VANAX 808 HP-50, a 50% active 3,5-diethyl-1,2-dihydro-1phenyl-2-propylpyridine, is also available.

VANAX 882B, composed of high molecular weight fatty amines, is a waxy flake accelerator for CPE. This product is often used with thiadiazoles, such as VANAX 829.

VANAX CPA, dimethylammonium hydrogen isophthalate, produces lower modulus stocks, especially in Neoprene GW Type compounds. When used

in combination with a blend of AGERITE[®] STALITE[®] S and VANOX ZMTI, vulcanizates have a higher modulus with excellent aging and outstanding resistance to flex fatigue. Finally this product offers outstanding organic color retention after processing and aging.

# Guanidines

VANAX PML, di-ortho-tolylguanidine salt of dicatechol borate, is a fast curing accelerator for Neoprene, especially in G, W, and T-type for both wire/cable and mechanical goods. This product can also be used in NR and other synthetic rubber compounds, including IIR. This product is listed in FDA21 CFR 177.2600, Rubber Articles for Repeated Use (in Contact with Food).

# Thioureas

THIATE[®] EF-2, trimethylthiourea, offers fast press cures that are less scorchy than THIATE H, and lower compression sets, in Neoprene compounds. Also, it is efficient in injection molding and liquid curing media (LCM) for extrusion stocks. The use of THIATE EF-2 in open steam cures is not recommended.

THIATE H, 1,3-diethylthiourea, is used in applications requiring a fast initial cure rate such as continuous cured sponge, LCM extrusion compounds, molded sponge, molded-on soiling, and hot air cures.

THIATE U, 1,3-dibutylthiourea, is similar to THIATE H with the exception of a slightly slower cure rate and improved scorch properties. It has a lower volatility than THIATE H.

Polymer	General Purpose		Fast Cure		Low Set/ Heat Resistance		Injection Molding	
Natural	AMAX	0.5	ALTAX	0.5	MORFAX	2.0	MORFAX	1.0
	TMTD	0.2	ZnDMC	0.3	DTDM	1.0	DTDM	1.0
	Sulfur	2.7	Sulfur	2.0	Sulfur	0.5	TMTD	1.0
SBR	MORFAX	1.5	MORFAX	1.0	DTDM	2.0	CAPTAX	1.2
	CUMATE	0.2	CUMATE	0.3	MORFAX	1.0	LEDATE	1.2
	Sulfur	2.0	Sulfur	1.7	TMTD	1.0	DTDM	1.0
							Sulfur	2.0
NBR	DURAX	2.0	CAPTAX	1.5	TMTD	1.0	TMTD	2.0
	TMTD	1.0	ZnDMC	1.5	DTDM	2.0	DURAX	1.0
	Sulfur*	1.5	Sulfur*	1.5	MORFAX	1.5	Sulfur*	0.5
EPDM**	CAPTAX	1.5	SULFADS	0.8	DTDM	2.0	ALTAX	1.0
	TMTD	0.6	TeDEC	0.8	ZnDMC	3.0	TMTD	0.6
	TETD	0.9	TMTD	0.8	ZnDBC	3.0	ZnDBC	2.0
	Sulfur	1.5	CAPTAX	1.5	TMTD	3.3	Sulfur	2.0
			Sulfur	2.0	Sulfur	0.5		
lir	CAPTAX	1.0	ALTAX	1.0	DTDM	2.0	CAPTAX	1.0
	TMTD	2.0	CADMATE	1.0	TMTD	2.0	SULFADS	1.0
	Sulfur	1.5	TeDEC	1.0	CADMATE	2.0	TMTD	2.0
			Sulfur	2.0			Sulfur	1.0
Neoprene	DOTG	1.0	VANAX PML	1.5	THIATE EF-2	1.5	THIATE U	1.0
(W&I Types)	UNADS	1.0	CaO	2.0				
13603)	Sulfur	1.0						
CSM	TMTD	2.0	SULFADS	2.0	VAROX DBPH	3.0	SULFADS	1.8
	Sulfur				TAC	4.0	VANAX MBM	1.0

A few factory proven accelerator systems can be found in the table below:

* Spider sulfur, elemental sulfur treated with magnesium carbonate, is suggested for good dispersion in NBR.

** The above EPDM acceleration systems are for non-metallocene polymers. These systems may be reduced by 40% to produce similar results in these newer EPDM polymers.

## Activators and Retarders

*Zinc Oxide* - The accelerators previously discussed normally require zinc oxide for activation in most polymers. The amount required for activation varies, but 3-5 phr has been found to give the desired effect in most polymers. Zinc oxide used for activation should be low in lead content and some compounders specify a lead free grade. With Neoprene, zinc oxide serves as a vulcanizing agent and acid acceptor as well.

Compounding materials which are alkaline can have an accelerating effect on vulcanization. Materials in this class include litharge, magnesia, certain precipitated calcium carbonates, furnace blacks, and amines. Conversely materials of an acidic nature may retard the curing rate if present in a sufficient quantity. A class of compound materials designated as "scorch retarders" is used in some highly accelerated stocks where unusually hot processing conditions are encountered. Phthalic anhydride, salicylic acid, and sodium acetate are examples of acidic materials that act as retarders. Another retarder is N-cyclohexylthiophthalimide, which is effective in small doses. The maximum recommended dosage is 0.4 phr, as additional quantities may bloom.

*Fatty Acids*: Natural polymers contain small, variable amounts of fatty acids such as stearic acid. Early research established that rubber deficient in fatty acids can be slow curing because fatty acids activate the zinc oxide needed for vulcanization. Therefore, it has become standard practice to include a fatty acid, normally stearic acid, in most rubber compounds. Generally 0.5 to 1.0 phr is used, but with SBR compounds, up to 3.0 phr may be needed.

OCTOATE Z, zinc 2-ethylhexoate, is an activator containing a soluble zinc carboxylate for bloom-free cures. It can be used as a substitute for zinc oxide and stearic acid in windshield wiper blades and adhesives where zinc oxide can be difficult to disperse and fatty acids would cause accelerators to bloom. OCTOATE Z can also be used for transparent to translucent rubber products. OCTOATE Z Solid (57% active on an inert carrier) provides an easily handled solid form of the activator.

Internal Lubricants or process aids are normally added to provide mold release and/or to promote flow in molding or extrusion (i.e., VANFRE® AP-2). These are described in detail later in this chapter. Internal lubricants also have the ability to reduce the heat history of "scorchy" compounds and allow faster accelerator systems to be used.

#### Antidegradants

The selection of an elastomer is dictated primarily by the application specifications, including the aging requirements of the rubber article. The curing system used also affects the aging of rubber products. There are a number of compounding materials used to impart aging protection, which, as a class, are known as antidegradants. The two main categories of antidegradants are antioxidants and antiozonants. Antioxidants include aromatic amines, phenols, and phosphites among others. Antiozonants are primarily paraphenylene diamines. Most synthetic polymers contain low levels of residual antioxidants, which are used to protect the polymers during manufacture and storage. Nevertheless, it is considered good compounding practice, and in many cases it is essential, to include additional antioxidants to protect the compound during processing, as well as the finished article.

## Antioxidants

Antioxidants are added to rubber compounds, generally in quantities of one to two parts per hundred rubber parts of rubber by weight (1-2 phr) depending on the degree of protection required by the end use. Combinations of antioxidants are often used, since some are specific as to the type of protection they impart. For example, some are particularly efficient for retarding the degrading forces of heat, oxygen, or ultraviolet light. Sometimes a combination of antioxidants will give synergistic results (better results than would be obtained by either antioxidant alone).

## Amine Antioxidants

AGERITE STALITE, octylated diphenylamine, is a liquid, general-purpose antioxidant for most elastomers. It is specifically recommended for use in CUMATE accelerated SBR formulations and is particularly effective in Neoprene and in adhesives.

AGERITE STALITE S, is a solid version of AGERITE STALITE that offers a comparable protection at equivalent dosages. It is a general purpose antioxidant that is effective in most elastomers, especially Neoprene. It is nonstaining and nondiscoloring, and may be used in adhesives and hot melts where good color retention is of particular concern. VANOX 1081, p,p'-dioctyldiphenylamine, is a purified version of AGERITE STALITE S.

AGERITE SUPERFLEX[®] Solid G, 75% active diphenylamine-acetone reaction product on an inert carrier, is used effectively for heat, oxidation, and flex-cracking protection in tires and heavy duty mechanical products.

VANOX AM, diphenylamine-acetone low temperature reaction product, provides good heat and oxidation resistance. Because it is staining and discoloring, this product should not be used in light colored compounds. When used with in a 1:1 blend with VANOX ZMTI, this product provides excellent high temperature heat resistance in non-peroxide cured compounds.

VANOX CDPA, 4,4' – Bis(a,a-dimethylbenzyl)diphenylamine, is a low volatility, high amine activity antioxidant that is especially effective in HNBR and ACM rubbers for high temperature applications. In combination with the antioxidant synergist Vanox ZMTI, it provides maximum heat resistance to EPR, EPDM, IR, NBR, NR, and SBR rubber compounds. This product should not be used in light colored compounds, as it is slightly staining and discoloring.

VANOX HT, a synergistic antioxidant blend, is designed for high temperature service and is especially effective in mineral filled EPDM compounds.

VANOX 1081, p,p'-dioctyldiphenylamine, is a general purpose antioxidant that is effective in most elastomers. This product is purified so that it may be used in many nonstaining and nondiscoloring applications. It is used in adhesives and hot melts where good color retention is of particular concern.

VANOX 1001, a mixture of alkylated diphenylamines, is a general purpose antioxidant for use in compounds required to be nonstaining and nondiscoloring.

# Phenolic Antioxidants

AGERITE SUPERLITE[®], a mixture of polybutylated bisphenol A is a nonstaining, nondiscoloring antioxidant for use in white and light colored compounds. This product can be used in automotive and appliance products where lacquer or enamel staining cannot be tolerated. It is non-blooming in most compounds. AGERITE SUPERLITE SOLID is 75% active ingredient on an inert carrier.

SONGNOX[®] 1010, Tetrakis [methylene 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate] methane, is a primary antioxidant for organic polymers PE, PP, POM, PA, PET, PBT, PVC, and elastomers. This product is effective for use in polymer processing for reducing viscosity change and gel formation. It provides long term heat stability and protects physical properties during the use and storage of the end-product. It exhibits a synergistic effect when used in combination with SONGNOX 1680 and other secondary antioxidants. It can be used with benzotriazoles or hindered amine light stabilizers (HALS) for thermal and light stabilization in outdoor use.

SONGNOX 1024, 1,2-Bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoly) hydrazine, is a metal deactivator and antioxidant for wire and cable, adhesive (both hot melt and solution), and powder coating applications. It is effective in PE, PP, Crosslinked PE, EPDM, styrenic elastomers, nylon, PU, polyacetal, and styrenic copolymers, and can be used as the primary antioxidant or can be used in combination with hindered phenolic antioxidants (particularly SONGNOX 1010) to achieve synergistic performance.

SONGNOX 1076, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, is a primary antioxidant for organic polymers PE, PC, PVB, PVC, PU, acrylics, styrenics, and elastomers. It is very effective in reducing viscosity change and gel formation in polymer processing, and it provides long term heat stability by protecting physical properties during storage and use of end product. It exhibits a synergistic effect in combination with SONGNOX 1680 and other secondary antioxidants. It can be used with benzotriazoles or HALS for thermal and light stabilization in outdoor use. Finally this product is FDA compliant for food packaging applications.

SONGNOX 1077, Isotridecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, a sterically hindered phenol which is a liquid at room temperature, is a primary antioxidant for organic polymers, including ABS, acrylics, PE, PU, PVC and elastomers such as BR, CR, EPDM, NBR and SBR. It can also be used in synthetic fibers, waxes, fats and oils.

SONGNOX 1135, iso-octyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, is a sterically-hindered liquid, primary antioxidant that can be used in a wide range of organic polymers such as ABS, PE, PVC, and rubbers such as BR, NBR, and SBR. It can be used in synthetic fibers, waxes, fats and oils. It is an effective nondiscoloring stabilizer that provides excellent long-term stability. It exhibits a synergistic effect in combination with phosphites, and can be used with benzotriazoles or HALS for thermal and light stabilization in outdoor applications.

SONGNOX 1290, 2,2'-ethylidene bis(4,6-di-t-butylphenol), is an antioxidant for both dry elastomers and latexes. It is nonstaining and nondiscoloring for light colored goods.

SONGNOX 3114, tris (3,5-di-5-butyl-4-hydroxybenzyl) isocyanurate, is a high melting point, trifunctional hindered phenol that is frequently used in combination with a phosphite antioxidant in high temperature hot-melts. The combination of hindered phenol and phosphite is recognized as an excellent stabilizer system for black polymer hot melts. When used by itself, it is both nonstaining and nondiscoloring. This product also provides excellent results when used in combination with BUTYL ZIMATE.

VANOX MBPC, 2,2'-methylene bis-4-methyl-6-t-butylphenol, is an antioxidant for NR and SR, both in dry rubber and latex form. This product is especially recommended for use in compounds for white and light colored goods. It is an effective copper inhibitor in natural and synthetic rubbers. It also offers high heat resistance in non-peroxide cured compounds.

#### Hydroquinoline Antioxidants

AGERITE RESIN D[®], polymerized 1,2-dihydro-2,2,4-trimethylquinoline, protects natural and synthetic elastomers against heat and oxidation under severe service conditions. At high dosages (7-12phr), it improves ozone resistance of many elastomers. It is used in radiation cured PE for improved heat aging. This product is especially useful with peroxide cures because it offers minimal interference in the peroxide crosslinking mechanism. For high temperature resistance in peroxide cured compounds, use with VANOX ZMTI. Generally, the use of this product is not recommended in Neoprene compounds, because it decreases scorch resistance. This product is available in both a powder and a pastille form.

AGERITE MA, polymerized 1,2-dihydro-2,2,4-trimethylquinoline, is a higher melting analog of AGERITE RESIN D, which may be preferred for extreme or higher temperature processing and aging conditions. This product is available in both a powder and a pastille form.

#### Other Antioxidants

ISOBUTYL NICLATE[®] Dustless Special, nickel di-iso-butyldithiocarbamate, is recommended as an antioxidant in SBR and CSM. This product is also recommended as an antioxidant and antiozonant in Epichlorohydrin.

METYL NICLATE, nickel dimethyldithiocarbamate, is a companion antioxidant to ISOBUTYL NICLATE for Epichlorohydrin. It is also suitable for peroxide cured EPR and EPDM elastomers because it has little effect on the cure characteristics of peroxides. This product produces a non-blooming, greenish color in mineral filled compounds. Finally, it offers superior non-blooming properties when compared to VANOX NDBC.

SONGNOX 1680, tris (2,4-di-tert-butylphenyl) phosphite, is a secondary antioxidant for organic polymers. It offers excellent melt flow and color protection during the thermal processing of polymers. It is an effective antioxidant in applications which include polyolefins, polycarbonate, polyester, and styrenics. It can be used in combination with hindered phenols to achieve synergistic performance. For better thermal and light stabilization in outdoor use, this

product can be used with benzotriazoles and HALS.

SONGNOX 2500, 2,5-di-tert-amyl-hydroquinone, is an excellent nonstaining and nondiscoloring heat stabilizer for natural and synthetic rubbers, providing effective protection against oxygen and sun cracking. It is an efficient stabilizer for raw polymers and is especially suitable for NBR. It is very effective in unvulcanized rubber adhesives, tapes, and film. This product is also particularly effective in water-based systems and is used in a wide variety of coatings. It can also be used with a lower volatility antioxidant to insure long lasting protection.

SONGNOX 6260, bis (2,4-di-tert-butyl phenyl) pentaerythritol diphosphite, is a high performance secondary antioxidant for organic polymers that provides excellent melt-flow and color protection during thermal processing. It can be used in combination with hindered phenols, such as SONGNOX 1010 and 1076 to achieve synergistic performance, and it can be used with benzotriazoles and HALS for thermal and light stabilizations in outdoor use. Please note, this product is moisture sensitive, so consult the MSDS for handling considerations.

SONGNOX DLTDP, dilauryl thiodipropionate, is a secondary thioester antioxidant for use during the processing of organic polymers. It decomposes and neutralizes hydroperoxides formed by the auto-oxidation of polymers. It is an excellent antioxidant for many applications including plastics, rubber, synthetic fibers, fats and oils, and petroleum products. This product can be used as a synergist in combination with phenolic antioxidants to enhance aging and light stability.

SONGNOX DSTDP, distearyl thiodipropionate, is a secondary thioester antioxidant for organic polymers. It decomposes and neutralizes hydroperoxides formed by auto-oxidation of polymers. It is an effective antioxidant for plastics, rubber, synthetic fibers, fats and oils, and petroleum products. This product can be used as a synergist in combination with phenolic antioxidants to enhance aging and light stability.

VANOX NDBC, nickel di-n-butyldithiocarbamate, is both an antioxidant and antiozonant for SBR, NBR, CR, CSM, and ECO. This product is not recommended for use in natural rubber compounds. With use of more than 1.0 phr, severe blooming may occur.

VANLUBE[®] 7723, methylene bis(dibutyldithiocarbamate), is an ashless antioxidant for halogenated polymers. It is especially recommended for use with CSM.

VANOX MTI, 2-mercaptotoluimidazole, is a synergistic, secondary antioxidant, for both natural and synthetic rubbers, which in combination with other antioxidants, provides superior heat aging and flex resistance.

# Antioxidant Selection Guide

	Properties							
Tradename	Form	Melting Temp. °C	Non- blooming Dosage, phr	Discoloration	Staining	Inhibits Oxygen Attack	Improves Heat Aging	Inhibits Flex Cracking
Amine Antioxidants		0	0	0				
AGERITE STALITE	liquid		2.0+	no	no	E	E	F
AGERITE STALITE S	powder	90-99	2.0+	no	no	E	E	F
AGERITE SUPERFLEX Solid G	powder		2.0+	br	st	E	E	E
VANOX 1081	powder	95-100	2.0+	no	no	E	E	E
VANOX AM	powder	85-97	2.0+	br	st	E	E	E
VANOX CDPA	powder	98 min.	2.0+	sl	sl	E	E	E
Hydroquinoline Antioxidant	S							
AGERITE MA	past/p*	115-135	2.0+	sl	sl	E	E	F
AGERITE RESIN D	past/p*	82-102	2.0+	sl	sl	E	E	F
Phenolic Antioxidants								
AGERITE SUPERLITE	liquid		2.0+	no	no	F	F	Р
AGERITE SUPERLITE S	powder		2.0+	no	no	F	F	Р
SONGNOX 1010	powder	110-125		no	no	E	E	Р
SONGNOX 1024	powder	221-232		no	no	G	G	Р
SONGNOX 1076	powder	49 min.		no	no	G	G	Р
SONGNOX 1077	liquid			no	no	G	G	Р
SONGNOX 1290	powder	160-165	2.0+	no	no	E	G	Р
SONGNOX 3114	powder	218-223	2.0+	no	no	F	E	Р
VANOX MBPC	powder	125 min.	2.0+	no	no	E	G	Р
Other								
BUTYLZIMATE	powder	103-110	2.0+	no	no	G	E	Р
ISOBUTYL NICLATE	powder	173-181	1.0	gr	no	F	E	Р
METHYL NICLATE	powder	290 min.	2.0	gr	no	F	E	Р
SONGNOX 1680*	powder	181-187		no	no	E	E	G
SONGNOX 2500	powder	175-185		no	no	E	E	G
SONGNOX 6260*	powder	170-180		no	no	G	G	
SONGNOX DLTDP*	powder	38-41		no	no	E	E	
SONGNOX DSTDP*	powder	63.5-68.5		no	no	E	E	
VANOX MTI*	powder	250 min.	2.0+	no	no	E	E	E
VANOX NDBC	powder	86 min.	1.0	gr	no	F	E	Р
VANOX ZMTI*	powder	300 min.	2.0+	no	no	E	E	E

*Normally used as a secondary antioxidant other antioxidants; rating refers to combination sI=slight, st=staining, br=brown, gr=green, gy=gray, E=excellent, G=good, F=fair, P=poor

Applications									
Polymer Stabilizer	Tires	Hose and Belts	Automotive & Appliance Molded Goods	Wire and Cable	Footwear	Adhesives & Cements	Hot Melts	Latex	FDA Listed**
		, <u> </u>				. <u> </u>			
x		×	x	x	x	x	x	x	
		×	x	x	x	x	x	x	~
	x		x	x		x			~
		x		x	x	x	х	х	~
	x		x	x			x	1	~
	x	x	x	x	x	x	x		
		·	•			•			
				x		x	x	x	
	x	x	x	x	x	x		x	
x	x			x	x	x	x	x	~
	х			x	x	x	х		~
x				x	x	x	x	x	~
		x		x		x	x		~
x		i i		x		x	x	x	~
						x		x	~
x								x	~
		ĺ					x	x	~
x		x			x	x	x	x	~
x						x	x		~
			x	x					
		x	x	x					
x				x		x	x		*
x						x	x	х	~
x			x				x		~
				x		x		x	~
				x		x		x	~
	x	x	x	x	x	x	x	x	
	x	x	x				x		
	x	x	x	x	x	x	x	x	

**Listed in 21 CFR Part 177.2600, Rubber Articles for Repeated Use (in Contact with Food) and/or 21 CFR Part 178.2010 Antioxidants and/or Stabilizers for Polymers X=recommended

VANOX ZMTI, zinc 2-mercaptotolimidazole, is a synergistic, secondary antioxidant for both natural and synthetic rubbers. Combinations, with amine and/or phenolic antioxidants and some antiozonants, provide superior heat aging in EPDM and NBR. This product provides excellent flex crack resistance in NR and CR. Above 2.0 phr, it may impart scorch in some CR compounds. For superior high temperature resistance, the use of 1 phr VANOX ZMTI with 1 phr antioxidant is generally recommended.

## Antiozonants

Most are derivatives of para-phenylenediamine (PPD) that are used to improve the resistance of finished rubber articles to attack by ozone. All PPDs will discolor the rubber article and stain adjacent surfaces.

#### Waxes

Certain waxy materials, when added in excess of their solubility in elastomers, will bloom to the surface after vulcanization. The waxy film that forms on the surface of the rubber provides protection from sun-checking and atmospheric cracking, as long as the film remains intact (static protection). Paraffin, microcrystalline, and various pre-blended combinations of waxes are used for this purpose. Generally the waxes are used in conjunction with a suitable antiozonant to provide resistance to both static and dynamic exposure to ozone.

VANWAX[®] H, a paraffin wax, blooms quickly and forms a somewhat fragile crystalline barrier to ozone. Typically 1.0 to 1.5 phr of this product is used for static applications.

VANWAX H Special, a blend of microcrystalline waxes, blooms slowly but forms a more amorphous, flexible barrier than paraffin waxes. In order to satisfy ASTM tests for resistance to ozone at 50 pphm, generally a minimum of 1.5 phr of this product in combination with 3.0 phr antiozonant and 1.5 phr of AGERITE RESIN D is recommended.

VANWAX OZ, a selected blend of waxes, is a sun-checking inhibitor that protects elastomers from ozone attack under static conditions. It is particularly effective at lower exposure temperatures.

#### **Processing Aids and Plasticizers**

Most natural and synthetic elastomers require processing aids and plasticizers. The basic benefit of these ingredients is the reduction of the internal friction of the compounds. With lower internal friction, the compounds incorporate fillers with less power consumption, have a lesser tendency to scorch, and extrude or calendar more smoothly. Plasticizers are also used in compounding to produce lower modulus, lower hardness, and higher elongation. Besides lowering the overall heat history of a compound, higher loading of either carbon black or mineral fillers can potentially reduce the net compound cost of a commercial product.

# Processing Aids

VANFRE® AP-2, a polymer processing lubricant, is a general purpose

processing aid for both natural and synthetic compounds. It reduces compound viscosity, improves mold flow and mold release, and has little effect on the optimum physical properties including adhesion. VANFRE AP-2 Special, specifically designed for FDA compliant applications, offers the same advantages as VANFRE AP-2.

VANFRE DFL, a buffered phosphate ester solution, is a mold lubricant that minimizes mold build-up or mold fouling. It also inhibits the corrosion of molds and dryer flights. Demolding silicone compounds may be improved by the use of this product, especially in critical, "hot-tear" areas.

VANFRE HYP, a polymer processing lubricant, is designed for use with CSM. It reduces plasticity, improves mold flow and mold release without adversely affecting physical properties. It is FDA compliant for Polymer Processing Lubricant with no limitations to FDA 21 CFR Sections 175.300 and 177.1210. For compliance with section 177.2600, a maximum of 30% by weight of total compound may be used.

VANFRE IL-2, a blend of fatty alcohols on an inert mineral carrier, is an internal lubricant that greatly improves flow and molding characteristics of highly filled compounds. It has little to no effect on tensile strength and water swelling characteristics of the compound.

VANFRE M, a select blend of waxes, reduces compound plasticity, improves mold flow, and has little effect on physical properties.

VANFRE UN, un-neutralized fatty acid phosphate, is mainly used in ethylene acrylic elastomers. It improves release from mill rolls, molds, and other processing equipment.

VANFRE VAM, blend of fatty alcohols on an inert mineral carrier, is a flaked processing aid for Vamac[®], ethylene acrylic elastomers, and potentially in other solvent-resistant polymers.

#### Plasticizers

Petroleum, vegetable oils, and synthetic plasticizers are used to reduce viscosity, promote flow, improve flexibility at low temperature, and provide softer vulcanizates.

LEEGEN[®], a blend of sulfonated petroleum and mineral oils on an inert carrier, is an easily handled and weighed dry-form plasticizer. This product is especially recommended for use in mill mixing and as a process aid for diene-type polymers.

VANPLAST[®] PL, a neutralized oil soluble sulfonate of high molecular weight in paraffinic oil, is a plasticizer and processing aid for all elastomers.

VANPLAST R, a neutralized oil soluble sulfonate of high molecular weight in paraffinic oil, is a plasticizer and processing aid for all elastomers. Its amber color is lighter, and it has more of the active plasticizing ingredient than VANPLAST PL.

VANPLAST 202, a neutral barium petroleum sulfonate, is a dark-brown liquid containing a minimum of 6.4% barium. This product not only behaves as a plasticizer, but is also a corrosion inhibitor, especially in halogenated compounds.

#### **Reinforcing Materials, Inert Fillers, and Diluents**

Pure gum natural rubber and *cis*-polyisoprene compounds, although high in tensile strength, are suitable for relatively few commercial applications, while most synthetic polymers are too low in tensile strength to warrant their consideration for use; therefore, rubber compounds often require the addition of reinforcing materials to improve their physical properties. These materials include carbon blacks, zinc oxide, precipitated calcium carbonates, hard and soft clays, silicas, talcs, micas, wollastonites, calcium silicate, and silicon dioxide. High-styrene copolymer resins are used extensively in non-black shoe sole compounds, where high hardness and good abrasion resistance are required. Various phenolic resins are also used in some compounding applications.

The successful incorporation of these materials into a rubber compound, requires a thorough understanding of how the reinforcing materials affect processing and rates of cure. For example, clays have a retarding effect on the rate of cure, while carbon blacks and some treated mineral fillers accelerate the rate of cure.

## R.T. Vanderbilt Company, Inc. supplies the following reinforcing agents:

DIXIE CLAY[®] and PAR[®] CLAY, hard kaolin air-floated clays, can be used alone, or in combination with other fillers, to provide low-cost compounds while adding reinforcing properties.

BILT-PLATES[®] 156, hard kaolin clay, is a grit-free, air-floated clay that provides reinforcement similar to water-washed clays, but at a lower cost.

LANGFORD[™] CLAY and McNAMEE[®] CLAY, soft kaolin clays, are used at high loadings to produce easily processed compounds. When compared to similar loadings of hard clay, lower tensile strength and higher elongation are obtained.

PYRAX[®] A, PYRAX B, and PYRAX WA, pyrophyllite clays, are used as a filler in some applications. Small quantities improve the calendaring operations of some compounds. The platy structure can also be used to maintain small cell structure in sponge, and in thick cross-section parts, it can assist in removing entrapped air during molding.

VANTALC[®] 6H and VANTALC F2003, hydrated magnesium silicate, are high purity, platy talcs. These products provide fast extrusion rates and low gas permeability. They wet out quickly in rubber compounds, and provide low moisture absorption since water solubles are removed during the washing process. These products are FDA listed in 21 CFR Part 177.2600, Rubber Articles for Repeated Use (in Contact with Food).

VANSIL[®] W-40, VANSIL W-50, VANSIL WG, VANSIL HR325, VANSIL HR-1500, and VANSIL HR-2000, wollastonites, improve physical properties of thermoplastic and thermoset compounds. They offer good color, thermal stability, including low coefficients of thermal expansion, and high dielectric strength.

VANCOTE[®] HR-325 AS, VANCOTE HR-1500 AS, VANCOTE HR-2000 AS, VANCOTE WG-AS, VANCOTE W-40 AS, and VANCOTE W-50 AS are wollastonites which are surface treated with an amino silane. They offer improved flex modulus, tensile strength, elongation, and scratch resistance. VANCOTE products also provide resistance to, or moderation of, heat deflection by "tempering" the filled substrate. Nylons and polyolefins will also have improved heat flow, lower coefficient of linear expansion, and surface paintability. VANCOTE W-40 ES and VANCOTE W-50 ES, wollastonite surface treated with an epoxy silane, provide similar physical properties to other VANCOTE products.

# **Miscellaneous Materials**

## Colors

White and colored articles are obtained through the use of mineral pigments and organic chemicals, which can be added as powders or in masterbatch form. Nondiscoloring accelerators and antioxidants should be selected for these compounds. Additionally, a nonstaining grade of rubber should be selected where applicable.

Titanium dioxide is considered to be the best white pigment. It is possible to make satisfactory white compounds for many applications with zinc oxide, zinc sulfide, or lithopone (zinc sulfide and barium sulfate). These products can be used in place of some or all of the more costly titanium dioxide. VANTALC 6H Mineral Filler and VANSIL/VANCOTE Wollastonite can also be used in a similar fashion. A small amount of blue dye, such as ultramarine blue, can be added to minimize off-white tints.

Various grades of iron oxide can be used for yellow brown or reddish colored articles. For open steam curing, any organic colors should be tested for stability prior to use.

#### Reodorants

Small quantities (1 to 2 ounces per 100 pounds of rubber stock) of essential oils may be added to some rubber compounds to neutralize unpleasant odors or to impart a pleasant scent. RODO[®] 0 is used to neutralize any odors caused by sulfur, and RODO 10 is used where a pleasing lilac scent is desired. The exact amount of reodorant must be experimentally determined for each particular stock.

#### Blowing Agents for Sponge

Cellular structures can be created by incorporating sodium bicarbonate and oleic acids into highly plasticized rubber compounds. The oleic acids react with the sodium bicarbonate to liberate carbon dioxide during the curing process. Nitrogen bearing organic compounds, which decompose at curing temperatures,

are also used extensively for this purpose. The nitrogen blowing agents are typically complex azodicarbonamides which provide a more uniform closed cell structure than the bicarbonate.

## Abrasives

Abrasive qualities, when required in articles such as erasers and polishing or grinding wheels, are obtained by adding fillers such as pumice, silica, tripoli (soft, porous silica), and carborundum.

## Flame Retardants

Most hydrocarbon rubbers will burn when exposed to a flame or a fire situation. Some, such as Neoprene, are self extinguishing, which means that they will not support combustion when the flame is removed. It is possible to add flame retardants to provide resistance to burning. Most often chlorinated paraffins or brominated aromatic resins are used in combination with antimony trioxide to impart flame resistance. Fillers that emit large amounts of inert vapor when heated are also helpful. Examples are aluminum trihydrate, magnesium hydroxide, and zinc borate.

# PEROXIDE CROSSLINKING of ELASTOMERS

# by Chris Nola

R.T. Vanderbilt Company, Inc.

# Introduction

Crosslinking and/or vulcanization are defined as a process for converting a thermoplastic material or elastomer into a thermoset or vulcanizate.¹ This process converts unbound polymer molecular chains into a single network which retains many desirable physical and chemical properties of the base polymer. The two major chemical processes by which crosslinking occurs are peroxide and sulfur cure systems. Peroxide systems are more versatile since they can be used to crosslink both saturated and unsaturated polymers, thereby providing a wider selection of elastomers, and more opportunities for cost savings.

Peroxide crosslinking systems can:

- Offer a truly nitrosamine-free finished product with predictable cure rates and cured physical properties.
- Provide a stable factory stock elastomer compound, as opposed to a sulfurcured compound with a short shelf life (sometimes days).
- Be made equivalent, and in many cases superior, to sulfur systems, by varying the ratio of many common additives.
- Produce thermosets and vulcanizates having better heat aging properties, lower compression set, less color, no reversion, reduced (if any) bloom, and lower odor levels than compounds cured by sulfur systems.

# What is an Organic Peroxide?

An organic peroxide is a molecule containing at least two oxygen atoms, connected by a single bond to organic chemical groups, as shown below in dicumyl peroxide (VAROX[®] DCP):



Depending on the groups attached, this oxygen-oxygen bond is designed to break on heating, leaving one unpaired electron on each oxygen, called a "free radical". These free radicals are able to promote certain chemical reactions, such as:

- · Polymerization of one or more monomers
- Curing of thermosetting resins (polymer + monomer)
- · Crosslinking of elastomers and polyethylene

Organic peroxides that are thermally decomposed generate free radicals that consequently create an active site on a polymer backbone. The reaction between two active sites creates a strong link between the polymer chains, forming a polymer network exhibiting very desirable mechanical properties, particularly excellent heat resistance and compression set. Another advantage of using a peroxide cure instead of sulfur vulcanization is the wide range of polymers that can be crosslinked (unsaturated polymers as well as saturated polymers like polyethylene). Due to the nature of the strong carbon-carbon crosslink bond created by the use of organic peroxides, it is possible to use the full engineering capabilities of these peroxide crosslinkable polymers. Tables 1 and 2 list the polymers which can and cannot be crosslinked by organic peroxides.

,	5
AEM	Poly(ethylene-co-methylacrylate) (Vamac®)
AU/EU	Polyurethane Rubber
BIIR	Bromobutyl Rubber
BR	Polybutadiene Rubber
CM	Chlorinated Polyethylene (Tyrin®)
CR	Polychloroprene Rubber (Neoprene)
CSM	Chlorosulfonyl Polyethylene (Hypalon®)
EBA	Ethylene Butylacrylate Copolymer
EEA	Ethylene Ethyl Acrylate
EPM	Ethylene Propylene Copolymer (Vistalon™)
EPDM	Ethylene Propylene Diene Terpolymer (Vistalon)
EVA	Ethylene Vinylacetate Copolymer
FKM	Fluoroelastomers (Viton [®] )
FVMQ	Fluorosilicone Rubber
HNBR	Hydrogenated Acrylonitrile-butadiene Rubber
IR	Polyisoprene Rubber
NBR	Acrylonitrile-butadiene Rubber (Nitrile Rubber)
NR	Natural Rubber
PE	Polyethylene (includes high, low and linear low density)
POE	Polyolefin Elastomer (Exact [™] )
SBR	Styrene-butadiene Rubber
Т	Polysulfide Rubber
VMQ (MQ)	Silicone Rubber

# Table 1: Polymers Crosslinkable with Organic Peroxides

# Table 2: Polymers Not Crosslinkable with Organic Peroxides

ACM	Polyacrylate Rubber
CIIR	Chlorobutyl Rubber
CO	Epichlorohydrin Rubber
ECO	Epichlorohydrin Copolymer
lir	Butyl Rubber
PB	Polybutene
PIB	Polyisobutylene (Vistanex [™] )
PP	Polypropylene
PVC	Polyvinylchloride

# Peroxides* vs. Sulfur and Sulfur Donor Cure Systems

(*Organic peroxides will be referred to as peroxides in the rest of this chapter.)

Advantages of crosslinking with peroxides instead of sulfur include:

· Formation of radicals which generate carbon to carbon linkages.

- · Best retention of properties after heat aging.
- True non-nitrosamine crosslinking.
- · Improved resistance to chemicals and oil.
- · Lower compression set, and improved resiliency.
- Superior electrical properties, since zinc oxide is not required.
- · Crosslinks both saturated and unsaturated polymers.
- Wide range of operating temperatures.
- Superior color retention, i.e., no discoloration.
- Wide variety of peroxide half-lives for crosslinking and processing.

Disadvantages of crosslinking with peroxides instead of sulfur include:

- · Restrictions on some ingredients (no aromatic oils or highly acidic fillers).
- Lower hot tear. However, certain blends of peroxides and coagents provide hot tear equivalent to sulfur cure.
- Bloom (some types of peroxides), although not as extensive as with most sulfur cure systems.
- Oxygen inhibition (surface tack in forced hot air oven cure).
- Cost of curatives. Although not necessarily in regard to the newer low nitrosamine accelerators and that of the entire formulation, particularly when lower cost elastomers can be readily substituted. More additives are required for a sulfur cure vs. a peroxide cure.

When polymers are crosslinked by peroxides, carbon to carbon bonds are formed between individual polymer chains. The C-C bond is stronger and more thermally stable than the S-S bond formed by elemental sulfur vulcanization. Efficient Vulcanizing (EV) systems (low sulfur and sulfur donor cure systems) primarily form C-S type bonds. The energy (kJ) or thermal stability of C-S bonds falls between that of S-S and C-C bonds. Because of the overwhelmingly higher strength of the covalent C-C bond network, the peroxide cure is the preferred crosslinking method to obtain optimum thermal stability and superior compression set properties. Table 3 compares the typical results of three standard cure systems for a 65 Shore A, black-filled, EPDM compound:

Test	Elemental Sulfur	Sulfur Donor	Peroxide
Crosslink Bond Energy, kJ	155-270	285	350
Compression Set After 70 hrs. @ 212°F, %	52	28	11
Elongation After 120 hrs. @ 300°F, % Retention	42	63	75

Table 3: A Comparison of Three Standard Cure Systems

# Peroxide Classification

All peroxides have a peroxy group (-O-O-). What makes certain peroxides more reactive than others? The answer is simply the chemical composition of the rest of the molecule. The general formula for organic peroxide is  $R_1-O-O-R_2$ ,

where  $R_1$  and  $R_2$  represent other chemical groups that are bonded to the -O-Ogroup. Depending on the chemical structure of  $R_1$  and  $R_2$ , the organic peroxides typically used for crosslinking elastomers can be classified as either Dialkyl, Diacyl, Peroxyketal or Peroxyester. A brief summary of these classes is provided in Table 4.

Class	Commercial Product	Advantages	Disadvantages
Dialkyl	VAROX DBPH	No odor. No bloom.	High cost. Less efficient cure.
Dialkyl	VAROX DCP	Very efficient. Low cost.	Odor (Acetophenone).
Dialkyl	VAROX VC-R	Very efficient. No odor.	Bloom.
Diacyl	VAROX A75	Fast cure in Silicone.	Scorchy. Low cure efficiency in carbon black- filled systems.
Peroxyketal	VAROX 231	Faster curing. Lower temperatures. No bloom.	Scorchy. High cost. Low efficiency in saturated polymers.
Peroxyester	VAROX 270-XL	Fast cure in unsaturated polymers.	Low cure efficiency in carbon black-filled systems.

Table 4: Peroxide Classifications

# **Dialkyl Peroxides**

 $\rm R_{_1}$  and  $\rm R_{_2}$  are alkyl groups. The structure of t-butyl cumyl peroxide is given below.



alkyl groups

The dialkyl peroxide class is the most important type of crosslinking peroxide because it produces high energy free radicals (105 kcal/mole) on thermal decomposition. High energy radicals are needed to efficiently crosslink the peroxide-curable elastomers described in this chapter. It is important to note that dialkyl peroxides can contain one or two -O-O- groups.

Table 5 gives examples of dialkyl peroxides containing one peroxy group; Table 6 gives examples containing two peroxy groups.
Trade Name	Chemical Name
VAROX DCP	Dicumyl peroxide
VAROX 801	t-butyl cumyl peroxide

## Table 5: Dialkyl Peroxides with One Peroxy Group

### Table 6: Dialkyl Peroxides with Two Peroxy Groups

Trade Name	Chemical Name
VAROX VC-R	m/p-di(t-butylperoxy)diisopropylbenzene
VAROX DBPH	2,5-dimethyl-2,5-di(t-butylperoxy)hexane
VAROX 130	2,5-dimethyl-2,5-di(t-butylperoxy)hexyne-3

VAROX DCP (dicumyl type) and VAROX VC-R ("bis" type, which includes the extended VAROX 802-40KE grade) have similar crosslinking efficiency. These two aromatic dialkyl peroxides generate the same high energy radicals.

## Dialkyl Peroxides - Free Radical Energies

Based on the known hydrogen bond dissociation energies (the energy required to remove a hydrogen from various chemical compounds), one can determine the energy of the free radicals formed from the decomposition of various organic peroxides. A list of these energy levels is given in Table 7.

Bond Type	Bond Dissociation Energy (kcal/mole)		
$(R)_{3}C - H$ $(R)_{2}CH - H$ $RCH_{2} - H$	Poor Hydrogen Abstractors 91.1 97.0 99.9	Low Energy Radicals	
$CH_3 - H$ $(CH_3)_3CO - H$ RC(O)O - H $C_6H_5 - H$	104.9 104.9 112 112 Good Hydrogen Abstractors	High Energy Radicals	

Table 7: Free Radical Energy Levels



VAROX VC-R (m/p-di(t-butyperoxy)diisopropylbenzene, para form shown below



1, 4 Diacetylbenzene

#### VAROX DBPH (2,5-dimethyl-2,5-di(t-butyperoxy)hexane)



VAROX DBPH, an aliphatic dialkyl peroxide, has a lower crosslinking efficiency compared to the other dialkyls. This is due to the generation of a combination of high energy and lower energy radicals. Lower energy radicals do not readily participate in crosslinking by hydrogen abstraction. However, VAROX DBPH has several outstanding advantages. It doesn't create bloom, generates very little odor, and, due to the safer decomposition by-products, it is used extensively in FDA-approved indirect food contact and medical applications.

VAROX DBPH-50-EZD, an easy to disperse version of the standard VAROX DBPH-50 product, is designed for softer elastomer compounds that are mixed under lower shear conditions. These elastomers may have difficulty in breaking up or dispersing harder particles of inert filler.

Table 8 compares the crosslinking efficiency of three dialkyl peroxides on a molar basis in a carbon black-filled general purpose EPDM compound:

-	-	-	
Peroxide Type	Parts per	Hundred Ru	ıbber (phr)
VAROX DCP-40KE	7.0		
VAROX 802-40KE		4.3	
VAROX DBPH-50			5.5
Moving Die Rheometer, 1° arc @ 180°C $M_H$ (dN-m) $t_S$ 0.4 (sec) t' 90 (min) Moles of Peroxide	14.6 18.6 2.93 0.010	15.66 22.2 5.36 0.011	16.05 22.8 6.32 0.017
Mooney Viscosity @ 135°C Minutes to 5 pt. rise	7.8	15.2	16.2

Table 8: Dialkyl Peroxide Crosslinking Efficiency in EPDM

### Peroxyketals

All peroxyketal peroxides contain two peroxy groups, which are bonded to the same carbon atom, as shown below in VAROX 231:



The chemical structure of the peroxyketals provides for fewer half-lives, so that the oxygen-oxygen bond has a lower thermal stability as compared to dialkyl peroxides.

The peroxyketals are non-aromatic, liquid peroxides which produce decomposition products with low odor and no blooming. In particular, two of the t-butyl type peroxides have found application in crosslinking: VAROX 230-XL and VAROX 231-XL. The "XL" indicates that the pure liquid peroxides are extended on an inert calcium carbonate and calcium silicate filler blend, creating a free-flowing powder. VAROX 231 is the more active of these two peroxides with the pure liquid at a minimum assay of 92%.

#### Reactions of Peroxyketals

Peroxyketals generate а combination of high energy radicals (105 kcal/mole) and low energy radicals (97 kcal/mole). The mechanisms of the thermal decomposition of peroxyketals are complex, and will vary depending on the specific structure. As a rule, only high energy radicals are suitable for efficient crosslinking applications, so peroxyketals are generally less efficient than dialkyl peroxides. However, low energy radicals are capable of crosslinking where unsaturation is present, whether the unsaturation source is the elastomer or the incorporation of a coagent in the formulation. The crosslinking efficiency of peroxyketals increases in proportion to the level of unsaturation (i.e. the type of coagent used). In fact, the use of coagents will increase the efficiency of all peroxides used for crosslinking.

The efficiency of any specific peroxyketal will also vary with the pH of the reaction system. One reason is the sensitivity of the peroxyketals to cationic decomposition (a non-radical decomposition of the peroxide) when low pH additives or fillers are used. Small quantities of stearic acid are acceptable, but highly acidic fillers, like unwashed clay, should not be used.

CH₃ CH₃ CH₃ CH₃ ć-CH₃--00 00 Ċ -CH₃ 00 CH₃ CH₂ • 0 ĊH₃ ĊH₃ ĊH₃ ĊH₃ CH₃ CH₃ Strong Radical, CH₃ CH₃ 104.9 kcal/mole CH3 CH₃ CH₃ CH₃ •0 00-Ć CH₃ CH₃ ĊH₃ CH₃ CH₂ ċ CH₃ CH CH₃ CHá CH₃ ĊH₃ ĊH₃ Weak Radical, 99.9 kcal/mole VAROX 230 (n-butyl-4,4-di(t-butylperoxy)valerate) CH₃ CH₃ CH₃ • 0 CH₃ С റ CH₃ CH₃ Strong Radical CH₂ CH₂ CH₃ nC₄H₉ CH₃ 0 CH₃ C 0 ĊH₃  $CH_2$ CH₂ • nC₄H₉· CH₃ Weak Radical CH₃-CH₃ C ĆH₃ CH₃ CH₃-CH₃ ĊH₃

VAROX 231 (1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane)

Strong Radicals

#### Peroxyketal vs. Dialkyl Peroxide Crosslinking Performance

Peroxyketal peroxides are widely used for crosslinking and polymer modification.² They have fewer half-lives than dialkyl peroxides, and therefore provide faster reaction times at a given temperature. The peroxyketal peroxides

should be considered as replacements for dialkyl peroxides when lower curing temperatures are required in order to reduce curing times. The type of elastomer or polymer to be crosslinked or modified will determine if peroxyketals will be a suitable choice.

Peroxyketal peroxides are non-aromatic and in their pure form are liquid at room temperature. Peroxyketals do not produce solid decomposition by-products and are therefore non-blooming.

Peroxyketals generate a combination of weak and strong free radicals, based on hydrogen bond dissociation energies, which means that peroxyketals are less efficient than dialkyl peroxides when crosslinking saturated polymers or polymers with low levels of unsaturation. The latter would require considerably higher concentrations of peroxyketal peroxide to replace dialkyl peroxide. With minimal unsaturation present in the polymer, hydrogen abstraction becomes important, and requires a high level of strong free radicals, like those provided by dialkyl peroxides. However, in certain polymerization systems, e.g., acrylic and styrenic, or in highly unsaturated elastomers, the peroxyketals are equivalent in crosslinking efficiency to the dialkyl peroxides.

Figure 1 compares the performance of dialkyl and peroxyketal peroxides in the curing of EVA, a saturated polymer which requires strong radicals to enable hydrogen abstraction for crosslinking. In the examples below, peroxyketals VAROX 231-XL and VAROX 230-XL provide low crosslinking efficiency, but fast cure rates. However, as shown in Figure 2, the proper selection of a crosslinking coagent, in this case triallyl cyanurate, improves the crosslinking efficiency of peroxyketals while retaining the desired faster cure rate.



Figure 1: Crosslinking EVA (9% Vinyl Acetate) Without a Coagent



Figure 2: Crosslinking EVA (9% Vinyl Acetate) With a Coagent

Table 9 shows that triallyl cyanurate (TAC) increases the degree of crosslinking by improving the efficiency of VAROX 230-XL, while maintaining its dramatically faster cure rate.

Peroxide Type	Parts per	Hundred Ru	bber (phr)
VAROX 802-40KE	2.5		
VAROX 230-XL		4.5	3.0
SR 507 (TAC)			1.0
ODR @ 165.5°C (330°F), 3° arc @ 180°C			
M _H (dN⋅m)	70.1	57.6	89.2
M _L (dN•m)	11.3	12.4	12.4
t _s 2 (min)	2.4	1.5	1.6
ť 90 (min)	17	5.4	5.3

Table 9: Crosslinking EVA using VAROX 230-XL and Sartomer® SR 507

# Summary of Peroxyketals

- 1. Peroxyketal peroxide efficiency increases when used with coagents:
- 1. Coagents add unsaturation to the system.
- 2. Coagents equalize peroxyketals and dialkyl peroxide cures.
- 3. Coagents can improve Mooney viscosity, scorch time, compression set, hardness, and modulus.
- 4. Peroxyketals exhibit equivalent efficiency to dialkyl peroxides in highly unsaturated elastomers.
- 2. Peroxyketals have lower half-lives, and provide much faster cures (a lower t' 90) than the dialkyl peroxides.
- 3. Peroxyketals provide the ability to cure at much lower temperatures, e.g., over curing EPDM on plastic parts while avoiding warpage.
- 4. Peroxyketals are stable liquids at room temperature.
- 5. Peroxyketals do not bloom, since they do not contain any solid decomposition by-products.
- 6. Peroxyketals are aliphatic, or non-aromatic in chemical composition.

7. Peroxyketals have low odor.

### **Diacyl Peroxides**

Diacyl peroxides decompose to useful free-radicals and have the least amount of decomposition by-products. In addition to the crosslinking of elastomers, diacyl peroxides are used in a variety of applications that include the curing of unsaturated polyester resins, and the manufacturing of PVC, polystyrene and polyacrylates.

The low half-life temperature of diacyl peroxides, i.e. 1 minute t ½ of 267°F, makes them unacceptable from a processing point of view for most crosslinking applications.³ However, applications requiring low processing temperatures can take advantage of the diacyl peroxide's efficiency.

Diacyl peroxides are primarily used for the crosslinking of silicone rubber; in carbon black-filled EPDM formulations they generally provide poor crosslinking performance, probably because of the peroxide's chemical sensitivity to the complex surface chemistry of the carbon black. This peroxide generates very high energy radicals and is therefore capable of the hydrogen abstraction of labile hydrogens on the silicone rubber. This peroxide is therefore well-known as a "non-vinyl specific" curative in the silicone rubber industry. One of the most common diacyl peroxides for crosslinking silicone rubber is dibenzoyl peroxide (VAROX A75), whose chemical structure is shown below.

### **Peroxyester Peroxides**



This is an **Acyl** group, hence the name Diacyl Peroxides

Peroxyesters are another class of peroxides that are used to crosslink elastomers such as EPM, EPDM, PE, and CPE. They are also used for crosslinking silicone, and in polymerization type reactions. They are very efficient in these types of applications, but their efficiency is reduced dramatically when introduced into compounds containing carbon black. Shown below is the structure of a *tert*-alkyl peroxyester (VAROX 270-XL).

Only tert-alkyl peroxyesters are commercially available because primary and



secondary alkyl peroxyesters are relatively inefficient and susceptible to induced decompositions which can create safety problems.⁴ In addition, it should be noted that the type of *tert*-alkyl group affects activity, showing decreasing thermal stability in the order of *tert*-butyl > *tert*-amyl > *tert*-cumyl.

## **Physical Forms of Peroxides**

*Liquids* — Pure liquids can be difficult to handle and are much harder to incorporate, especially in mill mixing. Also, safety precautions have to be taken when handling "neat" peroxides.

*Powders* – Peroxide powders give off dust, produce caking, and cause product loss by ventilation. Peroxide powders are normally formulated to a 40% activity on a variety of carriers. Those most common in the Rubber Industry include calcium carbonate, kaolin clay, and silica.

*Masterbatches* – Pre-dispersed peroxide masterbatches dramatically shorten mixing time and improve the quality of the elastomer by avoiding premature crosslinking (scorch) in soft or hard compounds. The final compound exhibits a lower and more consistent viscosity, which is essential to molding and extrusion operations. Consistency in the final physical properties of crosslinked technical articles is obtained by peroxide masterbatches, since they create factory compounds with an exceptionally uniform peroxide dispersion. Peroxide masterbatches are typically formulated to a 40% active material, and are uniformly dispersed on substrates such as EPM.

## Active Oxygen Content and Percent Assay

Active Oxygen Content – Each organic peroxide contains a certain amount of active oxygen, usually between 2% and 12%. This is a good indication of the expected activity of peroxides of the same class. The active oxygen content, A[O], is defined as the percentage between the atomic mass of oxygen in each O–O bond and the molecular weight of the peroxide.

Example: VAROX DCP-40 KE has one O-O group and a molecular weight of 270.37; its peroxide content is 40%, so its active oxygen content will be:

As a general rule, lowering the percent active oxygen of an organic peroxide, or reducing its assay, will increase its safety and ease of handling in the workplace. For example, when pure liquid VAROX DBPH peroxide is extended on an inert calcium carbonate filler, a safer and lower active oxygen content product is produced. This free flowing powder greatly improves safety and handling of the peroxide, while increasing the accuracy and uniformity of the final peroxide concentration in the elastomer compound.

Percent Assay – percent active oxygen content should not be confused with percent assay. Percent assay is the measure of active peroxide content. For example, VAROX DCP-40C contains 40% active dicumyl peroxide, with the

remaining 60% consisting of calcium carbonate.

## Half-life Time and Half-life Temperature

Decomposition rates of organic peroxides are reported in terms of half-life time or half-life temperature. The half-life time of a peroxide, at any specified temperature, is the time in which 50% of the peroxide has decomposed. Correspondingly, the half-life temperature at any specified time is the temperature at which 50% of the peroxide has decomposed in the specified time. Table 10 shows how the number of half-lives correlates to the percentage of peroxide decomposed.

Number of Half-lives	Percent Peroxide Decomposed
0	0
1	50
2	75
3	87.5
4	93.75
5	96.9
6	98.4
7	99.2
8	99.6
9	99.8
10	99.9

 Table 10: Half-lives vs. Percent Peroxide Decomposition

 The rate of crosslinking produced by a free radical initiator is determined by

its rate of thermal decomposition. Half-life data are essential in the selection of the optimum initiator for specific time/temperature applications. Over the years, Arkema Inc., has determined the rate of peroxide decomposition in various solvents at low concentrations, in order to determine the key Arrhenius first-order kinetic parameters required to estimate peroxide half-lives at various temperatures. This half-life data has been compiled into Arkema's copyrighted Half-life spreadsheet. This spreadsheet will permit various calculations, including the ability to estimate the percent peroxide decomposed versus time at a given temperature.

The polarity of the solvents used in these studies was found to influence the peroxide decomposition kinetics. Higher polar solvents tend to result in a faster peroxide decomposition. For this reason it is best to compare peroxide half-life data generated in the same solvent. Peroxide manufacturers commonly include the 1 hour and 10 hour half-life temperatures in their product bulletins. However, it is often useful to express peroxide stability in terms of 1 minute, 1 hour, and 10 hour half-life temperatures at which 50% of the initiator has decomposed in 1 minute, 1 hour and 10 hours, respectively.

Since crosslinking is directly related to the amount of peroxide decomposed, at least 6 to 10 half-lives of peroxide decomposition are recommended for crosslinking operations. One mole of crosslinked peroxide equates to one mole of decomposed peroxide. The t'90 (min) value is the time necessary to achieve 90% of the final cure. Thus, the t'90 (min) is equivalent to 90% peroxide decomposed, or approximately 3.33 half-lives. The percent of peroxide decomposed can be calculated by using the number of peroxide half-lives in the following equation:

Percent of Peroxide Decomposed =  $(1 - 0.5^{N}) \times 100$ (Where 'N' is the number of peroxide half-lives)

- At N = 3.33 half-lives, approximately 90% of the peroxide is decomposed.
- At N = 6 half-lives, the peroxide is 98.4% decomposed.
- At N =10 half-lives, the peroxide is almost completely decomposed at 99.9%.

Example 1: Calculate an estimated t'90 cure time for VAROX DCP at 340°F.

At a temperature of 340°F (171.1°C), dicumyl peroxide has a half-life time of 1.87 minutes as calculated using Arkema's HALF-LIFE[®] program (An Excel[®] half-life program which predicts half-life times for a given temperature). This program allows the compounder to compare various peroxides simultaneously, and is available from the local Vanderbilt Technical Sales Representative. Applying the principle that t' 90 (min) should relate to 3.33 half-lives of peroxide decomposition, the t' 90 cure time can be estimated.

Estimated t' 90 (min) = 3.33 half-lives x 1.87 min. = 6.23 minutes

Example 2: Calculate the minimum cure cycle for VAROX DCP at 340°F.

Six half-lives is the minimum number of peroxide decompositions for a crosslinking cure cycle. The theoretical minimum cure cycle is therefore 11.2 minutes (6 half-lives x 1.87). This time assumes an isothermal profile of  $340^{\circ}$ F, with zero warm-up time.

For best performance it is recommended that as much of the peroxide as possible be decomposed. To decompose 99.9% of the peroxide requires going through 10 half-lives. This is especially true in the manufacture of gaskets and seals, where compression set is important. Residual peroxide remaining in the rubber could react under further heat and stress, resulting in an undesirable increase in percent set values. The theoretical time to decompose 99.9% of the dicumyl peroxide would be 18.7 minutes (10 half-lives x 1.87 minutes) at 340°F.

Example 3: Determine the number of peroxide half-lives from rheometer data.

Table 11 shows actual t' 90 (sec) data from an Alpha Technologies MDR 2000E, at various temperatures, for a general purpose EPDM compound that was crosslinked with dicumyl peroxide.

The half-life program is used to calculate the theoretical half-life, in seconds, for dicumyl at each cure temperature in Table 11. These half-life time calculations are listed in the half-life column. The actual t' 90 (sec) is then divided by the

half-life time data to obtain the number of dicumyl peroxide half-lives needed to achieve the t' 90. The number of half-lives required to achieve t' 90 is usually in close agreement with the expected "3.33" theoretical value. The deviation in the number of half-lives at higher temperatures is attributed to non-isothermal conditions. Above 180°C, the nominal 30 to 40 seconds of warm-up time required to reach cure temperature becomes a significant part of the actual t' 90 cure times. It is therefore important to consider the "dead time" or "warm-up time" in the curing operation, when estimating the theoretical process cure times.

Ingredients				ł	ohr
EPDM	1	00.0			
N660 Carbon	Black				65.0
N990 Carbon	Black				35.0
Paraffinic Oil					25.0
Zinc Oxide					5.0
AGERITE® RE	SIN D [®]				1.0
VAROX DCP-	-40KE				8.0
Total				2	39.0
Temp	M _H	t _s 2	ť 90	Half-life	Number of
(°C)	(dN·m)	(sec)	(sec)	(sec)	Half-lives
170	21.80	35	415	125	3.32
175	21.13	28	260	78.4	3.32
180	20.43	24.6	164	49.7	3.30
185	19.61	20.4	110	31.8	3.46
190	19.99	18.0	79	20.6	3.83
200	19.38	14.4	44	8.8	5
210	18.83	12.0	29	3.9	7
220	17.93	9.6	22	1.8	12

Table 11: Effect of Cure Temperature on Peroxide Ef
-----------------------------------------------------

Table 12 provides percent assay, active oxygen content, and half-life times, along with suggested maximum compounding and curing temperatures, for peroxides used in crosslinking elastomers.

	VAROX DCP	VAROX DCP-40C, KE or MB	VAROX VC-R	VAROX 802-40C; KE or MB	VAROX DBPH Liquid	VAROX DBPH- 50	VAROX 230XL	VAROX 231XL
Assay, %	99	40	>96	40	91-93	45-48	40	40
Active Oxygen, %	5.86	2.34 to 2.46	9.08	3.73 to 3.92	10.03 to 10.25	4.96 to 5.29	3.78 to 3.97	4.13 to 4.34
1 min. Half Life, °C	178	178	181	181	181	181	169.8	153
10 min. Half Life, °C	157	157	157	157	157	157	145.7	131
1 hr. Half Life, °C	137	137	139	139	140	140	128.8	115
Max Mix Temp., °C	130	130	139	139	145	145	110	105
Cure Temp., C	154 to 199	154 to 199	160 to 204	160 to 204	160 to 204	160 to 204	130 to 175	138 to 182

 Table 12: Chemical and Physical Properties of Extended Peroxides

## COMPOUNDING CONSIDERATIONS

### Suggested Peroxide Dosage

Table 13 represents typical starting peroxide loading levels for various polymer systems. These levels should be used only as a guideline, since various compounding ingredients have different effects on the peroxide crosslinking mechanism.

Peroxide	VAROX	VAROX DCP-40C.	VAROX	VAROX 802-40C.	VAROX DBPH	VAROX	VAROX	VAROX
Polymer	DCP	KE or MB	VC-R	KE or MB	Liquid	DBPH-50	230XL	231XL
CPE	2.4-3.8	6.0-14.0	1.5-2.4	3.8-6.0	2.5-4.0	5.6-8.9	3.5-6.5	7.5- 14.0
CR	0.8-1.6	2.0-4.0	0.5-1.0	1.3-2.5	0.5-1.4	1.0-3.0	1.1-3.5	0.5-2.0
EPDM & EPM	2.4-5.4	6.0-14.0	1.6-3.2	4.0-8.0	1.7-3.4	3.8-7.6	7.5- 13.0	3.5-6.5
EVA	1.2-2.0	-	0.8-1.6	-	1.0-1.2	2.0-5.0	3.5-6.5	4.0-5.8
HDPE	-	-	-	-	0.5-1.2	-	-	-
HNBR	2.2-4.2	5.5-10.5	1.4-2.4	3.4-6.1	2.5-4.7	5.5-10.5	7.5- 13.0	3.5-6.5
LDPE	1.5-2.5	-	1.2-1.8	-	1.4-2.0	-	-	-
NBR	0.9-1.7	2.3-4.3	0.5-1.5	1.3-3.8	1.1-2.0	2.4-4.4	3.0-5.5	2.5-5.0
NR & IR	0.8-1.6	2.0-4.0	0.5-1.0	1.3-2.5	0.8-1.6	2.0-4.0	2.5-5.0	2.2-4.3
SBR	0.7-1.5	1.7-3.7	0.4-1.0	1.0-2.5	0.7-1.2	1.6-2.7	2.0-4.5	1.8-4.0
Q	0.5-2.0	1.2-5.0	0.2-1.0	0.5-2.5	0.4-1.5	0.9-2.0	-	-

Table 13: Suggested Peroxide Dosage Levels (phr)

## **Decomposition By-products**

As shown in Table 14, organic peroxides decompose to form various types of by-products. The type and quantity of decomposition by-products depend

on the amount of the specific peroxide used, together with the processing conditions. Postcuring of the crosslinked product will reduce the residual amount of decomposition by-products.

Peroxide	Major Decomposition Products (Hypothesized)	Minor Decomposition Products (Hypothesized)
VAROX A-75 dibenzoyl peroxide	benzoic acid	-
VAROX DCBP 2,4-dichlorobenzoyl peroxide	2,4-dichlorobenzoic acid	-
VAROX DCP dicumyl peroxide	methane; acetophenone; $\alpha$ -cumyl alcohol	$\begin{array}{l} \alpha \text{-methylstyrene;} \\ \alpha \text{-methylstyrene oxide; } \alpha \text{-cumyl} \\ \text{methyl ether} \end{array}$
VAROX VC-R m/p-di(tert- butylperoxy) diisopropyl benzene	methane; acetone; t-butyl alcohol; 1,3 &1,4-diacetyl benzenes; 1,3 & 1,4-di( $\alpha$ - hydroxyisopropyl) benzenes; 1-acetyl-3 or 4-( $\alpha$ -hydroxy- isopropyl)benzenes	isobutene; isobutene oxide, 3 or 4-( $\alpha$ -hydroxyisopropyl)- $\alpha$ -methyl styrene oxides; 3 or 4-( $\alpha$ -hydroxyisopropyl)- $\alpha$ -methylstyrene oxides; 3 or 4-( $\alpha$ -hydroxyisopropyl) $\alpha$ -methylstyrenes; 3 or 4-( $\alpha$ -hydroxyisopropyl)- $\alpha$ -methylstyrenes
VAROX DBPH 2,5-dimethyl-2,5- di(t-butylperoxy) hexane	methane; acetone; tert-butyl alcohol; tert amyl alcohol; ethane; 2,5-dihydroxy-2,5- dimethylhexane	isobutene; isobutene oxide; ethane; 2-methyl-3-butyn-2- ol; 2-butanone; methyl vinyl ketone; 2,5-hexanedione
VAROX 130 2,5-dimethyl-2,5- di(t-butylperoxy) hexyne-3	methane; acetone; tert-butyl alcohol; 2,5-dihydroxy-2,5- dimethyl-3-hexyne; 3-hexyne- 2,5-dione; 5-hydroxy-2-methyl- 3-hexyne-2-one	isobutene; isobutene oxide; 5-hydroxy-2,5-dimethyl-3-hexy- 1-ene oxide; 2-methyl-5-oxo-3- hexyn-1-ene oxide; 2-methyl-3- butyn-2-ol; 3-butyn-2-one
VAROX 230 n-butyl-4,4-di(t- butylperoxy) valerate	acetone; methane; tert- butyl alcohol; tert-butyl hydroperoxide; n-butyl levulinate; carbon dioxide; acetic acid; n-butyl propionate; n-butyl acrylate	t-butyl methyl ether
VAROX 231	acetone; methane; t-butyl alcohol; t-butyl hydroperoxide; 3,3,5-trimethylcyclohexanone; carbon dioxide; 2,2,4-trimethyl- 1-pentene; t-butyl trimethylpentyl ethers; 2,2,4-trimethylpentylene di-t- butyl ether	1,1,3-trimethylcyclopentane; 3,3,5-trimethylhexanoic acid; 3,5,5-trimethylhexanoic acid; 3,3,5-trimethyl-5-hexanoic acid
VAROX TBPB	methane; acetone; t-butyl alcohol; benzoic acid	ethane; t-butyl methyl ether

 Table 14: Peroxide Decomposition By-Products

#### Percent Peroxide Remaining vs. Time

Figures 3 and 4 compare the different amounts of peroxide that remain at the given temperatures of 325°F and 350°F.



Figure 3: Percent Peroxide Remaining at 325°F



Figure 4: Percent Peroxide Remaining at 350°F

## Processing Time (Scorch)

Experimental data were generated using a Mooney viscometer, as shown in Figure 5. The  $t_s05$  value is the scorch time at the processing temperature (usually at the polymer extrusion temperature). This value represents the time during which the compound can be safely processed before unwanted crosslinking or "scorch" takes place. The  $t_s05$  value is defined as the time needed at a specific temperature to obtain a 5 Mooney unit increase in the viscosity, as measured from the MV or minimum viscosity. This value provides the user valuable information on process safety. It is important to note that any premature crosslinking generated during compounding is not reversible; it can lead to an undesirable increase in elastomer viscosity.



Figure 5: Mooney Scorch vs. Temperature in an EPDM Compound ²

Example: If an EPDM compound containing VAROX VC-R is processed at 130°C, its viscosity will be increased by 5 Mooney Units after about 10 minutes.

# Cure Time (t' 90)

Experimental data were recorded using an ODR 2000E rheometer. The t' 90 value represents the time needed to reach 90% of the difference between the maximum and the minimum crosslinking density. The t' 90 value is one of the key parameters used to study improvements in productivity.



Figure 6: t' 90 vs. Temperature in an EPDM Compound²

Example: 90% of the crosslinking density of an EPDM compound cured with VAROX VC-R at 170°C will be obtained after 9 minutes. It takes 3 minutes at 185°C to obtain the same result.

## **Crosslinking Efficiency**

An ODR 2000E rheometer was used to generate the data in Figure 7.  $M_H$  (N·m) is the maximum torque developed in the compound, which is relative to the amount of crosslinking bonds created by the peroxide, and is an indication of some of the mechanical properties to be expected in the cured product.



Figure 7: Crosslinking of EPDM at 185°C* ²

Example: When curing EPDM at 185°C, data suggest that only 2.6 phr of pure VAROX VC-R are required to provide the same level of crosslink density as 4.3 phr of pure VAROX DCP.

## Effect of Compounding Ingredients

Antidegradants — One class of free radical scavengers consists of antidegradants. The amount of cure inhibition they exhibit depends on the particular chemical. Figure 8 shows the effects of various antioxidants in a formulation containing 100 phr of EPDM, dicumyl peroxide as indicated, and 0.5 phr of antioxidant.



Figure 8: Effects of Various Antioxidants⁵

As Figure 8 demonstrates, when using an amine antioxidant, it is necessary to use three phr of dicumyl peroxide to obtain the same state of cure as with one phr of dicumyl with no antioxidant. The quinoline antioxidant has the least effect on the state of cure, followed by the amine, while the hindered phenol antioxidant severely reduces the final cure. Antiozonants of the p-phenylenediamine type will reduce peroxide efficiency to the greatest extent. The best antioxidants for use with peroxide cures are AGERITE RESIN D, METHYL NICLATE[®], and

VANOX[®] MTI and VANOX ZMTI. Typically, sensitivity to this effect decreases in the following order: VAROX 231 > VAROX DCP > VAROX VC-R > VAROX DBPH > VAROX 130.

*Plasticizers* — Are additives used as processing aids, extenders (to lower the compound cost), and as active ingredients capable of imparting special properties to vulcanizates. Some plasticizers, especially aromatic oils, are not recommended because they can consume a portion of the radicals generated by the peroxides. In this regard, paraffinic type oils are preferred. Figure 9 shows the effect of various plasticizing oils in an EPM formula consisting of 25 phr of oil, and 1.1 phr of VAROX 130.



Figure 9: Effects of Various Plasticizing Oils⁵

Typically, sensitivity to this effect decreases in the following order: VAROX DBPH > VAROX VC-R > VAROX DCP > VAROX 231 > VAROX 130.

*Fillers* – Reinforcing and nonreinforcing fillers such as carbon black, silicates, silica, kaolin clay and calcium carbonate can be used in compounds cured with peroxides. However, acidic fillers such as "channel" carbon blacks, "hard clay" and "acidic silicas" can initiate ionic decomposition of the peroxide. Different peroxides are sensitive to acidic materials to varying degrees. The peroxyketals such as VAROX 231 are perhaps the most sensitive; VAROX DCP is somewhat less sensitive, followed by VAROX DBPH. VAROX 130 is the least sensitive to acidic fillers. If the use of acidic fillers is necessary, it is advisable to neutralize the compound with small quantities of basic metallic oxides (MgO, ZnO), or with amines (DPG, hexamethylene, tetramine, triethanolamine).

# Coagents

Coagents containing unsaturation can help increase the crosslink density. Coagents become part of the crosslink network, and can also affect the cure characteristics. Table 15 highlights common coagents available today.

Trade Name	Description
SR 297 (BGDMA)	Difunctional Liquid Methacrylate
SR 350 (TMPTMA)	Trifunctional Liquid Methacrylate
Saret [®] SR 516	Scorch-Retarded Liquid Dimethacrylate
Saret SR 517	Scorch-Retarded Liquid Trimethacrylate
Saret SR 519	Scorch-Retarded Liquid Triacrylate
Saret SR 521	Scorch-Retarded Liquid Dimethacrylate
Saret SR 522	Scorch-Retarded Solid Diacrylate
Saret SR 633 Saret 75 EPM 2A (75% active)	Scorch-Retarded Metallic Diacrylate
Saret SR 634 Saret 75 EPM 2M (75% active)	Scorch-Retarded Metallic Dimethacrylate
SR 507 (TAC)	Triallyl Cyanurate
SR 525/VANAX® MBM	Bis-maleimide
Ricon [®] 100	Styrene/Butadiene Copolymer (70% vinyl)
Ricon 153 Ricon 153 D (65% active)	85% Vinyl Liquid Polybutadiene
Ricon 154 Ricon 154 D (65% active)	90% Vinyl Liquid Polybutadiene
Ricobond [®] 1731 Ricobond 1731 HS (69% active)	Maleinized Liquid Polybutadiene (28% vinyl)
Ricobond 1756 Ricobond 1756 HS (69.5% active)	Maleinized Liquid Polybutadiene (70% vinyl)

Table 15: Common Coagents⁶

Acrylates, methacrylates, and maleimides are classified as Type 1 coagents which typically shorten scorch time in addition to increasing the state of cure. Type 2 coagents such as polybutadiene, triallylcyanurate (TAC), and triallylisocyanurate (TAIC) increase efficiency without significantly increasing the cure rate. While Type 1 coagents have the advantage of a faster cure rate, they also have a higher tendency to scorch. Figure 10 compares scorch values for common Type 1 acrylate/methacrylate coagents (Saret SR) with those of several Type 2 liquid polybutadiene coagents (Ricon/Ricobond) – at a level of 5 parts per 100 of rubber in peroxide-cured EPDM.



Figure 10: Scorch Comparison of Coagents in EPDM⁶

The key to an ideal cure is the correct choice of a proper coagent/peroxide system. The following pages describe the benefits coagents can provide in peroxide-cured compounds.

Improved Efficiency of Cure – Although all coagents will increase the efficiency of cure to some degree, there are several coagents which give the greatest boost in crosslink density. These include SR 350, SR 517, SR 519, Ricon 154, TAC, and SR 525 (VANAX MBM). Figure 11 illustrates the effectiveness of a bis-maleimide coagent.



Figure 11: Modulus Response of Bis-Maleimide in EPDM⁶

*Higher Tear Strength* – The tear strength of peroxide-cured systems is usually considered inferior to that of sulfur cures. Figure 12 illustrates hot tear values at 150°C in EPDM for several coagents as well as a sulfur/accelerator control.



Figure 12: Coagent Tear Strength Response in EPDM⁶

*Improved Heat Aging* – It is well known that peroxide-cured systems have superior heat aging as compared to sulfur systems. The addition of a coagent to the peroxide-cured formulation maintains excellent heat aging properties compared to sulfur, as shown in Figure 13.



Figure 13: Heat Aged Elongation and Modulus in EPDM⁶

*Improved Compression Set* – Liquid acrylate and polybutadiene coagents can be used to obtain improved compression set values. Figure 14 compares the compression set of several acrylate, methacrylate, and polybutadiene coagents to that of a peroxide control.



Figure 14: EPDM Compression Set with 5 phr Coagent⁶

Lower Mooney Viscosity—Liquid coagents can be termed "reactive plasticizers". They lower the viscosity of a formulation during processing, and add significant crosslinking upon vulcanization. By using these coagents, process oils and other extractable plasticizers can be reduced or even eliminated in some cases. Figure 15 illustrates the plasticizing effect in a non-oil-filled polyisoprene system.



Figure 15: Coagent Viscosity Response in Polyisoprene⁶

Improved Rubber to Metal and Rubber to Fiber Adhesion – Several coagents will increase a peroxide-cured rubber compound's adhesion to various metallic and fibrous substrates. These include Saret 633, Saret 634, Saret 75 EPM 2A, Saret 75 EPM 2M, Ricobond 1756, Ricobond 1756 HS, Ricobond 1731, and Ricobond 1731 HS. These coagents can be used alone or as blends (Saret/Ricobond) to achieve excellent adhesive properties. Table 16 shows the advantages of a blend of Saret 633 and Ricobond 1756 when a flexible, yet tough, bond to steel is required.

Compound (phr)	1	2	3
Vistalon 2504 & Vistalon 7500 (50:50) MB	256.0	256.0	256.0
AGERITE RESIN D	1.0	1.0	1.0
VAROX DCP-40KE	7.5	7.5	7.5
Saret 633	5.0	-	2.5
Ricobond 1756	-	5.0	2.5
Totals	269.5	269.5	269.5
Physical Properties			
T-Peel Adhesion (cold roll steel), lbs	44	76	69
Lap Shear Adhesion (cold roll steel), psi	1720	1279	1792

Table 16: Coagents and Adhesion to Steel

*Improved Dynamic Properties* — Metallic diacrylate and dimethacrylate coagents can be used to improve dynamic properties such as tan delta and dynamic flex. Figure 16 shows the advantages of using SR 633 and SR 634 in a dynamic flex application in synthetic polyisoprene.



Figure 16: DeMattia Flex Response of Polyisoprene with Coagent⁶

Several other performance advantages can be obtained by the use of a coagent. These include: improved resistance to oils and fuels, higher tensile strength, increased hardness and enhanced abrasion resistance.

### Fluoroelastomers and High Performance (HP) Peroxides

Fluoroelastomers (FKM) are extensively discussed in the "Fluoroelastomers" chapter of this publication; please refer to that chapter for detailed information on fluoroelastomer polymers and compounding.

Fluoroelastomers are often chosen for very high performance applications where odor and bloom cannot be tolerated, so the peroxide of choice for crosslinking fluoroelastomers (FKM) is the aliphatic dialkyl peroxide, VAROX DBPH. There are several forms of this dialkyl peroxide: VAROX DBPH (pure

liquid), VAROX DBPH-50 (extended product on calcium carbonate) and a high performance "HP" extended grade.

The HP grade provides two significant advantages when crosslinking FKM. The first is longer scorch time for either processing or compounding operations. This can be a true cost-savings feature, given the cost of these specialty elastomers. The second advantage is a significant improvement in physical properties, particularly thermal properties, leading to desirable lower percent compression set values at 200°C.

The VAROX DBPH-50-HP peroxide can lead to higher productivity and improved physical properties for FKM elastomers in the following operations:

- · Injection Molding
- Transfer Molding
- · Lay-up Compression Molding
- Extrusion

The dramatic increase in scorch resistance made possible by the use of VAROX DBPH-50HP in an FKM elastomer is illustrated in Figure 17.



Figure 17: Increased Scorch Time in FKM with HP Peroxide

Table 17 shows the significant improvements in percent compression set values obtained when crosslinking FKM with VAROX DBPH-50-HP at 200°C.

	Percent Compression Set (70 hrs. @ 200°C)		
Viton Grade	VAROX DBPH-50*	VAROX DBPH-50HP*	
GF-205NP	24.0%	14.9%	
GFLT-502	40.5%	35.8%	
GBL-200	30.4%	24.0%	
GBLT-601	34.2%	29.3%	

Table 17: Improved Compression Set in FKM with HP Peroxide

* Equal weight peroxide used @ 3 phr

### SILICONE RUBBER AND PEROXIDES

Silicone rubber is discussed in the "Silicone Elastomers" chapter of this publication; please refer to that chapter for information on silicone polymers and compounding.

Two specific peroxides are preferred for crosslinking silicone rubber: "non-vinyl specific" VAROX A-75, and "vinyl specific" VAROX DBPH.

#### Dimethyl Polysiloxane (MQ)

This type of silicone rubber, also known as polydimethylsiloxane, has the general structure shown below, where n = 3,000 to 10,000 units.



MQ Silicone

Polydimethylsiloxane does not contain any double bonds or unsaturation and must be cured by hydrogen abstraction of the labile hydrogens on the pendant methyl groups. A great deal of energy is required to remove a hydrogen from the methyl group (CH₃) of an MQ elastomer, and very few peroxides are capable of effectively crosslinking this polymer. VAROX A-75 (dibenzoyl peroxide), although having lower thermal stability than the dialkyl and peroxyketal peroxides, produces very high energy radicals (112 kcal/mole) that can abstract a hydrogen from the pendant methyl group to effectively crosslink MQ. Dibenzoyl peroxide, which is a member of the diacyl peroxide class, is often referred to as a "non-vinyl specific" peroxide for this reason. The VAROX A-75 crosslinking mechanism is shown as follows:



# Methyl Phenyl Polysiloxane (PMQ)

Manufacturers of PMQ advise that the additional phenyl groups (benzene rings) in PMQ improve low temperature flexibility and resistance to gamma radiation. This polymer also requires VAROX A-75 for crosslinking.



Methyl Phenyl Polysiloxane (PMQ)

## The Vinyl Containing Silicone Elastomers:

- Methyl Vinyl Polysiloxane (VMQ)
- Fluoro Methyl Vinyl Polysiloxane (FVMQ)
- Methyl Phenyl Vinyl Polysiloxane (PVMQ)



Methyl Vinyl Polysiloxane (VMQ)



Fluoro Methyl Vinyl Polysiloxane (FVMQ)



Methyl Phenyl Vinyl Polysiloxane (PVMQ)

The pendant vinyl groups in these rubbers are quite reactive to both low and high energy free radicals. The presence of the vinyl groups in the VMQ, FVMQ and PVMQ greatly increases the peroxide crosslinking efficiency, so that all the peroxides used for crosslinking can cure these elastomers. However, not all peroxides are suitable for crosslinking vinyl containing silicone and fluorosilicone elastomers.

Important considerations in the selection of peroxide are: no bloom, no color formation, non-aromatic decomposition products, low odor, and FDA indirect food contact clearance. VAROX DBPH [liquid 2,5-dimethyl-2,5-di-(t-butyl-peroxy)hexane and its extended forms] continues to be the favorite choice with regard to these properties.



2,5-dimethyl-2,5-di(t-butylperoxy)hexane (VAROX DBPH)

Peroxides for crosslinking silicone can be split into two classes: "vinyl specific" and "general purpose". These peroxides and their application to silicone are described in Table 18.

	Compounding Information		Inding ation	
Commerical & Chemical Names	Type	Dosage (phr)	Typical Curing Temp (°C)	Application Technology
VAROX DCP Dicumyl peroxide, bis(1-methyl-1- phenylethyl) and extended grades	VS	1.1 to 2.2	150 to >200	Requires a higher curing temperature than general purpose peroxides, and is unsuitable for hot air or UHF (microwave) curing. Normally used for molding, autoclave and continuous (steam or salt bath) vulcanization of insulation and tubing products. Does not form acidic decomposition products, so cure products do not require a postcure. Since it melts at approximately 40°C, good dispersion can be obtained by mixing at temperatures above the M.P. Acetophenone, a decomposition product, imparts a strong odor to the cured product, which can be reduced by postcure.
VAROX VC-R 1,3 & 1,4- di(tertbutylperoxy) diisopropyl benzene	VS	0.3 to 0.9	150	Very efficient crosslinker that is used instead of dicumyl because of its lesser odor.
VAROX 130 2,5-dimethyl-2,5- di(tertbutylperoxy) hexyne-3	VS	0.4 to 1.5	>150	High thermal stability peroxide used primarily for curing elastomers that must be mixed at elevated temperatures. This peroxide can be volatile at high temperatures.
VAROX DBPH 2,5-dimethyl-2,5- di(tertbutylperoxy) hexane	VS	0.4 to 1.5	160 to 205	Characterized by high thermal stability. Complies with FDA 21 CFR 177.2600. Liquid at room temp., it does not present any dispersion problems in silicone compounds. Because it is somewhat volatile, its silicone compounds should not be stored for long periods at relatively high temperatures. Has excellent scorch stability and is recommended for applications where UV stability and transparency are required.

# Table 18: Peroxide Applications in Silicone Rubber⁷ (continued)

	Compounding Info		unding D	
Commerical & Chemical Names	Type	Dosage (phr)	Typical Curing Temp (°C)	Application Technology
VAROX A75 Di-benzoyl peroxide and extended grades	GP	0.7 to 1.4	93 to 138	More suitable for thin cross-section moldings than 2,4-dichlorobenzoyl peroxide due to its scorch safety. Cannot be used in continuous hot air vulcanization because cross-sections tend to be porous, with tacky surfaces, when cured without external pressure.
VAROX TBPB Tert-butylperoxy benzoate	GP	0.3 to 0.6	140	Excellent processing safety. Used where scorch resistance is required.
VAROX DCBP Di(2,4- dichlorobenzoyl) peroxide	GP	1.1 to 2.3	90	Used for low temperature curing of silicone compounds. Can be cured without external pressure because of its low activation temperature (can be scorchy). Suitable for continuous hot air curing. Not suitable in carbon black-filled compounds. Postcure is required to prevent acidic decomposition of the rubber product.
Perkadox PM -BOS-ps Di(4-methylbenzol) peroxide	GP	0.8 to 1.6	105	Developed to overcome problems associated with the toxicity of certain decomposition products related to 2,4 dichlorobenzoyl) peroxide.

## FDA Compliance: Peroxide in Indirect Food Additives

The following substances are listed in FDA regulations covering polymers, resins, paper products, coatings or adhesives intended for food packaging or food-contact applications in accordance with Title 21, U.S. Code of Federal Regulations (21 CFR), as amended.

Chemical & (Commercial) Names	Regulation	Limitations ¹
Benzoyl peroxide ² (VAROX ANS, VAROX A75)	§175.105(c)(5)	None. ³
	§176.170(a)(5); §176.180(b)(1)	For use only as a preservative in paper coating compositions and limited to use at a level not to exceed 0.01 mg/in ² (0.0016 mg/cm ² ) of the finished paper and paperboard.
	§177.2420(b)3	For use as a catalyst in the production of crosslinked polyester resins for repeated contact with food; total catalysts not to exceed 1.5 percent. ⁴
	§177.2600(c)(4)(ii)(b)	For use as a vulcanization accelerator in rubber products for repeated contact with food; total vulcanizing accelerators not to exceed 1.5 percent by weight of rubber product.
	§184.1(a)	Generally recognized safe for use in food-contact applications subject to any limitations in parts 174, 175, 176, 177, 178, 186 or §179.45 of Chapter 1.
Di-tert-butyl peroxide	§177.2600(c)(4)(ii)(b)	For use as a vulcanization accelerator in rubber products for repeated contact with food; total vulcanizing accelerators not to exceed 1.5 percent by weight of rubber product.
tert-Butyl hydroperoxide	§175.105(c)(5) §176.170(a)(5); §176.180(b)(1)	None. ³ For use only as a polymerization catalyst in the production of paper and paperboard.
tert-Butyl peracetate	§177.2600(c)(4)(ix)	Total substances listed in paragraph $(c)(4)(ix)$ not to exceed 5 percent by weight of rubber product when used as an adjuvant substance in the production of rubber articles for repeated contact with food.
p-tert-Butyl perbenzoate (VAROX TBPB)	§175.300(b)(3)(xxxii); §175.390(b)(2)	For use as a catalyst for epoxy resin in side seam cements.
Cumene hydroperoxide	§175.105(c)(5) §176.170(a)(5) §176.180(b)(1) §177.2420(b)(3)	None. ³ For use only as a polymerization catalyst in the production of paper and paperboard. For use as a catalyst in the production of crosslinked polyester resins for repeated contact with food; total catalysts not to exceed 1.5 percent. ⁴
Dicumyl peroxide (VAROX DCP)	<pre>§175.105(c)(5) §175.300(b)(3)(xxxii); §175.390(b)(2) §177.2420(b)3 §177.2600(c)(4)(ii)(b)</pre>	None. ³ For use as polymerization catalyst in side seam cements. For use as a catalyst in the production of crosslinked polyester resins for repeated contact with food; total catalysts not to exceed 1.5 percent. ⁴ For use as a vulcanization accelerator in rubber articles for repeated contact with food; total
		vulcanizing accelerators not to exceed 1.5 percent by weight of rubber product

Chemical & (Commercial) Names	Regulation	Limitations ¹
Lauroyl peroxide	§175.105(c)(5) §177.2420(b)3	None. ³ For use as a catalyst in the production of cross- linked polyester resins for repeated contact with food; total catalysts not to exceed 1.5 percent. ⁴
2,5-Dimethyl- 2,5-di(tert-butyl peroxy) hexane [VAROX DBPH]; complying 1,1,4,4- Tetramethyl- (tetramethylene) bis(tert-butyl peroxide)	§177.1520(b) §177.2600(c)(4)(ii)(b)	For use as an initiator in the production of propylene homopolymer complying with §177.1520(c), Item 1.1 and olefin copolymers complying with §177.1520(c), Items 3.1 and 3.2 and containing not less than 75 weight percent of polymer units derived from propylene, provided that the maximum concentration of tert-butyl alcohol in the polymer does not exceed 100 parts per million, as determined by an FDA method titled "Determination of tert-Butyl Alcohol in Polypropylene." For use as a vulcanization accelerator in rubber articles for repeated contact with food; total vulcanization accelerators not to exceed 1.5 percent by weight of rubber product.
Methyl ethyl ketone	§177.2420(b)3	For use at up to 2 percent as the sole catalyst in the production peroxide of crosslinked polyester resins for repeated contact with food.
¹ The limitations listed in this summary are those applied by the regulation to the specific organic peroxide. Some regulations impose additional limitations on finited production over the over the		³ Section 175.105 requires food packaging adhesives produced from the substances listed in the regulation to be separated from food by a functional barrier. Alternatively, the upartite of adhesive contextring accharged agreeues and fattu

products, such as the limitations on finished Please consult the individual regulations for further information

² Benzoyl peroxide that meets the appropriate Food Chemicals Codex specifications has also been affirmed as generally recognized as safe (GRAS) for use as a bleaching agent in certain foods (i.e., flour, whey and milk used in the production of certain cheeses). See 21 C.F.R. §184.1157

quantity of adhesive contacting packaged aqueous and fatty maximum quantity of material that may be extracted. foods must not exceed the trace amounts at seams and at the edge exposure between packaging laminates that may occur within the limits of good manufacturing practice; the quantity of adhesive that contacts packaged dry food must not exceed the limits of good manufacturing practice.

> ⁴ Limits of addition expressed as percent by weight of finished resin.

## PEROXIDE SAFETY CHECKLIST⁸

The following checklist is provided as a summary of measures that will promote the safe storage, handling and use of peroxides. The list is a basic safety and information guide, pertaining to all organic peroxides.

1. Different classes of organic peroxides have their own particular characteristics, specifications and handling requirements. These are identified on the product labels and described in the appropriate bulletins and MSDSs. The product label is designed to indicate the recommended storage temperature, specific product hazard characteristics, special handling information and appropriate first aid instructions. Product bulletins provide chemical composition data, sales specifications (including shelf life), physical properties, and safety information such as storage temperature and SADT (Self Accelerating Decomposition Temperature).

- One of the most important factors to observe when working with an organic peroxide is the recommended storage temperature. Exposure to a temperature that can cause accelerated decomposition may result in the generation of flammable gasses, and in some cases spontaneous ignition.
- 3. Refer to NFPA 432 for storage guidelines. Proper storage is critical to the safe handling of organic peroxides, both those normally stored at ambient temperatures and those requiring controlled temperature storage. Ventilation is important because air circulation around peroxides stored at low temperatures reduces the chance of localized hot spots that can cause decomposition.
- 4. Storage areas for peroxides should have explosion proof electrical equipment.
- 5. Organic peroxide inventories should be rotated to avoid shelf life problems.
- 6. Any observable gassing or distortion of the container should be handled very carefully. Visible gassing of organic peroxide containers may be an indication of imminent, possibly violent, decomposition.
- 7. Only minimal quantities of peroxides should be kept in the immediate processing area.
- 8. Avoid contact with incompatible materials, such as oxidizers, reducing agents, promoters, acids or bases.
- 9. The safe use of organic peroxides requires that good housekeeping procedures be meticulously practiced.
- 10. Heat, flame, contamination, shock, friction, and static electricity are potential hazards when an organic peroxide is being charged to a reaction. Care should be taken to eliminate or minimize all of these.
- 11. Polymeric materials that may be soluble in organic peroxide solutions, as well as brass, copper and iron, should not be used in reaction or storage vessels, including piping and valving. Compatible construction materials include stainless steel 304 or 316 (preferred), HDPE, polytetrafluoroethylene, and glass linings.
- 12. Contaminants, such as iron or dirt, should be avoided when charging peroxides.
- 13. Pumps used for organic peroxides must be "dedicated" to avoid potential contamination.
- 14. Static buildup can be minimized by proper grounding and by keeping free fall distances to a minimum, especially when working with initiators sensitive to static, such as dry benzoyl peroxide or di-t-butyl peroxide.
- Friction caused by pumping increases the temperature of the pumping solutions. Extra care should be exercised when peroxide solutions are being re-circulated to avoid temperatures above the SADT (<u>Self Accelerating</u> <u>D</u>ecomposition <u>T</u>emperature).
- 16. When peroxide samples are used in analytical work, care should be exercised to avoid any contamination. Clean, dry plastic or glass containers

should be used to transfer peroxide samples. Dry ice should be available to cool samples in an emergency. Direct heat should never be applied to organic peroxides.

- 17. As a rule, dilution of pure peroxides with compatible solvents will assist the safe handling of peroxides.
- 18. Any spilled organic peroxides should be attended to immediately. Spills can normally be handled by spreading an inert absorbent substance directly on the spill, wetting with water, sweeping the area and placing the sweepings in polyethylene bags for appropriate disposal.
- 19. Where spills occur, allow for sufficient ventilation to aid in the removal of fumes that may be present.
- 20. In disposing of organic peroxides, or the absorbent material that has been used to remove spills, extreme care should be exercised. The wetted absorbent material should be placed in a plastic bag and incinerated. Federal, state and local laws, and environmental regulations, must be observed in choosing a disposal method.
- 21. The procedure for disposal of empty peroxide containers must include rinsing with water or a compatible solvent. This is especially important for refrigerated products. In accordance with federal, state and local regulations, these can then be sent to a landfill or incineration site.
- 22. Drums must always be thoroughly flushed and drained before being sent to a reconditioner.
- 23. Cutting torches should never be used on empty peroxide drums. Flammable vapors may be present.

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### **REINFORCING FILLERS - CARBON BLACKS**

#### by John T. Byers* & Alan A. McNeish*

Degussa Corporation * Retired

A wide spectrum of fillers is available for use in rubber compounding. These range from low cost, nonreinforcing fillers to more expensive, highly reinforcing materials. The choice of filler depends on the requirements of designing a compound. If the rubber part will not be exposed to any particularly high stresses or extensive dynamic flexing, nonreinforcing extender filler can be used at a fairly high loading in formulating a low cost compound for the application. For example, the primary filler for an auto floor mat would probably be a mineral filler. On the other hand, if the rubber part requires strength and durability to withstand the rigors of a demanding application a reinforcing filler like carbon black or silica would probably be chosen. Rubber compounds for applications with intermediate performance requirements often contain a blend of a mineral filler along with a carbon black or silica filler to achieve the best balance of cost and performance.

The U.S. rubber industry consumes about 2.5 million tons of fillers each year. Carbon blacks comprise about 75%, mineral fillers about 21%, silicas and silicates about 4% of the total use. Each variety of filler includes several types or grades that offer various degrees of rubber reinforcement.

#### **Filler Reinforcement**

A reinforcing filler adds stiffness and strength to the polymer-filler composite mixture without destroying its rubber-like flexibility. The degree of reinforcement relates to physical and chemical forces that restrict the mobility of the polymer chains.

Polymer-filler bonds are relatively weak interfacial cohesive forces that can be broken rather easily and reform readily as the rubber part is stretched or compressed. If these were strong covalent chemical bonds, the resulting composite would be stiff and rigid like a plastic or ebonite material. In order to achieve a high degree of reinforcement the surface of the filler particles or aggregates has to be compatible with the polymer and a substantial amount of surface must be available for intimate contact with the polymer chains. A high surface area carbon black that is well-dispersed in a hydrocarbon polymer at a sufficient loading level will yield a highly reinforced rubber compound. A silica with an equivalent surface area will not reinforce as well because it has a less compatible surface and achieve enhanced reinforcement characteristics.

The geometry and shape of filler aggregates can influence the physical restriction of the polymer chain's mobility and the resulting stiffness of the composite mixture. Asymmetrical particles can align with the polymer chains and contribute additional reinforcement. Clay and talc particles have an elongated

shape (platelet deposits) that yields more reinforcement than a whiting (more spherical calcium carbonate deposit) of similar surface area. High structure carbon black aggregates have a branched structure that can entangle polymer chains and restrict their mobility – a phenomenon that is called 'occlusion' of rubber.

Some of the lowest surface area mineral fillers can actually have a negative influence on reinforcement if their particles are too large to fit within the spacing of the polymer chains. Filler particles with a diameter greater than about 1.5 microns can act like a flaw or foreign body that decreases the strength and fatigue characteristics of the composite mixture.

A filler's surface area and the average diameter of its particles or aggregates are roughly the inverse of each other. The carbon blacks and silicas with very small particles and high surface area (greater than 100 m²/gram) have the greatest reinforcement potential, but are more difficult to disperse in a rubber compound. Smaller particle size fillers have a stronger tendency to agglomerate. The large agglomerates have less surface available to contact the polymer chains. Additional mixing energy is required to break up the agglomerates in order to achieve the full reinforcement potential.

## **Carbon Blacks**

Carbon blacks can be produced from hydrocarbon materials by a variety of combustion methods that produce a 'smoke' of finely divided carbon particles. Some of the older methods used to produce lamp blacks and channel blacks are not very efficient, but are still being used to produce some specialty pigment blacks. Small volumes of carbon black produced from acetylene are sometimes used in applications where greater thermal conductivity is needed (curing bladders, etc.).

More than 95% of the carbon blacks used in rubber compounding are now made by the oil furnace process, with thermal blacks accounting for most of the remaining 4 to 5%. The semi-reinforcing thermal blacks, made from natural gas in a cyclical batch process, have low surface area and very little structure. Their primary use is in applications where it is desirable to use a high loading of carbon black without much increase in stiffness (i.e. seals, diaphragms, etc.).

Variations of the furnace process have been used for more than 40 years to produce rubber grade carbon blacks covering the semi-reinforcing to veryreinforcing range. This method has proven to be both flexible and cost-effective. A hydrocarbon oil is used as feedstock and injected into a high temperature furnace (2000°F to 4000°F) fueled by a mixture of air and natural gas or fuel oil. The incomplete combustion in the furnace reactor occurs in milliseconds to yield nearly pure carbon in very fine particles. Graphitic layers of carbon atoms form initially, then combine and grow into nearly spherical particles as they spin in the rapidly moving gas stream. Subsequent collisions of these spherical particles in the turbulent atmosphere form structural aggregates of carbon black. The size of the initial particles and the amount of structure that forms are controlled by various parameters including the reactor design, temperature of the furnace, flow rates, feedstock injection method, chemical additives, cooling method, etc. The resulting aggregates contain a distribution of particle sizes and also a distribution of the number of particles that have combined to make up the structure. Figure 1 shows a carbon black aggregate containing about twenty individual particles or nodes (SEM at 120,000:1 magnification).¹



### Figure 1: Carbon Black Aggregate

The aggregate shown is actually a low structure lampblack, but it gives a good view of the individual particles fused together into a permanent aggregate structure. A more complex aggregate of a high structure furnace black may contain 200 or more particles fused together in a similar manner.

After some cooling of the 'smoke' stream, the carbon black is separated from the gas in bag filters. The fluffy carbon black is pelletized to increase its bulk density and make it easier (and cleaner) to handle and transport. The pelletized carbon black is dried and conveyed to a storage tank for subsequent packaging or bulk shipment.

### **Carbon Black Nomenclature**

The first furnace blacks were given names like SAF (Super Abrasion Furnace), HAF (High Abrasion Furnace), HS-HAF (High Structure HAF), FEF (Fast Extrusion Furnace), GPF (General Purpose Furnace), SRF (Semi-Reinforcing Furnace), etc. As new carbon blacks were introduced, the names grew increasingly unwieldy. A technical nomenclature system was first developed by ASTM in 1966 to simplify and classify the rubber grade carbon blacks. The system, described in ASTM Method D 1765, uses a letter followed by three numbers. Most of the carbon black names start with the letter N, which stands for 'normal' cure rate, but a few start with S (slower cure rate like the older channel blacks). The first number following the letter indicates the particle size and thus gives a rough estimate of the reinforcement potential. The last two
digits are arbitrarily assigned by ASTM when new grades are introduced. Among the furnace grades, the N100 series of grades has the smallest particles (the highest surface area) and the N700 series of grades has the largest particles (less reinforcing potential). Thermal blacks, with even larger particle sizes, make up the N800 and N900 series of grades. The ASTM nomenclature does not give an indication of structure, another important factor in reinforcement, but it is a considerable improvement over the original names. Method D 1765 contains a table of target values and typical values for a number of tests that characterize the standard grades, which are represented in Figure 2.



Figure 2: Carbon Blacks Listed in ASTM D 1765

#### **Primary Properties**

Surface Area and Structure are the most important properties that characterize the reinforcement potential of a carbon black. Increasing the amount of surface that is available to form cohesive bonds with the polymer leads to additional restriction of the polymer chain's mobility. Increasing the complexity of the aggregate structure contributes to more entanglement of the polymer chains (occlusion) and further restriction of their mobility.

Standardized laboratory test methods that are commonly used to measure the surface area of carbon blacks include: lodine Adsorption (ASTM D 1510), Nitrogen Adsorption (D 3037 single point and D 4820 multi-point methods), CTAB Surface Area (D 3765), and STSA - Statistical Thickness Surface Area (D 5816). The ideal test method would measure the effective surface area that is accessible to the polymer chains. Iodine and nitrogen adsorption results may include some surface area contained within small pores which is not accessible to the polymer. The CTAB method uses a larger molecule and gives a better measure of the effective surface area, but it is cumbersome and time-consuming. STSA is a modification of the multi-point nitrogen procedure that was developed as a less cumbersome alternative that correlates with CTAB results.

The highly branched aggregates of a high structure carbon black contain voids within the branching of the complex structure, even after the sample is compressed. Several test methods are used to characterize the structure of carbon blacks by measuring the volume of the voids within the carbon black sample. These methods include Oil Absorption Number (D 2414), Crushed OAN (D 3493 - also known as COAN or 24M4 OAN), and CVI – Compressed Volume Index (D 6086). The common Oil Absorption procedure measures the volume of oil (previously dibutyl phthalate) needed to fill the voids within the sample, but the result also includes voids that are trapped within larger agglomerates. In the Crushed OAN test the carbon black sample is crushed or compressed at 24,000 psi four times in a cylinder prior to testing in an absorptometer. Results from the Crushed OAN test are generally accepted as more indicative of the structure that remains after mixing the carbon black into a rubber compound. Compressed Volume Index is a more recent method utilizing an instrument to measure the volume that remains after compressing a carbon black sample.

*Tint Strength* (D 3265) is an indirect measurement that relates to aggregate size. It is a light reflectance measurement on a mixture of carbon black, zinc oxide and oil. Smaller aggregates give a 'blacker' paste that absorbs more light. Results are affected by structure differences, however.

Surface Activity is often listed as a third primary property, but there is not much variance in activity per unit of surface among the rubber grade furnace carbon blacks. Modifications of the processes that were introduced in the 1970s probably enhanced the activity of the surface somewhat compared to previous furnace grades. Some specialty blacks are oxidized or acid-treated to alter their surface chemistry and thus modify their surface activity. There are no standard tests that are commonly used to measure surface activity differences. Research using various analytical methods has shown that the edges of the bent and broken graphitic planes on the surface of a carbon black particle have higher electron density and are the active sites for cohesive attachment to the polymer chains.

Increasing the carbon black loading level magnifies the reinforcement effects by multiplying the amount of surface available to form cohesive bonds with the polymer chains, as well as increasing the degree of entanglement of the polymer chains by the branches of the aggregate structure (occlusion). Data shown in Figures 3 through 9 illustrate the effects of varying Nitrogen Surface Area, DBP absorption (Structure) and the carbon black loading levels in a natural rubber compound.² The surface area and structure variations for the five carbon black points are shown in Figure 3. The N300 central point is a composite made from averaging the data for three carbon blacks – N339, N351 and N375 – to give (N300 = 91 N₂SA, 118 DBP). The structure variations from the central point are: HS (N356 = 158 DBP) and LS (N326 = 74 DBP). The surface area extremes are:

Hi SA (N110 = 136  $N_2$ SA) and Lo SA (Composite of N650, N660, and N550 data to give N600 = 41  $N_2$ SA).



Figure 3: Carbon Blacks in Reinforcement Study

Figure 4 illustrates that both surface area and structure have an effect on compound viscosity. Increasing carbon black loading or increasing either primary property leads to more restriction of the mobility of the polymer chains and stiffening of the uncured compound. Modulus data on the cured compounds give similar curves. Shore A Hardness data, shown in Figure 5, again illustrate the stiffening effect as loading, surface area or structure is increased. The Hardness increase is linear as the loading of the carbon blacks is increased.



The rebound data, shown in Figure 6, and running temperature, shown in Figure 7, demonstrate that hysteresis losses accompany the increased stiffness as the carbon black loading increases. Higher loading levels result in reduced resilience (lower rebound) and more heat generation as the running temperature block is flexed. The carbon black surface area variation shows a significant effect on hysteresis, but structure shows considerably less effect. Both of these carbon black characteristics restrict the mobility of the polymer chains, but they act in

different ways. When the carbon black surface area is increased, there are more polymer-filler cohesive bonds and also more filler-filler network bonds to be broken when energy is input to deform the test block. Some, but not all, of the energy is returned when these bonds reform. The structure effect – the entanglement of polymer chains – is a physical effect and does not involve the rupturing of bonds. These differences in energy consumption are again evident when comparing the effects of carbon black surface area and structure on strength-related properties (tensile strength, tear resistance, abrasion resistance, etc.).



NR COMPOUND - 15 OIL

Figure 6: Rebound

NR COMPOUND - 15 OIL



Figure 7: Running Temperature

Figure 8 illustrates that high tear resistance can only be attained with higher surface area carbon blacks. For each carbon black, as the loading is increased the tear resistance reaches a maximum (at optimum inter-aggregate spacing in the polymer matrix) and then starts to decrease. Varying the carbon black structure alters the location of the optimum loading region, but does not change the maximum level of tear resistance that can be obtained. Low structure carbon blacks do not necessarily give better tear resistance than high structure carbon blacks, as commonly believed, if the loading is adjusted correctly.

NR COMPOUND - 15 OIL





The same comments apply to the abrasion resistance data, shown in Figure 9. The curves are similar to those for tear resistance, but the plateau regions are shifted to higher loading levels. Tensile strength data would show a similar pattern.



Figure 9: Abrasion Index

For all of these strength-related properties, a high surface area carbon black offers more potential to maximize the strength or abrasion resistance. Achieving greater strength requires the absorption of more energy, which is attainable with higher surface area, but is not influenced by the structure of the carbon black. Improving the strength or abrasion resistance of a compound by using a higher surface area carbon black also leads to higher hysteresis. A somewhat better trade-off of hysteresis and abrasion resistance can often be achieved by using a higher surface area carbon black that also has higher structure, along with reducing the loading level. The stiffening effect from the increased structure enables a reduction in the loading to match the original stiffness (or hardness), and the lower loading gives reduced hysteresis.

Similar trends occur with carbon blacks in the semi-reinforcing region (N500, N600 and N700 series). The least reinforcing N700 series furnace carbon blacks are commonly used in hoses, seals, molded goods and various other rubber products where high strength and abrasion resistance are not required. Even highly loaded compounds remain fairly soft, flexible, and process easily. N660, N650 and N550 would be greater reinforcing alternatives. N550 and N650 are high structure carbon blacks that are often used in extruded profiles. They contribute a smoother extruded surface and lower die swell.

Fatigue life decreases as the stiffness of the polymer-filler composite increases. Cut growth resistance is a combination of fatigue and strength. Using a higher surface area carbon black should improve cut growth resistance if the loading level is reduced slightly to the point where stiffness is maintained (equal hardness).

Several tools are available to help in compounding to equal hardness with various carbon blacks. One is a slide rule type 'Equal Hardness Calculator' and another is a chart such as the one shown in Table 1. The chart lists estimates of relative loading levels for various carbon blacks, several other fillers, and extender oil. These should be considered only as starting point estimates for initial laboratory studies in compounding to equal hardness. For example, the chart can be used as a guide in a project to reduce the material cost of a compound by substituting a more reinforcing carbon black and adding the appropriate amount of low cost extender oil to adjust to the original hardness.

Polymer	SBR	NR	BR	CR	NBR	EPDM	lir
N110	18	15	22	12	17	24	13
N234	19	16	23	13	18	25	14
N231	23	19	28	15	21	30	17
N358	20	17	25	13	19	27	15
N339	21	17	26	14	20	28	16
N330	23	19	28	15	21	30	17
(OIL)	-23	-19	-28	-15	-21	-30	-17
N326	26	21	32	17	24	34	19
N550	28	23	34	18	26	37	21
N650	28	23	34	18	26	37	21
N660	31	25	38	20	29	41	23
N774	34	28	42	22	32	45	25
N762	35	29	43	23	33	47	26
N990	51	42	65	35	48	68	38

Table 1: Equal Hardness Compounding Chart for "Starting Point" Compounds

#### **Secondary Properties**

In addition to the primary properties of carbon black discussed above, there are several other properties that can be critical for obtaining a well-dispersed mixture, handling and conveying of the carbon black, and for producing rubber parts of uniform quality.

Carbon black pellet properties can be very important for proper mixing and dispersion, especially in soft or highly extended compounds. Carbon blacks are pelletized to increase the bulk density and improve handling. The pellets have to be fractured and the agglomerates of carbon black broken down to achieve a well-dispersed mixture in order to realize the reinforcement potential of the carbon black. Large agglomerates of carbon black do not give the desired performance characteristics. Softer pellets are usually required for compounds that generate low shear forces during mixing. Pellet size distribution may also be important, because larger pellets require additional force to break. The standard ASTM test methods to assess pellet properties are: Individual Pellet Hardness (D 3313) and Pellet Size Distribution (D 1511). Soft pellets may break up more readily during transport and handling, generating higher "fines" that are more difficult to transfer in bulk systems, creating more dust, and possibly causing problems in incorporation and mixing. The fines content can be monitored using ASTM Method D 1508.

Carbon blacks that contain too many 'grit' particles can cause appearance and performance problems. Common sources of grit include particles of coke that have formed in the furnace reactor, pieces of refractory from the lining of the furnace, or metallic particles that have gotten into the carbon black product stream. Wet sieve residue tests are used to measure the grit content (ASTM D 1514).

Other common tests for carbon blacks include: Bulk density (D 1513), Ash content (D 1506), Toluene Extract (D 4527), Toluene Discoloration (D 3392), and pH (D 1512).

#### Silicas

Silicas are also used as reinforcing fillers for rubber compounds, but their processing and performance characteristics are different than those of carbon blacks. Both precipitated and fumed silicas are commercially available, but the fumed silicas (i.e. Aerosil[®], Cabosil[®], etc.) are primarily used in silicone rubber and a few specialty rubber compounds that must have very low moisture content. Fumed silicas are made in a high temperature gaseous process and are more expensive than the precipitated types.

Precipitated silicas are produced in water by adding an acid to a sodium silicate solution to form a precipitate of amorphous SiO, particles and aggregates. Their surface is hydrated silica in the form of silanol groups (=Si-O-H or =Si[OH]_) that contain active hydrogen atoms. This surface is considerably more reactive than the surface of carbon black, and it is not as compatible with most generalpurpose polymers. The silanol groups can attach to several rubber chemicals (including zinc activators and amine accelerators) that are integral parts of the cure system, and reduce their effective level. This can lead to longer cure times and fewer sulfur crosslinks in the cured rubber. A glycol or an active amine ingredient may be added to silica-filled compounds to tie up the active silica surface and reduce its affinity for curative chemicals. These additives include polyethylene glycol (Carbowax[®]), diethylene glycol (DEG), triethanol amine (TEA), hexamethylene tetramine (Hexa), and hexamethoxy methyl melamine (HMMM). Guanidine accelerators, such as DPG or DOTG, are also quite effective. Silicas are hygroscopic, and the moisture that remains after mixing can interfere with some non-sulfur cure systems, including peroxides.

Compared to carbon black, the aggregates of silica contain fewer permanently fused particles, but they have a much stronger tendency to agglomerate into clusters of aggregates. High surface area silicas, such as Ultrasil[®] VN3, can form a strong filler-filler network that probably contributes to enhanced tear resistance and adhesion properties, but makes the mixing and processing of compounds more difficult. The highly dispersible silicas, such as Ultrasil 7000 GR, feature greater persistent structure and a reduced tendency to agglomerate. The benefits include easier mixing, improved processing and better dispersion of the silica – which usually results in improved abrasion resistance.

Silane Coupling Agents have proven to be very effective in altering the surface chemistry of silicas and enhancing their performance in rubber compounds. The typical use includes a fairly hot mix of the compound masterbatch ingredients, sometimes a second hot mixing stage to complete the reaction between the silane and the silica, and then the addition of curatives in a lower temperature

mixing stage. An effective coupling agent contains an additional chemical group that will attach to the polymer during vulcanization. In addition to the coupling bonds that are formed between the silica and the polymer, the modification of the silica surface improves compatibility with the polymer, reduces the silanol group effect on curative ingredients, reduces filler-filler network formation and reduces agglomeration. The overall result is performance more like that obtained with carbon black; typically with the benefit of lower hysteresis. The use of the silicasilane combination in the tread compounds of low rolling resistance tires has demonstrated this benefit very well.

Silane coupling agents designed for use with sulfur-cure systems include a sulfur or mercapto-functional group. Silane coupling agents designed for use with peroxide-cure systems typically include a vinyl- or methacryloxy-group. A silane coupling agent with a chloro-group would be used with halogenated polymers.

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#### **REINFORCING FILLERS – SILICA**

#### by Anke Blume, PhD and Werner Niedermeier, PhD

Evonik Degussa GmbH Inorganic Materials Applied Technology Frankfurt, Germany

#### INTRODUCTION

Precipitated silica and silicates today play a very important part as reinforcing fillers for the rubber industry. The commercialization of white fillers started in 1942 with the production of pyrogenic silica with the trade name Aerosil[®] introduced by Degussa AG. The main application for this silica is its use in silicone rubber. Precipitated silica was first introduced in 1948 by the Columbian Chemical Division of the Pittsburgh Plate Glass Co. In Europe the commercial production of precipitated silica started in 1951 with the product Ultrasil[®] VN 3 developed by Degussa AG. This silica has been for many decades the state-of-the-art product all over the world.

In the following years the shoe sole industry was the most important consumer of white reinforcing fillers.1 The use of silica resulted in a nonmarking "nuclear" sole with good abrasion, tear and flex resistance (all premium guality soles made in the US contained silica in those times).24 A further great advantage of applying silica is the possibility of satisfying requirements such as transparency or a particular color in combination with high reinforcement, which can not be achieved by natural fillers like clays, chalk or talc. Silica was also used to improve tear and tensile strength. In particular, it was applied in small amounts in earth mover tire treads as well as truck tire treads, where tear resistance and cut & chip properties are highly requested. It is also used in belts, in wires, in cable jackets and in rubber adhesion compounds for improved rubber-metal bonding.² Furthermore, silica was inserted in some types of hoses which require a high abrasion resistance and to be colored for identification or easy visibility. In the late 1960s research showed that the use of silica results in remarkably good reinforcing properties only when a coupling agent, like the 3-methacryloxypropyltrimethoxysilane in peroxide-cured, and the 3-mercaptopropyltrimethoxysilane in sulfur-cured compounds, is added.⁵⁻¹³ Using high amounts of the reactive mercaptosilane was limited because of too short scorch times. When Degussa introduced the slower curing coupling agent Si 69® (TESPT, bis-(3-triethoxysilylpropyl)tetrasulfane) in 1972, the basis for a breakthrough of the silica-silane filler system in the rubber industry in new applications, especially in tires, was achieved.14-19

This new filler system was launched for the first time in winter tire tread compounds in 1974 by Metzeler with the introduction of the so-called "Blue Tire" and led to a significant improvement in winter performance.²⁰ But the hardening effect of the tread compound over time was too strong and therefore the overall tire performance was not satisfactory. This changed in the early 1990s with the introduction of the so-called "Green-Tire Technology" by Michelin in Europe.²¹

Part of the concept was a tread compound based on a blend of S-SBR and BR filled with highly dispersible (HD) precipitated silica with an optimized amount of sulfur-functional organosilane resulting in a lower rolling resistance and a better wet traction in comparison to traditional tread compounds.

Since then the demand from the rubber industry for precipitated silica and silane has been increasing continuously, and today more than 90% of the original equipment passenger car tires in Europe contain this filler system in the tread compound. In the US, 110 kilotons of silica were used in rubber materials in 2008, with 68 kilotons of this total used in tires.²² In addition to this major application, the combination of precipitated silica with a silane as coupling agent is also used in various industrial rubber goods.²³ For these applications not only the sulfur-functional silanes, but also vinylsilanes, methacryl- or aminosilanes are in use.

## PRODUCTION PROCESS OF PRECIPITATED SILICA

Precipitated silica is produced in a batch process by the addition of acid to a water glass solution. During the precipitation process, initially primary particles are formed, followed by the formation of clusters. Figure 1 shows the general formation of silica during the precipitation process²⁴ and Figure 2 pictures a typical production line. After the drying process the silica can be delivered in powder form or as small spherical particles, so-called micro pearls or micro granulates, respectively and further processed to granulates.





Precipitation process parameters such as time, temperature and acid addition predefine the main properties of the silica, which are surface area and structure. In the following production steps the silica is filtered, washed, dried and in most cases compacted for the transportation and later incorporation into the rubber.²⁵



Figure 2: Typical Silica Production Line

Table 1 shows an overview of the influence of the parameters of each process step on the product properties. For the development of new products a fundamental knowledge of these parameters is essential as well as a carefully controlled reaction.

Process step	Parameter	Product property
Precipitation	pH-value, reaction temperature and time, concentration, dosage and mixture of educts	specific surface area, structure, silanol group density, particle size distribution, pore size distribution
Filtration	filling and washing time, solid content	structure, pH, conductivity, pore size distribution
Drying	type of dryer, temperature, solid content, time	specific surface area, structure, moisture content, particle size distribution, pore size distribution
Granulation	feed rate, pressure	structure, sieve residue, bulk density, particle size distribution, pore size distribution

 Table 1: Main Product Properties Influenced by the Production Process

## MORPHOLOGY OF PRECIPITATED SILICA

It is essential to gain a deep knowledge of the morphology of precipitated silica in order to understand the reinforcement mechanism of the silica-silane system in rubber compounds.^{26, 27} The three most important characteristics to describe the morphology of silica are the following:

- · Specific surface area
- Structure
- Surface chemistry

Moisture content, pH value, sieve residue, fines content and conductivity are further parameters influencing the processing, vulcanization and the final rubber product properties as well.

## **Specific Surface Area**

The specific surface area of a silica is generally determined using an adsorption method according to Brunauer, Emmett and Teller (BET)²⁸ or a modified method^{29, 30} (ISO 5794-1). At low temperatures, nitrogen is adsorbed on the silica surface. The quantity of adsorbed gas is a measure of the surface area.

The CTAB method (ISO 5794-1), initially known from the characterization of carbon black, is also used in the case of silica.³¹ The preferred adsorption site for these large CTAB (cetyltrimethylammonium bromide) molecules is the outer, geometrical surface. In comparison to the CTAB, the BET surface area describes the total (outer + inner) surface of a silica. The bigger CTAB-molecule is used for a first approximation of the surface area which is accessible for the polymer molecules.

Besides the specific surface area indicating the average particle size, the distribution of the particle sizes of a filler is also an important parameter influencing the in-rubber properties of the final product. The particle size distribution can be defined on the one hand for primary particles and on the other hand for clusters of aggregated and/or agglomerated primary particles. Depending on the sample preparation and applied measuring technique the maximum of the particle size distribution can be on the order of a few tens of a nanometer up to a micrometer. A proposal for the determination of the particle size distribution by using a light scattering aerosol spectrometer is described in ISO 21501-1.

#### Structure

The term "structure" of filler particles in general should depict the 3-dimensional arrangement of primary particles in clusters. The shape and the number of primary particles define the structure of a cluster. The structure of silica influences the incorporation of the silica into the rubber mixture, the dispersibility as well as the processability.

To characterize the structure of a cluster the void volume inside the cluster is measured. The predominately used measurement (ASTM D 6854) up to now is the absorption of dibutylphthalate (DBP).³²⁻³⁴ This largely automated measurement technique provides an indication of the total volume of liquid which can be absorbed by a silica sample. The magnitude of the DBP number gives an indication of the structure of a silica sample. A higher DBP absorption number in this context means that the clusters are higher branched or built up of more primary particles. Owing to the toxicity of DBP, attempts are being made to replace it, for example, by paraffinic oil or dioctyladipate (DOA), the latter initiated by the European Council of Chemical Manufacturer's Federation CEFIC.³⁵ Another possibility to detect the silica structure is the direct measurement of the void volume³⁶ as a function of pressure applied on the sample. As a result the void volume at different pressure levels is obtained.

A further method to characterize the structure of silica is to measure the pore volume. The pore volume of silica can be understood as the micro- and submicro-pore volume within the particles or clusters. There are different specific evaluation methods described in the literature^{37,38}, e.g., ISO 15901.³⁹ The most common method of determining the pore volume of silica is by applying mercury porosimetry.^{40,41} The pressure required to force the mercury into the pores of the silica sample is used to calculate the pore volume. The adopted pressure is inversely proportional to the pore diameter. If the volume of mercury at this pressure is known, the pore volume of the silica can be calculated. The outcome is the pore size distribution expressed by pore volume over the pore diameter (Figure 3). Comparison of the measured curves of different silica reveals distinct differences in intrusion and is indicative of different structures of the measured products.



Figure 3: Pore Size Measurement by Mercury Porosimetry Intrusion

## **Surface Chemistry**

The Sears number is a measure of the number of silanol groups on the surface.^{42, 43} It is equivalent to the quantity of 0.1 n NaOH required to titrate a suspension of silica from pH 6 to pH 9. The acidic silanol groups on the silica surface react with NaOH. The Sears number gives an indication of the number of reactive centers on the surface of silica.

By using ²⁹Si NMR⁴⁴⁻⁴⁶ it is possible to look into detail in the surroundings of the Si-atoms in the silica sample. With this technique it is possible to distinguish between three main groups around the silicone atom in silica: siloxane bridges (bulk), isolated, vicinal and geminal SiOH (Figure 4).



Figure 4: Various OH-groups on the Silica Surface

IR spectroscopy is another method to analyze various silanol groups. It has to be noted that with this method a differentiation between geminal and isolated groups is not possible. On the other hand the grafting of silanes to the surface

of silica can be studied by an IR operando study. An overview of the detectable groups is given in Table 2.  $^{\rm 47,48}$ 

	isolated / geminal	vicinal SiOH	
	Si-OH	(bonded)	
IR band at / cm ⁻¹	3738	3500	

Table 2:	Silanol	Groups	Detectable by	v IR S	nectroscopy
	onunor	Groups	Detectuble b	y 11 X O	pecchoscopy

Silanol groups are able to react with coupling agents (e.g., TESPT). This reaction changes the polar hydrophilic silica surface to a less polar hydrophobic one. The different silanol groups are assigned to different reactivities to organosilanes.⁴⁹ An operando approach displays that the isolated (together with the geminal) SiOH groups (see Figure 4 and Table 2) are the most reactive ones.⁵⁰

The comparison of the silanol group densities measured with different techniques results in varying values. The reason for this is the different accessibility of the SiOH groups depends on the measuring principle as well as on the probe molecules used for adsorption measurements. The silanol group density is within the range of 4-10 SiOH/nm², which fits with the theoretical calculation.⁵¹

## NOMENCLATURE

There is no internationally accepted classification for silicas like for carbon blacks.⁵² The attempt at classification according to the specific surface area in grade A to F was made within the ISO 5794-1, but found no acceptance. Nevertheless a tentative listing of silica currently available on the market for tires and technical rubber articles from the four main global manufacturers is shown in Table 3.⁵³⁻⁵⁶ Products are also classified according to their specific surface areas (in this case CTAB adsorption) but only in three categories. Furthermore, the silicas for the rubber-processing industry are distinguished according to their dispersion behavior as "conventional", "semi highly dispersible" or "easily dispersible" and "HD" silica (Figure 5). This classification has gained acceptance in the literature.

	CTAB Surface Area (m²/g)				
	Up to 140	160 +/- 20	200 +/- 20		
	Low Surface Area Silica		High Surface Area Silica		
	Hi-Sil [®] 315	Hi-Sil 233	Zeosil 195 Gr		
	Hubersil [®] 1613	Hi-Sil 255			
	Hubersil 1633	Hi-Sil 243 LD			
	Hubersil 1635	Hi-Sil 210			
lal	Ultrasil 360	Hubersil 1714			
Itior	Ultrasil AS 7	Hubersil 1715			
UVEC	Ultrasil 880	Hubersil 1743			
ပိ	Zeolex [®] 23	Hubersil 1745			
	Zeolex 80	Zeolex 25			
	Zeosil [®] 125 Gr	Zeosil 175 Gr			
		Zeosil 145 Gr			
		Ultrasil VN 3 (GR)			
	Huberpol [®] 135	Hi-Sil 243 MG	Hi-Sil 190 G		
분	Ultrasil VN 2 (GR)	Zeosil 145 MP	Zeosil 195 MP		
Sem	Zeosil 115 Gr	Zeosil 165 Gr			
	Zeosil 1135 MP				
	Ultrasil 5000 GR	Hi-Sil 160	Hi-Sil [®] 2000		
	Zeopol [®] 8715	Ultrasil 7000 GR	Ultrasil 7005		
Р	Zeosil 1115 MP	Zeopol 8745	Zeosil 1200 MP		
		Zeopol 8755	Zeosil Premium 200 MP		
		Zeosil 1165 MP(S)			

Table 3: Classification of Rubber Silicas by CTAB and Dispersion

In general, the methods developed to determine the dispersion of fillers in a rubber matrix are either subjective (Phillips method – ISO 11345), only qualitative, or time-consuming (TEM). Most methods are based on the fact that aggregates or agglomerates of undispersed particles (carbon black, silica, zinc oxide...) are harder than the surrounding rubber matrix. Therefore these agglomerates are deflected to the one side of the slice or to the other during the cutting of the sample by a razor blade to create a fresh surface. The surface roughness is used as a measure for the filler dispersion. Therefore these methods are so-called indirect methods.

The light optical methods like the DIAS method⁵⁷ of the German Institute of Rubber Technology and the measurement with the Dispergrader (ISO 11345) are common and well accepted methods, but are not automated. For light-

colored compounds, rubber samples with different contrasts and silica containing mixtures the use of optical measurements is sometimes limited. The Topography method^{58,59}, which is automated and also an indirect method, uses a tiny needle to scan the surface and to monitor the surface roughness. Conventional silica shows a lot of undispersed particles in a Green Tire tread compound. There are less undispersed particles when semi-HD silica is used. Only the use of a highly-dispersible silica results in a very small amount of undispersed particles of a smaller size (Figure 5a). The measurement of the topography also delivers detailed information about the dispersion of the silica (Figure 5b).



Figure 5a: Filler Dispersion – DIAS Method⁵⁷ (450 µm x 650 µm)



Figure 5b: Filler Dispersion – Topography Measurement^{58,59}

# THE SILICA-SILANE FILLER SYSTEM FOR RUBBER APPLICATION

## Silica in Rubber

The use of silica without any coupling agent in a rubber compound was limited for a long time, in most cases, to small parts (10 - 15 phr) together with carbon black, to improve tear strength and cut resistance⁶⁰, for example in conveyor belts. Furthermore, silica has been used in tread compounds for off-road and heavy-duty tires to reduce cut & chip properties.⁶¹⁻⁶³ Shoe soles⁶⁴ and adhesive compounds are further applications.⁶⁵

The reason for this limited use of silica in rubber is its polar surface which, on the one hand, creates a strong silica-silica agglomeration via hydrogen bonding (Figure 6), but on the other hand, gives a weak interaction potential with the rubber. This agglomeration process results in a high filler-filler but low filler-polymer interaction^{66,67} and is responsible for an increased Mooney viscosity leading to poor processing behavior, reduced scorch time during vulcanization and a lower reinforcement. The low reinforcement given by silica without a coupling agent leads to poor abrasion resistance in tire tread applications compared to carbon black. Due to the strong hydrogen bonding, the filler network and hence the Payne effect formed by silica, is much stronger in comparison to carbon black with a similar surface area.



Figure 6: Formation of the Silica Network by Hydrogen Bridging

The crack growth rate as a function of the applied deformation analyzed by the Tear Analyzer^{68,69} shows the benefit of using small amounts of silica compared to carbon black. Three silica filled compounds without silane are compared in Figure 7. The silicas differ in their specific surface area. The filler loading of the silicas Ultrasil VN2 GR (120 m²/g), Ultrasil 7000 GR (160 m²/g) and Ultrasil 7005 (175 m²/g) was adjusted to their specific surface area to obtain the same total silica surface area in the compound. A clear trend to a better tear resistance behavior can be seen with increasing specific surface area of the silica used. The best performance regarding tearing can be observed by using silica with a high specific surface area. A reason for this improved tear resistance by using silica could be the strong filler-filler network, which is even stronger for a high surface area silica.^{62,63}



(Dosage adapted to the Specific Surface Area (CTAB) of the Silica: Ultrasil VN2 GR @ 120 m²/g; Ultrasil 7000 GR @ 160 m²/g; Ultrasil 7005 @ 175 m²/g)

#### Figure 7: Crack Growth Rate of Carbon Black vs. Silica Blends

## Silica-Silane Rubber Coupling

The use of silanes allows a modification of the polar silica surface area and increases the compatibility of the silica with the rubber matrix. The monofunctional alkylalkoxysilanes, which couple only to the silica, make the silica surface more hydrophobic. This leads to a strong reduction of the silica-silica network.⁷⁰⁻⁷² Lower viscosity and an improved processability are the benefits. Furthermore, the cure behavior is improved but the reinforcement of such modified silica is still low due to the lack of a strong filler-polymer interaction.

To achieve the desired reinforcement a chemical linkage between the silica and the rubber matrix is needed. Usually, bi-functional silanes are used to provide a covalent bonding between silica and rubber. The principle of the formation of chemical silica-silane-rubber bonding by a bi-functional silane (e.g., sulfur-functional) as coupling agent is displayed in Figure 8.



mixing

vulcanization

Figure 8: Principle of the Silica-Silane-Rubber Coupling

This coupling agent is characterized by three parts: a silica-active site, a hydrocarbon spacer and a rubber-active site.

The alkoxysilyl group, preferably a triethoxysilyl group, provides the coupling of the silane to the silica surface under release of alcohol. The spacer, most often a propylene group, is mainly responsible for the hydrophobation of the surface to make the silica more compatible with the rubber and to reduce the degree of the silica-silica aggregation. Furthermore it is reported that the length of the spacer correlates directly with the scorch safety and modulus.⁷³

The rubber-active site reacts with the polymer during vulcanization and therefore couples the silica chemically to the rubber. This chemical bond between the silica and the rubber matrix is responsible for the reinforcement of the silica-silane filler system.⁷⁴ Special attention has to be paid to the selection of the right silane, depending on the application, and therefore on the polymer and accelerating system.

The consequences of this chemical bonding can be seen in Figure 9. On the one side (top photo), the stretching of thin rubber parts compounded with silica without silane investigated by TEM leads to polymer displacements. This clearly displays that the interaction of pure silica with hydrocarbon polymer is very poor. On the other side (bottom photo), if the compound contains the bi-functional sulfur-silane Si 69[®] bound rubber and occluded rubber are formed and no polymer displacements take place, which leads to high tensile strength, moduli and good abrasion resistance.



Silica Compound Without Silane: Polymer Displacements



Silica Compound With TESPT: Almost No Polymer Displacements

Figure 9: TEM Photos of Silica-filled Polymer Under Stress

The efficiency of coupling sites between the silica and the polymer via the silane bridge increases with a rising silane amount. The higher the silane content of the coupling agent the better is the abrasion resistance in different polymers (Figure 10).



## **Silanes for Rubber Applications**

Several types of rubber silanes depending on the polymer and accelerating system are used in the rubber industry. The tetrasulfane-silane Si 69[®] is still the most widely used coupling agent for sulfur-cured rubber compounds. Table 4 gives an overview of the most common rubber silanes.

Chemical Name and Structure	Trade Name	Application
Bis-(triethoxysilyl-propyl)sulfane $(C_2H_5O)_3Si(CH_2)_3-S_{x-}(CH_2)_3Si(OC_2H_5)_3$	Dow Corning® Z-6940 Dow Corning Z-6920 Evonik Degussa Si 69 Evonik Degussa Si 75 Evonik Degussa Si 266 Shin-Etsu® KBE-846	Tire treads, industrial rubber goods, shoe soles
Mercaptopropyltrialkoxysilane (R'O) ₃ Si(CH ₂ ) ₃ -SR (R':alkyl; R:H or oxoalkyl)	Dow Corning Z-6062 Evonik Degussa VP Si 263 Evonik Degussa VP Si 363 Momentive NXT® Shin-Etsu KBM-803 Silquest® A-189	Tire treads, industrial rubber goods, shoe soles
Vinyltriethoxysilane + oligomer $(C_2H_5O)_3SiCH=CH_2$	Dow Corning Z-518 Dynasylan◎ VTEO Dynasylan 6498 Shin-Etsu KBE-1003	Industrial rubber goods (peroxide curing)
3-Aminopropyltriethoxysilane $(C_2H_5O)_3Si(CH_2)_3-NH_2$	Dynasylan AMEO Shin-Etsu KBM-903 Silquest A-1100	Industrial rubber goods
Thiocyanato-triethoxysilane $(C_2H_5O)_3Si(CH_2)_3$ -SCN	Evonik Degussa Si 264	Industrial rubber goods, shoe soles
Propyltriethoxysilane $(C_2H_5O)_3Si(CH_2)_2$ -CH ₃	Dow Corning Z-6535 Dynasylan PTEO	Processing Aid
3-Chloropropyltriethoxysilane $(C_2H_5O)_3Si(CH_2)_3$ -Cl	Dow Corning Z-6376 Dynasylan CPTEO	Industrial rubber goods (metal oxide curing)
$\begin{array}{l} 3\text{-}Glycidyloxytrimethoxysilane (GLYMO) \\ (CH_3O)_3Si(CH_2)_3\text{-}C_3H_5O_2 \end{array}$	Dynasylan GLYMO Shin-Etsu KBM-403	Industrial rubber goods
3-Trimethoxymethacrylate ( $CH_3O$ ) ₃ Si( $CH_2$ ) ₃ - $C_4H_5O_2$	Dynasylan MEMO Shin-Etsu KBE-503 Silquest A-174 Dow Corning Z-6030	Industrial rubber goods (peroxide curing)

Table 4: Common Rubber Silanes and Their Application⁷⁵

#### Silica-Silane Reinforcement System

Apart from the gain in reinforcement expressed by, e.g., moduli and DIN abrasion, the use of silanes influences nearly all vulcanizate properties. However, the main reason for the introduction of the silica-silane technology was its positive influence on wet-grip and hysteresis of rubber compounds by maintaining a high level of abrasion resistance.

Consequently, one main application of the silica-silane filler system is the use in modern passenger car tire tread compounds for reduced fuel consumption and improved wet traction properties. The use of the silica-silane filler system in combination with a high Tg solution-styrene-butadiene copolymer and a low Tg 1,4-polybutadiene results in an extension of the "Magic Triangle" of tire performance (Figure 11).



## Figure 11: The "Magic Triangle" of Tire Performance

Figure 12 displays the ongoing wet traction improvement by the stepwise replacement of carbon black N 234 by the silica-silane system in an S-SBR/BR compound.⁸¹



LAT 100 Wet Traction Test @ 15°C

(N234 Carbon Black/Ultrasil 7000 GR phr + 8 phr Si 69)

According to LAT 100 measurements, the wet-traction performance can be further improved by using higher amounts of silica, as shown in Figure 13.



Figure 13: Wet Traction vs. Silica Loading

This system is also applied successfully in passenger car tire tread compounds for winter tires to improve wet traction properties as well as snow traction.⁷⁶⁻⁸⁰ Snow traction is improved through the less pronounced stiffening effect at low temperatures of the silica-silane system. Due to the lower stiffness of the silica-silane containing compound at low temperatures the sipes of the tread pattern can open and close more easily and therefore create a better grip on snowy roads.

## Summary

Precipitated silica without a coupling agent is used in high amounts in the non-marking shoe soles market. However, silica without a coupling agent is mostly used only in small amounts in tire compounds in combination with carbon black to improve tear resistance properties. In contrast to the common filler carbon black, high reinforcement of silica-filled rubber compounds is only attained by the usage of organosilane coupling agents. This increase in reinforcement and wear resistance is due to the formation of chemical bonds between the silica and the polymer which occurs during the vulcanization process. Most commonly used are sulfur-functional organosilanes like TESPT and TESPD. The small primary particle size of precipitated silica, in combination with the chemical coupling of the silica to the rubber, results in much higher reinforcement than that for natural fillers like silicates and clays. The silica-silane filler system is the best choice for colored rubber articles, shoe soles, special sealants and hoses, which require high abrasion resistance. Today the "silica-silane technology" is state-of-the-art in passenger car tire tread compounds requiring low rolling resistance and high wet grip performance. This system is also state-of-the-art in winter tire tread compounds.

Developments in the field of silica, as well as in the silane technology, are ongoing specifically to improve the rolling resistance of tires and thereby reduce the fuel consumption of passenger cars. In the future a higher product diversification for silicas and for silanes can be expected. Low specific surface area HD silicas, as well as high specific surface area HD silicas, are already available. The newly developed high surface area silicas should help to perfectly balance rolling resistance and abrasion resistance. New mercaptosilanes^{82,83} have been developed, providing a higher coupling yield and reducing rolling resistance compared to the current silica-silane system based on TESPT.

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## MINERAL FILLERS FOR RUBBER

## by Peter Ciullo

## R.T. Vanderbilt Company, Inc.

The use of minerals in rubber products was a practical response to the sticky nature of rubber and arguably an inevitable consequence of Thomas Hancock's invention of the rubber masticator in 1820. Prior to the discovery of vulcanization in 1839, the tackiness of rubber goods was subject to correction by the traditional remedy for wet or sticky surfaces – sprinkling with talcum powder. The conceptual leap from applying talc to the outside to incorporating it within the rubber was facilitated by the masticator. In fact, this machine enabled the incorporation of all types of fine particles, including fine-ground natural minerals–calcium carbonate, clay, mica, barite, iron oxides, kieselguhr (diatomite) and litharge (lead oxide). The addition of particulates such as these may have been motivated by control of tack, adjustment of color, and improvement in compound cost, but, in time, two conclusions were unavoidable:

- Certain fillers, calcium carbonate in particular, could be added in large amounts without detracting from desirable rubber properties.
- Certain fillers, kaolin clay in particular, could actually improve rubber properties, usually by increasing hardness and durability.

In time, carbon black and precipitated silica became firmly established as the primary reinforcing fillers in rubber, but minerals have maintained their utility as supplements and complements to these.

#### **FILLER PROPERTIES**

The characteristics that determine the properties a mineral filler will impart to a rubber compound are particle size, particle surface area, particle surface activity and particle shape.

## Particle Size

The general effect of a filler in rubber can be estimated according to particle size:

- Fully reinforcing fillers range from 0.01 to 0.1 micrometer
- Semi-reinforcing fillers range from 0.1 to 1 micrometer
- Diluent or extending fillers, those with minimal effect on compound properties, range from 1 to 10 micrometers.

When the size of the filler particle significantly exceeds the polymer interchain distance, it introduces an area of localized stress. This can contribute to elastomer chain rupture on flexing or stretching. Fillers with particle size greater than 10 micrometers are therefore generally avoided because they can reduce compound performance rather than extend or reinforce.

This relationship of filler size to compound properties is a reasonable guide, but the stated particle size of a mineral filler is not necessarily straightforward. Filler size is usually reported as median size. This means that half the particles are larger and half are smaller than the stated size. This does not, however, represent or imply its actual particle size distribution, as indicated in Figure 1. Both distributions in this illustration have the same median size, but the lower one may, for example, have particles large enough to compromise compound properties, while the upper one may have a more substantial fraction of particles in the semi-reinforcing and reinforcing ranges. In matching a filler's properties to its intended effect in a compound, knowledge of its particle size distribution is often more useful than reliance on median size.



Figure 1: Median Particle Size

This is somewhat complicated, however, by the fact that in most cases particle size is actually measured as equivalent spherical diameter rather than actual size or dimensions, since most automated particle sizing instrumentation will match the behavior of a particle to that of an idealized round particle of specific diameter. For round or block-shaped particles, such as natural calcium carbonate, there is no significant difference. For platy minerals, such as clay and talc the equivalent spherical diameter will inaccurately represent actual particle dimensions, as illustrated in Figure 2. This makes true particle size matching difficult for two dissimilarly shaped fillers in compounding studies.



## Particle Shape and Surface Area

For platy, needle-shaped and fibrous fillers, the particle aspect ratio is an additional essential consideration. As illustrated in Figure 3, for platy minerals

this is the ratio of the diameter of a circle with the same area as the face of the plate to the thickness of the plate. For needle- and fiber-shaped fillers, the aspect ratio is the ratio of length to diameter. Isometric fillers, those that are approximately round, cubic or blocky in shape, are considered low aspect ratio. Low, in this context, means less than about 5:1 aspect ratio. Platy, needle-shaped and fibrous fillers are considered high aspect ratio.



Figure 3: Filler Particle Aspect Ratio

A filler must make intimate contact with the rubber matrix if it is going to contribute to the rubber-filler composite. Fillers that have a high surface area have more contact area available with which to interact with the elastomer chains. For a given weight of filler, surface area is increased simply by reducing particle size, as illustrated in Figure 4.



Figure 4: Particle Size vs. Surface Area

The shape of the particle is also a factor. For example, particles with a planar shape have more surface available for contact with the rubber matrix than isometric particles with an equivalent particle diameter. Among the calcium carbonates, for example, only the finest precipitated grades expose a surface area equivalent to the surface area of hard clay, as seen in Table 1.

Mineral	Median Size, µm	Surface Area, m²/g
Ground Calcium Carbonate	1-5	2-4
Precipitated Calcium Carbonate	0.7-1.0	8-10
Ultra-Fine Precipitated Calcium Carbonate	0.07-0.09	19-28
Soft Clay	1.2-2.0	15-20
Hard Clay	0.2-0.5	20-26

Table 1:	Particle	Shape vs	s. Surface	Area
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#### Matrix Compatibility and Matrix Adhesion

Intimate contact between the matrix and mineral particles is essential, since air gaps represent points of permeability and zero strength. The surface chemistry of the filler will determine affinity for the matrix, or the ability of the rubber matrix to "wet" the filler surface. In very general terms, nonpolar fillers are suited to nonpolar elastomers and polar fillers to polar elastomers. Although the hydrophilic surfaces of clays and silicas can react as acids and are capable of forming hydrogen bonds, the compatibility and activity of most mineral fillers is improved with suitable surface treatments.

The conventional surface treatment for calcium carbonate is stearic acid, which creates a hydrophobic surface to improve matrix compatibility, but does not provide for filler-matrix adhesion. Maleated polybutadiene (polybutadiene with grafted maleic anhydride functional groups) has been used as an *in situ* coupling agent to improve matrix adhesion to calcium carbonate fillers. Precipitated calcium carbonate is also available pre-treated with maleated polybutadiene. With either sulfur or peroxide cure, crosslinking occurs between the polybutadiene chain and the rubber matrix, significantly improving tensile and tear properties.

The surface hydroxyls on silica and silicate mineral fillers allow for particle treatment with hydrophobizing and/or coupling grades of organosilanes. The general chemical structure of organosilanes is RSiX₃, where X is a hydrolysable group, such as methoxy or ethoxy, and R is a nonhydrolysable organofunctional group. The organo group may be reactive toward the rubber matrix, or it may be unreactive and serve solely as a hydrophobe or wetting agent.

Modification with organosilane depends on the ability to form a bond with silanol groups, -Si-OH, and/or aluminol groups (-AI-OH) on the filler surface. As illustrated in Figure 5 for silicate surfaces, the hydrolysis of an alkoxysilane forms silanetriol and alcohol. The silanetriol slowly condenses to form oligomers and siloxane polymers. The -Si-OH groups of the hydrolyzed silane initially hydrogen bond with -OH groups on the filler surface. As the reaction proceeds, water is lost and a covalent bond is formed. The reaction of hydrolyzed silane with filler surface -OH will ultimately result in the condensation of siloxane polymer, encapsulating the filler particle if sufficient silane is used. Once the filler is reacted with the silane it exposes an organophilic or organofunctional surface for interaction with the rubber matrix. When the organol group is non-reactive, it aids in the wetting by the matrix and dispersion in the matrix. If this group is functional, the bonding of filler and matrix promotes increased modulus and tensile strength, and improved tear and abrasion resistance.



Figure 5: Silane Reaction With Filler Surface

Sulfur-functional silanes are usually used in sulfur-cured rubber compounds, in particular those with mercapto, polysulfide and thiocyanate active groups. The silanes typically used in non-sulfur-cured compounds have amino or epoxy functionality. The structures of these silanes are shown in Figure 6.

#### Silanes for Sulfur Cure: Eto oCH₃ CH₃o-Si-(CH₂)₂-SH Eto -Si-(CH₂)₃-SCN oCH₃ Mercapto Eto Thiocyanate Eto oEt Eto-Si-(CH₂)₃-S_n-(CH₂)₃-Si-oEt Eto Polysulfide oEt n = 2 or 4Silanes for Non-Sulfur Cure: Eto oCH 3 Eto - Si-(CH₂)₃-NH₂ CH30 -Si-(CH2)3-0-CH2 όCH₃ Eto Amino Epoxy

Figure 6: Silane Treatments for Rubber Fillers

## MINERAL FILLER EFFECTS

The principal characteristics of mineral fillers: particle size, shape, surface area and matrix compatibility/adhesion, are interdependent in modifying rubber properties. In considering fillers of adequately small size to provide some level of reinforcement, the general influence of each of the other three filler characteristics on rubber properties can be generalized as follows:

- Increasing surface area (decreasing particle size): higher Mooney viscosity, greater tensile strength, greater abrasion resistance, greater tear resistance, greater hysteresis, and lower resilience.
- Increasing aspect ratio: higher Mooney viscosity, higher modulus, greater hysteresis, lower resilience, less extrusion shrinkage, and longer incorporation time.
- Increasing matrix adhesion: greater abrasion resistance, greater chemical adsorption or reaction, higher modulus, and greater hysteresis (except for silane-treated fillers).

**Tensile Properties** - The presence of filler in a vulcanizate tends to increase modulus by providing resistance to elongation. A filler with no matrix adhesion simply creates viscous drag as the matrix stretches and slides across its surfaces. Higher surface area, greater aspect ratio, and higher loading (the latter two effectively increasing the surface area exposed to the elastomer) increase drag and raise the modulus. Resistance to elongation is maximized in relation to filler-matrix adhesion. Mineral fillers with good matrix adhesion, as from organo-functional silane treatment, therefore generally provide the greatest effect on modulus and on tensile strength because the coupling bonds between the filler and matrix must be broken.

**Impact and Flexural Strength** testing have in common test specimens that are subjected to compression on one side and tension on the other. Very fine high aspect ratio particles and strong filler-matrix adhesion resist the movement of elastomer chains under compression, as under tension. High aspect ratio fillers are particularly resistant to compression because this force is exerted perpendicular to the filler's rigid planar or elongate dimension, as pictured in Figure 7. Similar filler-matrix dynamics apply to the resistance to compression that is manifest as compound hardness.

**Tear Strength and Flex Resistance** are both a measure of resistance to the propagation of a crack or slit under tension. Large or poorly bound filler particles will act as flaws and initiate or propagate cracks. Very fine, high aspect ratio and matrix-adhering filler particles act as barriers to the propagation of microcracks, as illustrated in Figure 8, in addition to providing the higher tensile strength required to resist failure.


Figure 7: Compression/Tension vs. Filler Size and Shape



Figure 8: Tear Resistance vs. Filler Size, Shape and Adhesion

**Abrasion Resistance** – Filler particles are considerably harder than the matrix and can thus insulate the rubber against wear. Large and poorly bound filler particles are most easily dislodged by abrasion. This subjects to wear the relatively soft surrounding matrix, especially the edge of the depression left by the dislodged particle. Small size, high surface area and good matrix adhesion resist dislodging of filler particles.

**Resilience and Hysteresis** – Resilience is the ratio of energy released on recovery to the energy impressed on deformation. Essentially, it is a measure of rubber elasticity – the ability to quickly return to the original shape following deformation. Unfilled elastomers are at their peak resilience because there is no obstacle to elastomer chain extension and contraction. The introduction of a filler creates such an obstacle in proportion to the strength of the particle-matrix interaction. A compound's resilience is therefore generally in inverse proportion to filler loading and filler-matrix adhesion.

Hysteresis is the amount of impressed energy on deformation that is converted to heat instead of to mechanical energy as elastic rebound. In unfilled rubber the conversion to heat energy is related to the friction of elastomer chains sliding past each other. Fillers tend to increase hysteresis due to polymer-filler friction and the dislodging of polymer segments from filler surfaces. Reinforcing fillers, which adhere more strongly to the elastomer chains, usually provide the greatest increase in hysteresis, with the notable exception of silane-treated kaolin.

#### THE MINERAL FILLERS

The common mineral fillers for rubber are kaolin clay, calcium carbonate, talc, barite, and diatomite. Of these, the most widely used, by volume and by functionality, are kaolin clay and calcium carbonate.

## **Kaolin Clay**

Kaolin clay is a platy aluminosilicate. Its continuous sheet structure produces thin particles which exist in nature as overlapping flakes.

**Kaolin grades** – Rubber filler clays are classified as either "hard" or "soft" in relation to their particle size and stiffening affect in rubber. Hard clay has a median particle size of approximately 0.25 to 0.50 micrometers. It provides stiff uncured compounds and will impart high modulus, high tensile strength, stiffness, and good abrasion resistance to cured rubber compounds. Soft clay has a median particle size of approximately 1.0 to 2.0 micrometers. It provides softer uncured compounds and does not improve the properties of cured compounds to the same extent as hard clay. Soft clay is used where high loadings, for economy, and faster extrusion rates are more important than strength.

Most of the kaolin used as a rubber filler is airfloat clay. This is dry-ground kaolin that has been air-separated to minimize impurities, such as quartz, mica and bentonite, and to control the particle size distribution. About 80% of the kaolin used in the rubber industry is airfloat hard clay. The comparison in Table 2 of hard clay, soft clay and fine-ground calcium carbonate graphically illustrates the affects of particle size, surface area and shape on reinforcement of an SBR compound.

Hard Clay Soft Clay FGCC							
Median particle size, µm	0.3	1.3	3.0				
BET surface area, m ² /g	23	16	3				
Original Physical Properties							
Hardness, Shore A	61	62	53				
300% Modulus, MPa	3.2	2.8	1.2				
Tensile, MPa	12.8	8.8	1.6				
Die A Tear, kN/m 24.6 20.2 5.3							
SBR 1006 (100), filler (100), VANFRE® AP2 (2), ZnO (5); Stearic Acid (2), AGERITE® STALITE® S (1.5), Sulfur (2), METHYL CUMATE® (0.1), ALTAX® (1.5)							

Table 2: Reinforcement vs. Size, Shape and Surface Area

More hard clay (DIXIE CLAY[®] and PAR[®] CLAY) than soft clay (LANGFORD[™] CLAY and McNAMEE[®] CLAY) is used in rubber because of its semi-reinforcing effect and its utility as a low cost complement to other fillers. It is used, for example, to improve the tensile and modulus of ground calcium carbonate compounds. It also serves as a cost lowering partial replacement for carbon black or precipitated silica without sacrificing physical properties, as seen in the equal volumes studies in Table 3 and Table 4 respectively.

Ingredients	phr	phr	phr			
N990 Carbon Black	100.0	_	_			
Hard Clay	_	130.0	104.0			
N650 Carbon Black	_	—	20			
Original Physical Properties						
Hardness, Shore A	70	70	78			
300% Modulus, MPa	5.3	1.9	7.0			
Tensile, MPa	10.0	14.2	18.6			
Die C Tear, kN/m	14	16	18			
Abrasion Index	23	27	27			
SBR 1502 (100), ZnO (5), Stearic Ac Sulfur (3), TEA (3 in clay compound o	id (1), METHYL TUA only)	ADS [®] (0.1), ALTA	X (1.5),			

# Table 3: Hard Clay as Carbon Black Complement

Table 4: Hard Clay as Precipitated Silica Complex
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Ingredients	phr	phr		
Silica, 150 m²/g	45	30		
Hard Clay	—	23		
Original Physical Properties				
Hardness, Shore A	66	65		
300% Modulus, MPa	3.6	3.1		
Tensile, MPa	20.5	20.9		
Trouser Tear, kN/m	27	25		
Abrasion Index	68	67		
SBR 1502 (100), DEG (3), Stearic Acid (1), Zn Carbonate (1), Sulfur (2), ALTAX (0.7), CAPTAX [®] (0.4), UNADS [®] (0.3), VANOX [®] DPG (0.1)				

In addition to the designation hard and soft airfloat clays, kaolin clays are further classified according to how they are processed.

*Water-washed clay* is slurried in water and centrifuged or hydrocycloned to remove impurities and produce specific particle size fractions. To improve brightness, these clays are often chemically bleached and/or subjected to high intensity magnetic separation to remove dark impurities.

Delaminated clay is made by attrition milling the coarse clay fraction from water washing. This separates the overlapping kaolin particles into thin, wide individual plates. Delaminated clay is the most planar form of kaolin clay available and is preferred when high stiffness and low die swell are needed, as shown in the comparison of delaminated clay to hard clay in Table 5.

	<b>Delaminated Clay</b>	Hard Clay			
Original Physical Properties					
Hardness, Shore A	74	70			
300% Modulus, MPa	16.5	15.2			
Tensile, MPa	21.2	20.7			
Olsen Stiffness	27	17			
Die Swell	100	150			
NR Smoked Sheet (100), Clay (156), ZnO (5), Stearic Acid (4), Cumar [®] MH 2½ (7.5), Sulfur (3), CAPTAX (1)					

### Table 5: Delaminated Clay, Improved Stiffness and Die Swell

Calcined clay for filler uses is made by heating water-washed clay to partially remove surface hydroxyl groups. This provides a corresponding decrease in surface activity, and thus reinforcement, but calcined clay is commonly used in wire and cable insulation and jackets because it provides excellent dielectric and water resistance properties.

Kaolin surface activity – Kaolin's surface silica  $(SiO_2)$  groups readily hydrolyze to silanols (-SiOH) in the presence of moisture and can react as acids (-SiO-H+). This might be considered an advantage for a rubber filler, but it can cause problems with other compounding ingredients. Most of the accelerators used in sulfur cure systems contain an amine group. Strong adsorption or reaction with kaolin silanols will decrease the amount of accelerator available for vulcanization reactions. This results in slower cure rates and a reduced state of cure. Similar effects can result from the reaction of soluble zinc ions with kaolin. The adsorption or reaction of accelerators by hard clay usually requires about a 15-25% increase in acceleration. These negative effects on the cure system can be reduced or completely avoided, however, by adding other chemicals that will preferentially associate with the silanol groups and reduce their activity. As illustrated in Figure 9, triethanolamine (TEA), diethylene glycol (DEG) and high molecular weight polyethylene glycol (PEG) typically serve this function. These are mixed into the compound prior to the addition of the accelerators.



Figure 9: Protecting Accelerators from Kaolin Reactivity

Reactivity with accelerators is effectively avoided, and reactivity with the rubber matrix is optimized, by treatment of kaolin clay with organofunctional silanes. The combination of platy shape and chemical reactivity enable the silane-treated kaolins to impart a unique blend of properties to elastomers. These include high modulus, low hysteresis, good abrasion resistance, low viscosity, low set, and resistance to heat and oxidative aging. The unusual combination of high modulus and low hysteresis, in particular, allows silane-treated kaolins to be used alone or as a partial carbon black replacement in products requiring good dynamic properties, such as transmission and V-belts, and non-tread tire components.

Table 6 demonstrates the significant improvement in hard clay reinforcement provided by mercaptosilane treatment.

Clay Pretreatment None Mercaptosilane							
Original Physical Properties							
Hardness, Shore A	60	65					
M300, MPa	5.3	12.2					
Tensile, MPa	21.2	22.3					
Die C Tear, ppi	155	235					
<i>Compression Set B</i> 29.6 14.0							
Polyisoprene (100), DIXIE CLAY (75), ZnO (5), Stearic Acid (2), AGERITE STALITE S (1), VANOX ZMTI (1), Sulfur (2.75), AMAX [®] (1.25), METHYL TUADS (0.2)							

Table 6: Reinforcement From Mercaptosilane-Treated Hard Clay

## **Calcium Carbonate**

Calcium carbonates for rubber fall into two general classifications: ground natural calcium carbonate (limestone) and precipitated calcium carbonate. Ground natural carbonates (GCC) are further characterized as dry-ground products and wet-ground products. Of the wet-ground products, fine ground (FG) calcium carbonates range from about 3 to 12 micrometers in median size, with a 44 micrometer top size. Ultrafine ground (UFG) grades range from about 0.7 to 2 micrometers in median size, with a 10 micrometer top size.

GCC products are characterized by their low aspect ratio, low surface area and low surface activity. Matrix compatibility can be improved with stearate treatment, but matrix adhesion is generally poor, as are tear and abrasion resistance with these fillers. They are widely used, nevertheless, because of their low cost, and because the properties that make them poorly suitable for reinforcement allow them to be used at very high loadings with little loss of compound softness, elongation or resilience. Dry-ground limestone is probably the least expensive compounding material available, and more can be loaded into rubber than any other filler. Wet-ground carbonate is somewhat more expensive, but offers better uniformity and finer particle size.

Precipitated calcium carbonate (PCC) is produced for applications requiring any combination of higher brightness, smaller particle size, greater surface area, lower abrasivity, and higher purity than is generally available from ground natural products. Fine PCC has typically a 0.7 micrometer median size, while ultrafine PCC has typically a 0.07 micrometer median. The shape of PCC crystals can be manipulated according to end use requirements; precipitated calcite, with isometric prismatic particles, is the form generally used in rubber compounding. As previously noted, PCC products are available with stearate surface treatments for better matrix compatibility and maleated polybutadiene treatment for matrix adhesion and compound reinforcement.

Table 7 compares PCC products to a fine-ground natural calcium carbonate. Tensile strength, tear strength, and modulus are all a function of particle size, while hardness is nearly unaffected.

	<u>GCC</u>	PCC	UF-PCC
Avg. particle size, µm	3.0	0.7	0.07
BET surface area, m ² /g	4	8	19
Loading, phr	175	175	150
Original Physical Properties			
Hardness, Shore A	70	75	70
M300, MPa	1.7	2.9	3.8
Tensile, MPa	4.5	7.2	13.0
Crescent Tear, ppi	45	125	200
SBR 1502 (100), ZnO (5), Stearic Aci	d (1), Cumar MH 1½	⁄₂ (15), Sulfur (2	2.75), METHYL
TUADS (0.35), ALTAX (1.5)			

|--|

## **OTHER MINERAL FILLERS**

Talc, barite and diatomite are also used as fillers in rubber, although at relatively small volumes. They are used where there characteristic physical properties provide more or less unique functionality.

**Talc** - Talc products are alkaline platy magnesium silicates processed using various combinations of dry grinding, air separation and flotation depending upon the quality of the crude ore and the properties required for intended applications. Talc is characteristically soft, white, alkaline and high in plate aspect ratio. It is unique among mineral fillers in that it is naturally hydrophobic. Most talc products are too coarse for use as reinforcing fillers, but the relatively large plates are used to advantage, nonetheless. Talc is used in extruded rubber because the plates orient and provide smooth surfaces at high extrusion rates. Talc is also included in filler systems to reduce moisture and gas permeability, as

in hoses and innerliners. Micronized talc products with all particles finer than 10 micrometers are useful for reinforcement, but they compete with kaolin products that are typically less expensive.

**Barite** – Barite is natural barium sulfate; the highest quality filler grades are made by flotation, followed by wet grinding, bleaching with sulfuric acid, washing, drying, and milling. Barite has a high specific gravity (4.5), so it is used in compounds where weight is required, It is also chemically inert and therefore used in acid resistant compounds. Barite has no significant effect on compound cure, hardness and stiffness. *Blanc fixe* is precipitated barium sulfate for uses where higher brightness and purity and finer particle size is required. *Blanc fixe* is available in adequately small particle size to be semi-reinforcing, providing equivalent compound resilience and softness but better tensile strength and tear resistance.

**Diatomite** – Diatomite is the microscopic skeletons of diatoms, unicellular algae found in fresh and sea water. These silica skeletons are naturally fine in particle size, chemically inert and have a lace-like structure that accounts for the high porosity, high surface area and low bulk density of diatomite fillers. Diatomite's absorptive capacity finds use as a process aid in high-oil compounds. It is also used as a semi-reinforcing filler, imparting hardness, stiffness and low die swell, but its absorbtive capacity for accelerators can affect cure.



#### COMPOUND DESIGN

#### by Jennifer Forgue

#### R.T. Vanderbilt Company, Inc.

This chapter is intended to serve as a guide in formulating elastomeric compounds for a wide range of applications. The purpose of formulating a rubber recipe or compound, typically known as "compounding", is to achieve specific physical properties. This is accomplished by combining inherent elastomer properties with particular chemical additives as needed for each application. Compound requirements may be specified by the customer or determined by final consumer needs. With many types of elastomeric polymers available, and a large selection of additives for every polymer class, there is an almost infinite number of compound ingredient combinations.

The challenge in compounding is to obtain the desired physical properties with acceptable processing characteristics, while keeping overall material and manufacturing costs as low as possible. Tantamount to this is the importance of quality to a successful operation. Building upon past compounding experiences can help realize future improvements.

This chapter's "Figures" and "Tables" should be used as a reference in understanding how various changes to compound ingredients affect compound processing and physical properties, as well as how test result data trends can provide knowledge of how other compounds may be optimized. The comparative properties of elastomers are outlined in Figure 1 and Table 1. In the instances where a wide range is indicated for a particular property, careful selection of compounding ingredients is required to obtain the exact value desired.



Figure 1: Performance by Heat and Oil Resistance ASTM / IISRP / ISO Designation

Polymers	NR, IR	SBR	EPM, EPDM	CR	IIR	BIIR, CIIR	NBR	CSM
ASTM Classifications								
D 2000 Density, Mg/m ³ Hardness, Shore A	AA 0.93 20-90	AA 0.94 40-90	DA 0.86 40-90	BC 1.23 20-95	AA 0.92 40-75	BA 0.92 40-75	BF 1.00 20-95	CE 1.10 45-95
Typical Tensile Streng	ıth							
Pure Gum, MPa Reinforced, MPa	21 21	7 14	3 21	21 21	10 14	10 14	7 14	14 19
<i>Resilience</i> Room Temperature Hot	E E	G G	VG VG	VG VG	L VG	L G	G G	G G
Resistance to Tear Abrasion Compression Set Weathering Oxidation Ozone	E E G E G P	F G G V G P	G G G VG E E E	G E F-G E VG VG	G G F VG E G	G F-G VG VG VG	F G G F-G G P	F E F E E O
<i>Temperature Range</i> High Temperature Low Temperature	G E	G G	E E	G G	G G	VG F	VG G	VG F
Aqueous Fluid Resistance								
Dilute Acid Concentrated Acid Water	E F-G VG	F-G F-G VG	E G E	VG G G	E E VG	E G VG	G G F-G	E E G
Organic Fluid Resista	nce							
Aliphatic Oxygenated Chlorinated Aromatic Fuels Fats and Oils	P F P P P-G	P F P P P-G	P G P P G	G P-F F G G	P G P P VG	P G P P VG	E P-F G E	G P-F F-G E G
Permeability	F	F	P-F	L	VL	VL	L	L
Flame Resistance	Р	Р	Р	G	Р	Р	Р	F-G
Dielectric Properties	E	G	E	VG	G-E	VG	Р	E

Table 1: Comparative Properties of Rubbers

O = Outstanding, E = Excellent, VG = Very Good, G = Good, F = Fair, P = Poor, L = Low, VL = Very Low

	ECO,			AU,				
Polymers	Со	СМ	ACM	EU	т	MQ	FKM	FVMQ
ASTM Classifications								
D 2000	CH	BC	DH	BG	AK	FE	ΗK	FK
Density Ma/m ³	1.27-	1.16-	1 00	1 02	1 20	1.10-	1 85	1 4 7
Hardness, Shore A	40-90	40-95	40-90	60-95+	20-80	10-85	60-95	40-70
Typical Tensile Streng	th							
Pure Gum, MPa		10	3	42	1	1	14	
Reinforced, MPa	14	14	12	42	9	8	14	10
Resilience								
Room Temperature	P-F	F	L	L-G	F	VG	L	G
Hot	P-F	F	VG	G	F-G	VG	VG	VG
Resistance to								
Tear	F	G	Р	0	Р	Р	F	Р
Abrasion	G	VG	F	0	P-F	P	G	P
Compression Set		VG	G			VG	VG	VG
Ovidation	E	E	E	E	E	E	E	E
Oxidation	VG	E	G	G	E		0	E
	- 00	L	0	L	L	L	0	L
Temperature Range	-	NO	-	0	ГO	0	0	0
High Temperature	E	VG	E	BC	F-G	0	D D C	0
	1-0	0	Г	1-0	L	0	1-0	0
Aqueous Fluid Resista	ance	1/0	-		0	-	_	-
Dilute Acid	G	VG		Р	G		E	E
Wotor	F	VG	г D	P	P E	F C	E VC	VC
	0	0	Г	г 		0		vG
Organic Fluid Resistai	nce	-	_	_	_	-	_	_
Aliphatic	G	G	E	E	E	Р	E	E
Oxygenated		Р	Р	P-F			P	P
Aromotio	P-F	P F	P F	P-F	P-F	P-F	E	G
Fuelo	G	Г С	Г С	г-G	VG E			
Fats and Oils	F	G	VG	F	G	F	F	F
Permeability						F		 F
Elame Resistance	 P_F	 G	 P	 F	 P	F	 G	G
Dielectric Properties	G	 G			F-G	 	G	 G
Disidentie Fropenties	9	9			1-0	L	9	9

Table 1: Comparative Properties of Rubbers (continued)

O = Outstanding, E = Excellent, VG = Very Good, G = Good, F = Fair, P = Poor, L = Low, VL = Very Low

# NATURAL RUBBER (NR)

### Natural Rubber Base

A practical base or "pure gum" compound of natural rubber contains the following essential parts:

Ingredients	Gum Compound	phr
1. Elastomer	SMR-5	100.00
2. Processing Aid	VANFRE® AP-2	2.00
3. Activators		
Fatty Acid	Stearic Acid	2.00
Metal Oxide	Zinc Oxide	5.00
4. Antioxidant	AGERITE [®] STALITE [®] S	1.00
5. Accelerators of Vulcanization		
Primary	ALTAX [®] (MBTS)	1.00
Secondary	METHYL TUADS®	0.10
6. Vulcanizing Agent	Sulfur	2.75
	Total	113.85

Pure gum vulcanizates of natural rubber develop good physical properties, and are used as such in commercial applications where low modulus, light weight translucent products are desired.

r nysicar r topenies							
Cures @ 153°C (min.)	500% Modulus, MPa	Tensile, MPa	Elongation, %	Hardness, Shore A			
5	1.3	25.5	780	38			
10	1.4	23.8	750	39			
15	1.4	22.6	750	38			

# Physical Properties

It is generally accepted practice to include stearic acid or a metal stearate in all natural rubber base compounds, since a deficiency of fatty acid in the nonhydrocarbon constituents is known to cause a slow rate of cure.

Antioxidant selection is based on anticipated service requirements.

Accelerator content and type varies with curing, color and aging requirements of the final product.

Sulfur may be varied between 0 and 3 or more parts, with lower sulfur contents allowing for better aging. Maximum heat resistance is obtained by compounding with sulfur bearing accelerators such as METHYL TUADS, METHYL SELENAC[®] or SULFADS[®], alone or in combinations as vulcanizing agents.

## Fillers in Natural Rubber

Most of the rubber fillers used today offer some functional benefit that contributes to the processability or utility of the rubber product. The properties imparted by the filler are determined by the following filler particle characteristics: size, surface area, surface activity and shape. Functional fillers transfer applied stress from the rubber matrix to the strong and stiff filler.

Fillers with particle size greater than 10,000 nm are generally avoided because they can reduce performance rather than extend or reinforce. Fillers with particle sizes between 1,000 and 10,000 nm are used primarily as diluents and usually have no significant effect, positive or negative, on rubber properties. Semi-reinforcing fillers range from 100 to 1,000 nm. The truly reinforcing fillers, which range from 10 nm to 100 nm can significantly improve rubber properties.



Figure 2: Filler Sizes and Their Reinforcing Effects

As noted in the MINERAL FILLERS FOR RUBBER chapter,

"The principal characteristics of rubber fillers: particle size, shape, surface area and matrix compatibility/adhesion, are interdependent in improving rubber properties. In considering fillers of adequately small particle size to provide some level of reinforcement, the general influence of the other filler characteristics on rubber properties can be generalized as follows:

- Increasing surface area (decreasing particle size): higher Mooney viscosity, greater tensile strength, greater abrasion resistance, greater tear resistance, greater hysteresis, and lower resilience.
- Increasing aspect ratio: higher Mooney viscosity, higher modulus, greater hysteresis, lower resilience and extrusion shrinkage, and longer incorporation time.
- Increasing matrix adhesion: greater abrasion resistance, greater chemical adsorption or reaction, higher modulus, and greater hysteresis (except for silane –treated fillers)."

The following two studies show the loading level effects of various carbon black (Table 2) and mineral fillers (Table 3).

	300% Mod., MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML	
MT N990	Carbon Black							
25 phr	2.8	22.1	660	43	28.2	13	14/11	
50 "	4.4	21.4	620	49	45.8	15	11/13	
75 "	6.3	18.8	600	55	42.2	14	9/17	
100 "	8.5	15.3	530	60	44.9	15	9/17	
125 "	10.3	11.6	430	67	35.2	15	7/18	
SRF N77	0 Carbon Black	(						
25 phr	4.2	24.7	660	48	45.8	15	12/14	
50"	8.9	22.8	560	58	58.1	16	10/19	
75"	13.9	20.7	460	66	66.0	18	8/31	
100 "	17.0	18.8	350	74	26.4	16	7/18	
GPF N66	0 Carbon Black	ſ						
25 phr	4.6	25.0	630	48	59.9	11	12/16	
50"	9.3	23.2	540	57	66.0	15	10/27	
75"	15.0	25.1	440	68	52.8	16	8/36	
100 "		18.4	280	76	22.9	15	6/48	
FEF N55	0 Carbon Black	•						
25 phr	5.6	26.0	650	51	66.0	11	10/23	
50 "	11.8	24.8	530	62	77.4	12	7/30	
75"	18.1	22.2	400	72	38.7	12	6/39	
100 "		18.6	260	78	24.6	15	5/60	
HAF N33	0 Carbon Black	(						
25 phr	5.1	27.6	640	51	92.4	12	10/22	
50 "	11.9	28.5	570	64	101.2	15	8/39	
75"	21.2	24.7	400	74	73.9	16	6/62	
ISAF N22	0 Carbon Blac	k						
25 phr	5.0	27.6	730	52	72.2	14	11/22	
50"	11.0	28.2	560	65	116.2	18	9/38	
75"	20.3	23.0	360	74	58.1	19	7/78	
Base Co	mpound	Ingredier	nts			phr		
		SMR-5				100.00		
		VANPLAS [®]	T® R			2.00		
		Stearic Aci	id			2.00		
		Zinc Oxide	;		5.00			
		AGERITE	STALITE S	5	2.00			
		ALTAX (MI	BTS)			1.00		
METHYL TUADS 0.10								
Sulfur 2.75								
		Total				114.85		
Mooney r	neasured @ 13	32°C						
All compo	ounds cured 10	min. @ 153	°C					
Tear mea	sured on Die A	samples		-				
Compress	sion set measu	red after 22	hrs. @ 70°	C				

Table 2: Carbon Black Loading in Natural Rubber

	300% Mod., MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
Calcium C	arbonate (grou	ınd)					
50 phr	2.1	17.8	700	44	10.6	17	17/12
75 [.] "	2.3	16.6	680	47	14.0	18	17/13
100 "	2.6	14.4	640	51	13.2	19	16/17
150 "	2.5	10.8	620	56	13.2	22	13/20
DIXIE CLA	<i>\Y</i> ®						
50 phr	5.0	21.9	660	45	14.0	37	25/16
75 [.] "	6.8	19.1	570	48	14.0	45	24/21
100 "	9.1	20.0	530	53	15.8	49	18/28
150 "	11.7	16.0	400	62	19.4	52	9/34
DIXIE CLA	AY/Calcium Ca	rbonate (gro	und) 50/50	)			
50 phr	3.0	18.8	660	45	15.8	22	21/15
75 '"	3.9	17.4	620	49	22.0	25	22/15
100 "	4.3	15.7	560	51	13.2	29	21/15
150 "	5.4	13.1	520	56	33.4	38	16/23
Hi-Sil® 233	3						
25 phr	1.9	20.8	760	40	35.2	27	16/20
50 [.] "	1.9	20.0	790	50	81.8	34	15/26
75"	3.1	17.8	680	65	40.5	44	15/78
McNAME	® CLAY						
50 phr	4.2	20.4	660	46	13.2	15	15/15
75 "	5.7	20.2	610	50	13.2	32	21/21
100 "	7 1	17.8	550	52	17.6	36	20/22
150 "	8.8	14.6	450	58	17.6	43	17/25
Silene® 73	2D						
25 phr	2.1	18.1	700	41	31.7	26	7/14
50 "	2.8	18.3	680	48	47.5	34	6/17
75 "	4.0	16.6	650	52	38.7	38	6/25
Base Cor	mound	Ingredien	ts			phr	
2000 001		SMD 5			1	00.00	
		JIVIR-J	D			2 00	
		VAINFLAST	1			2.00	
		Steand Acid	1			2.00	
						5.00	
		AGERITE		•		2.00	
			15)			1.00	
		Sulfur	UADS			2.75	
		Total			1	14.85	
Mooneym	assured @ 12	2°C			I	14.00	
All compoi	unds cured 10	∠ ⊂ min. @ 153°	°C				
Tear meas	ured on Die A	samples	-				
0	ion sot moasu	od after 22 k	nrs @ 70°	C			

Table 3: Mineral Filler Loading in Natural Rubber

#### Processing Aids in Natural Rubber

Heavily loaded and highly accelerated stocks require additives to promote easy and fast mixing and to inhibit scorch in stock preparation. VANPLAST R and VANPLAST PL are effective liquid processing aids. LEEGEN[®] is a solid which functions in a comparable manner to VANPLAST R and is preferred in open roll mixing operations. VANFRE AP-2 is a solid processing aid that is of proven value in both natural and synthetic elastomers.

The comparison in Table 4 demonstrates how these materials improve viscosity and flow characteristics without adverse changes in optimum physical properties of the rubber compound.

		VANPLAST	VANPLAST	VANFRE
Ingredients (phr)	Control	PL	R	AP-2
SMR-5	100.00	100.00	100.00	100.00
Stearic Acid	2.00	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00	5.00
AGERITE SUPERFLEX [®] SOLID G	1.50	1.50	1.50	1.50
N990 Carbon Black	25.00	25.00	25.00	25.00
N550 Carbon Black	35.00	35.00	35.00	35.00
ALTAX (MBTS)	1.00	1.00	1.00	1.00
METHYL LEDATE®	0.25	0.25	0.25	0.25
Sulfur	2.50	2.50	2.50	2.50
VANPLAST PL		5.00		
VANPLAST R			5.00	
VANFRE AP-2				2.50
Totals	172.25	177.25	177.25	174.75
Mooney Viscosity, ML 1+4 (100°C)	37.5	32.0	32.0	32.5
Mooney Scorch @ 121°C				
Minimum Viscosity	27	26	26	26
Minutes to 5 pt. rise	12.5	13.5	13.5	12.5
Original Physicals, Press Cured 5 m	n. @ 153°	C		
Hardness, Shore A	62	58	60	62
300% Modulus, MPa	13.9	11.5	11.4	12.9
Tensile, MPa	25.3	25.2	24.3	23.8
Elongation, %	550	570	560	540
DuPont Spider Mold, 6.4 mm Orifice,	20 Tons F	Pressure, 30.0	g Charge	
Press Cured 5 min. @ 153°C				
Weight, g	17.0	17.8	18.0	18.1

#### Table 4: Process Aid Comparison in Natural Rubber

## Accelerators in Natural Rubber

In combination with vulcanizing agents, accelerators reduce vulcanization time (cure time) by increasing the rate of vulcanization. In most cases, the physical properties of the products are also improved.



The various classes of accelerators are compared in Figure 3.

Figure 3: Cure Curve Comparison of Accelerator Classes

The guanidines and thiazoles type accelerators provide a slow rate of cure that is useful in thick cross-section parts. With these accelerators, the interior of the part can come up to cure temperature without the surface becoming overcured.

Sulfenamides type accelerators exhibit a prolonged period of flow before crosslinking begins. The exact amount of delayed action depends on the specific amine. In general, the delay before crosslinking increases in this order: cyclohexylamine > tertiary butylamine > morpholine.

The thiurams and dithiocarbamates type accelerators provide the fastest rate of crosslinking. These products are known as "ultra accelerators".

Accelerators play an important role in the vulcanization of rubber and they affect the scorch safety, the rate of cure and the length and number of the crosslinks which form. The different types of accelerators and the effect of the levels used are shown in Tables 5 thru 8 on the following pages:

	M300 MPa	Tensile, MPa	Elong., %	Duro, Shore A	Comp. Set, %	Rheo., t _s 2/t' 90	Mooney, t5/ML
Cured 15 min. @	153°C						
ALTAX (MBTS)	6.1	19.5	580	50	26	2.3/14	11/15
CAPTAX [®] (MBT)	5.8	17.6	550	48	25	1.3/11	8/16
ZETAX [®] (ZMBT)	5.7	17.0	550	48	24	1.7/14	8/18
AMAX®	8.3	20.0	510	55	19	4.0/10	21/15
DURAX® (CBS)	9.1	19.2	490	56	18	4.0/8	17/14
MORFAX®	8.6	19.2	510	56	19	4.3/11	17/16
VANAX® NS	10.0	19.7	490	56	19	5.0/10	20/15
CURE-RITE [®] 18	8.8	18.6	490	56	19	4.3/10	17/15
Cured 5 min. @ 1	71°C						
ALTAX MBTS	5.5	16.3	550	49	38		
CAPTAX (MBT)	5.3	15.5	550	47	28		
ZETAX (ZMBT)	5.3	16.7	560	47	26		
AMAX	7.0	18.0	500	50	20		
DURAX (CBS)	7.9	19.4	530	57	20		
MORFAX	7.4	18.8	530	54	23		
VANAX NS	8.9	19.9	510	54	19		
CURE-RITE 18	7.5	18.6	510	54	19		
Base Compour	nd	Ingredie	nts			phr	
		SMR-5				100.0	
		VANFRE	AP-2			2.0	
		VANPLAS	STR			2.0	
		Stearic Ad	cid			2.0	
		Zinc Oxid	е			5.0	
		AGERITE	STALITE	S		2.0	
		N990 Car	bon Black			25.0	
		N550 Car	bon Black			25.0	
		Sulfur	Don Diaon			2.5	
		Accelerate	or (as abo	ve)		1.0	
		Total				166.5	
Mooney measure	ed @ 13	2°C					
Rheometer meas	sured @	153°C					
Compression set	Compression set measured after 22 hrs. @ 70°C						

 Table 5: Thiazoles and Sulfenamides in Carbon Black Filled NR

	M300 MPa	Tensile, MPa	Elong., %	Duro, Shore A	Comp. Set, %	Rheo., t _s 2/t' 90	Mooney, t5/ML
Cured 15 min. @	153°C						
ALTAX (MBTS)	3.9	11.0	530	51	51	3.6/12	19/7
CAPTAX (MBT)	3.9	7.9	460	52	42	0.9/9	6/10
ZETAX (ZMBT)	3.4	8.4	510	48	59	1.7/12	8/9
AMAX	4.5	11.1	510	56	46	4.3/12	23/9
DURAX (CBS)	4.8	14.9	530	60	45	3.8/7	17/9
MORFAX	5.0	11.7	530	57	48	3.6/9	17/8
VANAX NS	5.0	12.9	530	60	45	4.9/7	21/9
Cured 5 min. @ 1	71°C						
ALTAX MBTS	3.4	10.0	570	53	44	1.7/4	
CAPTAX (MBT)	3.4	8.8	550	52	46	0.8/4	
ZETAX (ZMBT)	2.8	8.2	560	50	49	1.2/5	
AMAX	3.7	12.6	570	55	45	1.8/4	
DURAX (CBS)	3.9	13.2	590	59	46	1.8/3	
MORFAX	3.5	13.0	600	57	45	2.2/4	
VANAX NS	4.1	14.5	500	59	44	1.9/3	
Base Compour	nd	Ingredie	nts			phr	
		SMR-5			100.00		
		VANPLAS	TR		2.00		
		Stearic Ac	id			2.00	
		Zinc Oxide	5			5.00	
		AGERITE	- SUPFRI ITI	=® SOLID		1 50	
			Y			50.00	
		Calcium C	Carbonate	(around)		50.00	
		Diethylene	Glycol	(9.00.00)		2 00	
		Sulfur	S Olycol			2.00	
		Accelerate	or (as abo	ve)		1.00	
		Total		,	2	216.25	
					-		
Mooney measure	ed @ 13	2°C					
Rheometer meas	sured @	153°C and	d @ 171°C	;			
Compression set measured after 22 hrs. @ 70°C							

Table 6: Thiazoles and Sulfenamides in Mineral Filled NR

	M300 MPa	Tensile, MPa	Elong., %	Duro, Shore A	Comp. Set, %	Rheo., t _s 2/t' 90	Mooney, t5/ML
Control	5.4	13.6	560	55	53	3.3/33	11/18
BISMATE®	15.9	21.4	420	71	19	0.5/4	6/21
ETHYL CADMATE®	13.8	19.7	450	68	20	1.0/5	5/21
AMYL LEDATE*	14.1	21.4	460	68	25	1.7/5	7/20
METHYL LEDATE	12.4	20.1	480	66	24	1.0/10	7/18
METHYL SELENAC	15.9	18.8	350	70	23	1.6/9	5/20
ETHYL TUADS®	14.5	19.5	370	69	20	2.0/6	7/19
METHYL TUADS	15.3	19.3	420	70	20	1.4/7	5/21
UNADS®	15.4	17.9	370	69	20	2.3/6	8/17
BUTYL ZIMATE®	13.3	19.4	450	67	25	1.9/6	7/19
ETHYL ZIMATE	14.2	18.8	420	68	23	1.5/6	6/19
METHYL ZIMATE	14.7	18.6	400	69	22	0.9/4	5/22
Base Compound	In	gredient	S			phr	
	SN	/IR-5				100.0	
	VA	NPLAST	R			2.0	
	VA	NFRE AP	2-2			2.0	
	St	earic Acid				2.0	
	Ziı	nc Oxide			5.0		
	AC	GERITE S	TALITE S		1.5		
	NS	990 Carbo	n Black			35.0	
	N	330 Carbo	n Black			30.0	
	Si	ilfur	Diation			25	
		TAX (MR)	IS)			0.5	
	111	tra Accele	rator (as a	above)		0.5	
* (1.0 for AMYL LEDATE)						0.0	
Total						181.0 *(	181.5)
Mooney measured @ 132°C Rheometer measured @ 143°C Compounds cured 15 min. @ 143°C Compression set measured after 22 hrs. @ 70°C							

Table 7: Ultras as Primary Accelerators in NR

	M300 MPa	Tensile, MPa	Elong., %	Duro, Shore A	Comp. Set, %	Rheo., t _s 2/t' 90	Mooney, t5/ML
Control	10.1	16.5	510	59	30	3.1/26	9/20
<b>BISMATE POWDER</b>	13.0	21.8	470	65	22	1.5/9	7/16
ETHYL CADMATE	12.8	12.8 21.9 480 65				2.3/11	8/14
AMYL LEDATE**	12.3	21.0	480	64	23	3.3/12	9/18
METHYL LEDATE	12.6	21.0	480	65	22	2.5/10	8/18
METHYL SELENAC	13.3	20.9	450	66	22	3.0/13	8/18
SULFADS	12.4	21.2	480	64	24	3.1/12	9/13
ETHYL TUADS	13.6	20.8	440	65	22	2.0/9	9/13
METHYL TUADS	13.2	19.0	420	65	21	2.1/12	8/14
UNADS POWDER	13.9	22.3	500	66	22	2.7/14	9/14
BUTYL ZIMATE	12.9	21.9	490	65	25	2.7/15	10/14
ETHYL ZIMATE	13.7	22.3	480	65	22	2.7/12	9/13
METHYL ZIMATE	13.8	22.3	480	66	24	2.7/10	9/14
Base Compound	In	gredient	S			phr	
	SN	/IR-5				100.0	
	VA	NPLAST	R		2.0		
	VA	NFRE AP	P-2		2.0		
	Ste	earic Acid			2.0		
	Zir	nc Oxide			50		
	AC	FRITE S	TALITE S		1.5		
	NC	990 Carbo	n Black			35.0	
	N	30 Carbo	n Black			30.0	
	S	lfur	II DIACK			2.5	
	٥u ۸i		re)			2.5	
			rotor (on (	abovo)		0.1	
	**/	0 2 for AM	12101 (85 8	TE)		0.1	
^^(U.2 for AMYL LEDATE)							* / 1 0 1 0
Total						181.1 *	*(181.2)
Mooney measured @	D 132°C	;					
Rheometer measured @ 143°C							
Compounds cured 1	5 min. (	D 143°C					
Compression set measured after 22 hrs. @ 70°C							

Table 8: Ultras as Secondary Accelerators in NR

## **Cure Systems in Natural Rubber**

The process of vulcanization involves heating the gum-like mixture of all ingredients under pressure to form the shape of the finished rubber article. Charles Goodyear coined the term after Vulcan, the Roman god of fire and metalworking. Before Goodyear's discovery, the use of rubber was limited by its tendency to become soft, tacky and smelly during the summer and to get stiff and brittle in the winter. Elemental sulfur was the first material discovered that "cured" these problems of rubber when exposed to heat or cold. Sulfur is still the most frequently used vulcanizing agent today. It is inexpensive and provides parts with good physical properties.

The types of sulfur crosslinks can vary from monosulfidic to polysulfidic. The resulting properties of the vulcanizate depend a great deal on the number and the type of crosslinks. Polysulfide crosslinks have poor thermal stability. These longer crosslinks easily cleave and reform under stress or heat. They provide high mechanical strength resulting in improved tensile strength, tear strength and fatigue properties. On the other hand, shorter mono- and disulfidecrosslinks contain stronger sulfur bonds. These more thermally-stable crosslinks give improved thermal and oxidative stability as well as better compression set.

The length of the crosslink can be altered by changing the sulfur to accelerator ratio. As the proportion of accelerator to sulfur increases, the cure system moves from a conventional, to a semi-EV (where EV stands for Efficient Vulcanization), to an EV cure system. This process produces progressively shorter crosslinks.

The three types of sulfur-based cure systems are outlined in Figure 4.

Conventional Cure System (high proportion of polysulfides)							
High Sulfur: 2.5-3.5 phr							
Low Accelerator: 0.3-1.0 phr							
<ul> <li>Poor heat and compression set resistance</li> </ul>							
<ul> <li>High mechanical strength and cut growth resistance</li> </ul>							
EV Cure System (high proportion of monosulfides)							
Low Sulfur: 0.2-0.7 phr							
High Accelerator: 2.5-5.0 phr							
<ul> <li>High heat and compression set resistance</li> </ul>							
Poor strength							
Semi-EV Cure System							
Intermediate Sulfur: 1.0-2.0 phr							
Intermediate Accelerator: 1.0-2.5 phr							
Good compromise between heat resistance and flex life							

## Figure 4: Types of Sulfur Cure Systems

## Sulfurless and Soluble Cure Systems in Natural Rubber

Even greater heat resistance can be obtained with a sulfurless cure system, which produces exclusively the very-thermally-stable monosulfide crosslinks. This is done by using sulfur donors, accelerators used as a source of sulfur. Unfortunately, fatigue properties become progressively poorer as one goes from polysulfide to disulfide to monosulfide crosslinks, especially in natural rubber compounds.

Thus, in practice, a compromise between thermal stability and fatigue resistance must be achieved for each particular application.

The Malaysian Rubber Producer's Research Association has suggested a low- sulfur curing system for natural rubber that results in improved properties over conventional systems. All additives such as accelerators, activators and antioxidants should be soluble in the rubber where possible. This eliminates crystallization of the curatives and other materials to produce homogeneously crosslinked vulcanizates. Some of the more important advantages of a lowsulfur soluble cure system are listed below:

- · Better heat-aged tensile retention
- · Lower compression set
- Greater reversion resistance
- Better resiliency (higher rebound)
- Better fatigue resistance
- Improved hot tear
- Reduces the stress relaxation or creep rate
- Elimination of sulfur bloom

Figure 5 and Table 9 show sulfurless and soluble cure systems' effects on heat and flex resistance, and Table 10 and Table 11 provide specific examples of efficient vulcanization and soluble cure systems.



Figure 5: Trade-off to Maximize Both Heat and Flex Resistance

Ingredients (phr)	Conventional	Sulfur Donor	Soluble
Smoked Sheet	100.00	100.00	100.00
Stearic Acid	5.00	5.00	5.00
Zinc Oxide	3.00	3.00	3.00
N220 Carbon Black	45.00	45.00	45.00
AGERITE STALITE S	2.00	2.00	2.00
Sulfur	2.00		0.75
AMAX	1.00		1.75
MORFAX		2.00	
DTMD		1.00	
BUTYL TUADS			0.50
OCTOATE Z			1.50
Totals	158.00	158.00	159.50
Retained Physical Properties After Heat	t Aging in Test Tube	es, 48 hrs. @ 100	°C
Tensile, %	22	46	51
Elongation, %	36	73	79
DeMattia Flex Fatigue			
Kilocycles to 1.9 cm	85	50	50

	-			•			
Table 9:	Property	Effects	of Cure	Systems	ın	Natural	Rubber

	Black Filled		Mineral Filled		
Ingredients (phr)	Sulfur	EV	Sulfur	EV	
Smoked Sheet	70.00	70.00			
High Modulus Crepe			70.00	70.00	
Polyisoprene (high cis)	30.00	30.00	30.00	30.00	
VANPLAST R	2.00	2.00	2.00	2.00	
VANFRE AP-2	2.00	2.00	2.00	2.00	
Process Oil (Naphthenic)	10.00	10.00			
Stearic Acid	2.00	2.00	3.00	3.00	
Zinc Oxide	5.00	5.00	5.00	5.00	
AGERITE STALITE S	2.00	2.00	2.00	2.00	
N990 Carbon Black	40.00	40.00			
N330 Carbon Black	35.00	35.00			
DIXIE CLAY			50.00	50.00	
Whiting (Water Ground)			50.00	50.00	
Hydrated Silica			30.00	30.00	
Sulfur	2.50		2.50		
ALTAX (MBTS)	1.25				
AMAX				1.00	
METHYL TUADS	0.15				
METHYL ZIMATE (ZDMC)			0.25		
MORFAX		1.50	1.50	1.00	
ETHYL CADMATE		1.50		1.00	
Totals	201.90	201.00	248.25	247.00	
Mooney Scorch @ 121°C					
Minimum Viscosity	28	29	45	42	
Minutes to 5 pt. rise	13	19	22	25	
ODR @ 143°C					
t₅2 (min)	2.7	5.4	3.4	4.6	
ť 90 (min)	7.5	15.0	7.3	12.5	
Original Physicals, Press Cure	d 20 min. @	143°C			
Hardness, Shore A	63	56	63	60	
300% Modulus, MPa	11.8	8.6	5.6	5.2	
Tensile, MPa	19.1	20.0	14.5	15.9	
Elongation, %	480	570	570	570	
Compression Set Method B	70 hrs @ 100	°C.			
%	46	32	44	27	
Physical Properties After Heat	Aging in Test	Tubes, 96 hrs.	@ 100°C		
Hardness, Pts. Change	+6	+4	+7	+5	
Tensile, % Change	-42	-10	-62	+2	
Elongation, % Change	-60	-25	-67	-14	

Table 10: Efficient Vulcanization (EV) Systems in Natural Rubber

Compound	1	2	3	4
Ingredients (phr)				
Smoked Sheet	100.00	100.00	100.00	100.00
VANPLAST R	2.00	2.00	2.00	2.00
AGERITE STALITE S	2.00	2.00	2.00	2.00
Process Oil (Naphthenic)	10.00	10.00	10.00	10.00
N990 Carbon Black	40.00	40.00	40.00	40.00
N330 Carbon Black	35.00	35.00	35.00	35.00
Sulfur	2 50	0.60	0.60	0.60
Zinc Oxide	5.00	3 00	3 00	3 00
Stearic Acid	2 00			
ALTAX (MBTS)	1.00			
METHYL TLIADS	0.15			
MOREAY	0.10	1 50	1 50	1 50
		0.50	0.50	0.50
		1 50	1.50	1.50
		1.50	0.75	1.50
			0.75	0.92
Totals	199.90	196.10	196.85	197.02
Mooney Scorch @ 132°C				
Minimum Viscosity	22	26	27	28
Minutes to 5 pt. rise	8	15	10	9
Original Physicals, Press Cure	d 30 min. @	143°C		
Hardness Shore A	64	56	58	57
300% Modulus MPa	14.3	11 7	12.3	12.4
Tensile MPa	20.6	20.3	20.9	20.6
Elongation %	460	480	480	470
Original Dhusiash, Drass Our	al d mains @ d	-00	-100	470
Unginal Physicals, Press Cure	an min. @ 10	82°C	<b>F</b> 4	50
Hardness, Shore A	59	51	54	52
300% Modulus MPa	11.0	8.8	9.1	9.5
Iensile, MPa	20.7	20.3	21.4	20.4
Elongation, %	500	550	550	530
Compression Set, Method B, 7	0 hrs. @ 70°	С		
%	14	14	12	12
Physical Properties After Heat	Aging in Test	Tubes, 48 hrs.	@ 100°C	
Hardness, Pts, Change	+5	+4	-4	-3
Tensile, % Change	-33	-16	-19	-10
Elongation, % Change	-50	-14	-25	-21
Goodrich Flex, 6.4mm stroke, 1 Temp, rise above 93°C, °C	113kg load, te	emp. 93°C		
15 Minutes	9	27	17	11
30 Minutes	40	60	20	16
45 Minutes		00	12	21
FO Minutes			+2 50	26
			00	20
				39
time to blowout	36 min.	30 min.	ьо min.	>90 min.

Table 11: Soluble Cure Systems in Natural Rubber

## Peroxide-Cured Natural Rubber

Table 12 shows how peroxide cures provide natural rubber vulcanizates with maximum thermal and oxidative stability, as well as superior resistance to compression set. This natural rubber compound was protected with AGERITE SUPERFLEX SOLID G and VANOX[®] ZMTI because this synergistic antioxidant combination offers the best thermal stability and maximum flex-fatigue resistance in conventional sulfur systems, while being fully compatible with peroxide cures.

la sue dia sta (s b s)	Normal		VAROX
Ingredients (pnr)	Sultur	DBPH-50	DBPH-50
SMR-L	100.00	100.00	100.00
Stearic Acid	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00
N330 Carbon Black	50.00	50.00	50.00
VANPLAST R	5.00	5.00	5.00
Ultramarine Blue	0.25	0.25	0.25
ALTAX (MBTS)	1.25	1.25	1.25
METHYL TUADS	0.15	0.15	0.15
Sulfur	2.50		
VAROX DBPH-50		3.50	3.50
AGERITE SUPERFLEX SOLID G	2.00	2.00	1.00
VANOX ZMTI	1.00	1.00	2.00
Totals	169.15	170.15	170.15
Mooney Scorch, @ 121°C			
Minimum Viscosity	24	21	21
Minutes to 5 pt. rise	13	60+	60+
Original Physicals, Press Cured:	<u>10 min. @ 160°C</u>	<u>20 min. (</u>	<u>D 171°C</u>
Hardness, Shore A	64	52	55
300% Modulus, MPa	12.1	11.3	13.6
Tensile, MPa	27.8	18.8	20.7
Elongation, %	550	420	410
Compression Set			
%	24	16	16
DeMattia Elex Fatique After Heat Ag	ina 24 hrs. @. 100°C		
Kilocycles to 1.9 cm	374	929	808
Retained Physical Properties After H	leat Aging in Test Tub	oes, 96 hrs. @ 1	100°C
Hardness, Pts. Change	+4	-6	-4
Tensile, %	75	72	90
Elongation, %	64	90	95
-			

Table 12: Comparing Peroxide and Sulfur Cures in Natural Rubber

## Antioxidants in Natural Rubber

Antioxidants are materials that protect rubber against reaction with oxygen. Just a small percentage of oxygen chemically combined with the rubber can seriously degrade the physical properties of a rubber part. Heat can significantly increase the rate at which oxygen reacts with rubber; the rate approximately doubles for each 10 degree Centigrade increase in temperature. Compared to room temperature, aging a vulcanizate in a 70°C oven provides about a 50-fold increase in reaction rate. Work in the Vanderbilt Rubber Laboratory shows that in general, one day of oven aging corresponds to one year of environmental or shelf aging for natural rubber.

The major types of antioxidants are phenols, amines, quinolines, peroxide decomposers and synergists.

- Phenols are most effective in non-black compounds and provide minimal discoloration.
- Amines provide moderate to severe discoloration and are typically used in black-filled compounds. Diphenylamine antioxidants are general purpose antioxidants.
- Polymerized quinolines are relatively permanent in most polymers and cure systems.
- Peroxide decomposers are typically used in uncured applications as polymer stabilizers or to protect adhesives.
- Antioxidant synergists, such as VANOX ZMTI, increase the performance of antioxidants. The mechanism by which synergists work has not been fully understood, but it may be that they are peroxide decomposers that can survive the vulcanization process.

In general, there is a trade-off between the discoloration that an antioxidant develops during exposure to light and the oxidative protection provided by the antioxidant. In moving from phosphites to phenols to amines, the discoloration increases but the resistance to oxygen, heat, metal-catalyzed degradation and flex fatigue generally improves. For maximum effectiveness, the combination of a radical trap phenol or amine antioxidant with a synergist will often be the best means to obtain a high standard of performance.

Tables 13 thru 17 provide examples of antioxidants in natural rubber, as well as how a synergist can improve the performance of antioxidants.

		Tensile, MPa	Elong., %	Duro, Shore A			
Original Physical Properties, Press Cured 10 min. @ 153°C							
Control		25.3	480	69			
AGERITE STALITE S		26.0	510	67			
AGERITE SUPERFLEX	SOLID G	25.4	520	68			
AGERITE RESIN D [®]		26.0	520	69			
AGERITE MA		25.2	510	68			
		Tensile,	Elong.,	Points			
		%	%	Change			
Retained Physical Prope	erties After Heat A	ging 48 hrs. @	2 100°C				
Control		47	42	+1			
AGERITE STALITE S		80	61	+7			
AGERITE SUPERFLEX	SOLID G	88	63	+6			
AGERITE RESIN D		71	48	+5			
AGERITE MA		76	51	+3			
Base Compound	Ingredients		phr				
	SMR-5		100.0				
	VANFRE AP-2		2.0				
	VANPLAST R		2.0				
	Stearic Acid		2.0				
	Zinc Oxide		5.0				
	N550 Carbon Bla	ack	50.0				
	ALTAX (MBTS)		1.0				
	METHYL TUADS	5	0.1				
	Sulfur		2.5				
	Accelerator (as a	above)	2.0				
	Total		166.6				

Table 13: Antioxidants in Carbon Black Filled Natural Rubber

		Tensile, MPa	Elong., %	Duro, Shore A		
Original Physical Propert	ies. Press	s Cured 10	min. @ 15:	3°C		
Control		14.7	570	60		
AGERITE STALITE S		13.9	600	55		
AGERITE SUPERLITE S	OLID G	15.3	590	60		
SONGNOX [®] 3114		13.9	570	60		
VANOX MBPC		15.6	600	59		
VANOX MTI		16.0	600	60		
VANOX ZMTI		15.6	590	60		
		Tensile,	Elong.,	Points	GE Bri	ghtness
		%	%	Change	Orig.	24 hrs.
Retained Physical Prope	rties After	· Heat Aging	1 48 hrs. @	100°C		
Control		52	68	+4	55	44
AGERITE STALITE S		83	80	+6	52	17
AGERITE SUPERLITE S	OLID G	75	76	+6	54	38
SONGNOX 3114		64	74	+5	54	40
VANOX MBPC		88	80	+9	54	35
VANOX MTI		68	85	+3	56	36
Base Compound	Ingredi	ents			phr	
	SMR-5			100	0.00	
	VANFRE	AP-2		2	2.00	
	Zinc Oxio	de		5	5.00	
	DIXIE CI	LAY		50	0.00	
	Whiting			50	0.00	
	Titanium	Dioxide		20	0.00	
	ALTAX (I	MBTS)		1	00.1	
METHYL TUADS			(	).10		
	Sulfur			2	2.75	
Antioxidant (as above)			ve)	2	2.00	
Total				232	2.85	
GE Brightness original and after 24 hrs. under RS lamp						

Table 14: Antioxidants in Mineral Filled Natural Rubber

Some antioxidants provide protection to natural rubber when copper contamination is present. A combination of AGERITE STALITE S and VANOX ZMTI provides excellent protection against copper deterioration, with minimal discoloration.

Ingredients (phr)	Control	AGERITE STALITE S	VANOX ZMTI + AGERITE STALITE S
	400.00	100.00	100.00
SIVIR-D Stoaria Aaid	100.00	100.00	100.00
Zine Oxide	5.00	5.00	5.00
	10.00	10.00	5.00
Titanium Dioxido	10.00	15.00	10.00
	0.25	0.25	15.00
	1.00	0.25	0.25
	2.50	2.50	2.50
Sulfur	2.50	2.50	2.50
Coppor Oloato	0.25	0.25	0.25
	0.10	2.00	1.00
VANOX ZMTI		2.00	1.00
			1.00
Totals	135.10	137.10	137.10
Original Physicals, Press Cured 20 min. @	143°C		
Hardness, Shore A	52	48	46
500% Modulus, MPa	12.4	12.4	12.8
Tensile. MPa	28.3	26.6	25.2
Elongation, %	650	610	600
Retained Drugiant Draparting After Lloot Ag	ing in Toot	Tubaa 160 hra	@ 101%
Retained Physical Properties Alter Heat Ag	ing in rest		@ 121°C
	meiled	-0	-0
Tensile, %	meited	31	44
Elongation, %	meited	12	82
Retained Physical Properties After Aging in	Oxygen Bo	omb, 168 hrs. @	0 80°C
Hardness, Pts. Change	-11	-4	-1
Tensile, %	70	98	100
Elongation, %	89	95	97
GE Brightness			
Original	61	62	63
48 hrs. exposure to LIV light	32	24	31
TO THO. EXPOSULE TO OV LIGHT	52	47	01

Table 15: Antioxidants as Copper Inhibitors in Natural Rubber

In sulfur cured natural rubber compounds, the addition of 1 phr of VANOX ZMTI to 2 phr of AGERITE SUPERFLEX SOLID G greatly improves flex resistance while also showing an increase in heat stability.

Ingredients (phr)	Control	AGERITE SUPERFLEX SOLID G	AGERITE SUPERFLEX SOLID G + VANOX ZMTI
Smoked Sheet	100.00	100.00	100.00
Stearic Acid	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00
VANPLAST R	5.00	5.00	5.00
N330 Carbon Black	50.00	50.00	50.00
ALTAX (MBTS)	1.25	1.25	1.25
METHYL TUADS	0.15	0.15	0.15
Sulfur	2.50	2.50	2.50
AGERITE SUPERFLEX SOLID G		2.00	2.00
VANOX ZMTI			1.00
Totals	165.90	167.90	168.90
Mooney Scorch @ 121°C			
Minimum Viscosity	35	31	30
Minutes to 5 pt. rise	12	13	14
t 2 min	13	15	16
$t_{s}^{2}$ , 11111.	1.5	3.7	3.5
t 90, mm.	4.0	0.7	0.0
Original Physicals, Press Cured 5 min.	@ 153°C		
Hardness, Shore A	70	70	70
300% Modulus, MPa	15.2	15.4	13.7
Tensile, MPa	25.9	27.0	26.5
Elongation, %	480	500	540
Tear Die C, kN/m	77.4	86.2	99.4
DeMattia Flex Fatique			
Kilocycles to 1.9 cm	14	34	185
Compression Set. Method B. 22 hrs. @	70°C		
%	20	20	22
Retained Physical Properties After Hea	t Aging in Te	st Tubes, 96 hrs.	@ 100°C
Hardness, Pts. Change	+2	+7	+6
Tensile, %	20	48	57
Elongation, %	19	34	37

# Table 16: Improving Natural Rubber Flex Resistance with VANOX ZMTI

The synergistic effect of VANOX ZMTI with a primary antioxidant in Natural Rubber is very evident in the retained elongation property after heat aging, as shown in Figure 6 and Table 17.



Figure 6: VANOX ZMTI Synergy with a Primary Antioxidant in NR

			AGERITE	
		VANOX	SUPERLITE	VANOX
Ingredients (phr)	Control	ZMTI	SOLID	ZMTI + AO
Smoked Sheet	100.0	100.0	100.0	100.0
Stearic Acid	3.0	3.0	3.0	3.0
Zinc Oxide	5.0	5.0	5.0	5.0
VANPLAST R	2.0	2.0	2.0	2.0
DIXIE CLAY	50.0	50.0	50.0	50.0
Calcium Carbonate	50.0	50.0	50.0	50.0
Hi Sil 233	30.0	30.0	30.0	30.0
MORFAX	1.5	1.5	1.5	1.5
ETHYL CADMATE	1.5	1.5	1.5	1.5
VANOX ZMTI		3.0		2.0
AGERITE SUPERLITE S			3.0	1.0
Totals	243.0	246.0	246.0	246.0
Original Physicals, Press Cu	red 20 min.	@ 143°C		
Hardness, Shore A	62	63	61	61
300% Modulus, MPa	7.6	8.3	7.6	7.9
Tensile, MPa	13.9	15.6	15.6	15.9
Elongation, %	460	460	480	480
Retained Physical Properties	After Heat	Aging in Tes	st Tubes, 72 hrs. @	⊉ 121°C
Tensile, %	24	42	57	72
Elongation, %	65	82	70	85

Table 17:	VANOX ZMTI	Synergy with	AGERITE	SUPERLITE	SOLID

## Polyisoprene (IR) Compounding

Much of the information on natural rubber compounding applies to its synthetic counterpart. Synthetic polyisoprene, unlike natural rubber, doesn't contain any fatty acid, so it requires a minimum of two parts fatty acid for cure activity and development of optimum vulcanizate properties. The sulfur level required is 2 to 3 phr. In gum, and in black compounds, 2 phr is recommended. In high levels of non-black, 3 phr is generally used.

Because natural rubber contains some naturally occurring accelerators and antioxidants, it is usually advisable to increase the levels of both when changing a natural-based compound to synthetic polyisoprene.

The suppliers of IR may recommend slightly different curing systems for use in their *cis*-polyisoprene rubber. Therefore, synthetic polyisoprene polymers should be selected individually for each requirement and the best state of cure. Table 18 provides example of a pure gum base synthetic polyisoprene compound.

Ingredients	phr
Natsyn 2200	100.0
Stearic Acid	2.0
Zinc Oxide	3.0
AGERITE SUPERLITE	1.5
DURAX (CBS)	1.0
UNADS	0.2
Sulfur	2.0
Total	109.7
Mooney Scorch @ 132°C	15
Minutes to 5 pt. rise	24
ODR @ 138°C	
t₅2, min.	6.1
ť 90, min.	10
Original Physicals, Press Cured 20 min. @ 153°C	
Hardness, Shore A	44
300% Modulus, MPa	2.0
Tensile, MPa	24.1
Elongation, %	620

## Table 18: Polyisoprene Gum Compound

## STYRENE-BUTADIENE RUBBER (SBR)

## SBR Base

SBR compound design, for all types and grades of these elastomers, follows the same basic compounding guidelines as natural rubber. Essential ingredients are the same, but quantities differ.

Sulfur for vulcanization is calculated on the unsaturated (butadiene) portion of the elastomer. Accelerator requirements are generally higher than for natural rubber, since SBR is inherently slower curing.

Although some residual fatty acids are present as soaps in all SBR elastomers, stearic acid is customarily added along with zinc oxide for cure activation.

The type of antioxidant present as a process stabilizer in the specific polymer should be determined, and selection of a supplemental protective material is then based on compound requirements.

A typical SBR gum compound consists of the following:

Ingredients	Gum Compound	phr
1. Elastomer	SBR	100.0
2. Processing Aid	VANFRE AP-2	2.0
3. Activators		
Fatty Acid	Stearic Acid	2.0
Metal Oxide	Zinc Oxide	5.0
4. Antioxidant	AGERITE STALITE S	2.0
5. Accelerators of Vulcanization		
Primary	ALTAX (MBTS)	1.5
Secondary	METHYL CUMATE	0.1
6. Vulcanizing Agent	Sulfur	2.0
	Total	114.6

Vulcanization over a range of 5-45 minutes at 153°C produces poor physical properties of tensile strengths of 1.7-2.1 MPa. Styrene-butadiene rubber has virtually no commercial use as an unfilled compound.

Useful properties are obtained by the addition of reinforcing carbon blacks, mineral, or modified hydrocarbon fillers as demonstrated in Tables 19 thru 22 on the following pages.

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
MT N990 Carbon Black							
25 phr	1.8	5.0	680	44	7.9	19	19/28
50 [°] "	2.1	10.1	770	50	15.8	21	19/32
75"	3.4	11.0	750	54	26.4	18	17/29
100 "	5.0	11.2	730	59	37.0	17	15/44
125 "	7.2	8.9	570	64	40.5	14	13/52
SRF N770 C	Carbon Black	(					
25 phr	1.5	11.6	760	48	24.6	25	16/30
50 [°] "	7.6	16.4	550	58	32.6	16	13/38
75"	14.5	18.0	410	65	37.8	17	11/52
100 "	19.0	19.0	300	72	39.6	15	8/78
GPF N660 (	Carbon Black	k					
25 phr	2.8	11.4	610	51	17.6	19	15/32
50 [°] "	7.9	15.9	530	60	22.9	17	13/42
75"	15.6	18.3	400	66	45.8	16	10/66
100 "		20.0	250	75	40.5	13	6/97
FEF N550 C	arbon Black	[					
25 phr	3.4	13.8	650	51	22.0	21	14/32
50 "	10.9	18.5	500	63	39.6	18	11/47
75"	18.6	20.2	330	72	37.8	17	7/88
100 "		18.3	260	78	30.8	17	
HAF N330 C	Carbon Black	(					
25 phr	4.1	13.9	540	52	21.1	17	13/32
50"	13.0	22.6	450	64	36.1	17	10/52
75"		22.1	280	73	32.6	20	7/91
ISAF N220 (	Carbon Blac	k					
25 phr	3.9	14.8	550	52	26.4	15	13/32
50 "	13.1	23.2	450	64	36.1	16	10/54
75"		21.7	280	76	38.7	18	
Base Com	pound	Ingredien	ts			phr	
		Dlioflev® 15	000	0		100.0	
			D_2			2.0	
		Stearic Acid	1 - 2			2.0	
		Zinc Ovide	A			5.0	
		AGERITE S	STALITE S			1.5	
AGERITE STALITE S					1.5		
					0.1		
Sulfur					2.0		
Total						114.1	
Compounds	cured 10 m	in. @ 153°C					
Tear measured on Die A samples							
Compression set measured after 22 hrs. @ 70°C							
Mooney mea	asured @ 13	32°C	-				

Table 19: Carbon Black Loading in SBR 1500
	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
Calcium Ca	arbonate (gro	ound)					
50 phr	1.2	1.9	500	50	7.9	36	20/26
75 "	1.2	2.3	540	53	7.9	34	20/30
100 "	1.3	2.3	550	55	8.8	37	21/32
150 "	1.2	2.5	560	60	8.8	43	21/35
DIXIE CLA	Y						
50 phr	2.2	9.6	860	51	18.5	38	24/28
75 "	2.6	10.9	920	55	25.4	41	24/34
100 "	3.9	11.4	850	60	38.7	41	23/38
150 "	6.1	12.4	760	68	35.2	37	16/57
Hi-Sil 233							
25 nhr	13	54	690	47	12.3	24	21/28
50 "	1.0	13.9	740	59	32.5	31	21/54
50 75"	22	15.9	800	68	44 0	43	20/89
	2.2	10.0	000	00	0	40	20/00
MCNAMEE	CLAY				10.0		
50 phr	2.0	5.4	740	50	13.2	34	22/27
75	2.8	8.3	800	55	20.2	36	24/30
100 "	3.4	9.1	850	59	26.4	38	23/35
150 "	5.0	10.0	820	66	35.2	36	22/45
Silene 732L	C						
25 phr	1.7	7.5	640	51	12.3	14	13/26
50"	2.1	9.4	670	58	17.6	18	17/35
75"	2.2	9.3	700	58	20.2	23	18/40
Base Corr	npound	Ingredien	ts			phr	
		Plioflex 150	0C			100.0	
		VANERE A	P-2			2.0	
		Stearic Acid	4			2.0	
		Zinc Oxide				5.0	
		AGERITE S	STALITE S			1.5	
		ALTAX (MB	TS)			1.5	
		METHYL C	UMATE			0.1	
		Sulfur				2.0	
		Total				114.1	
Compounds	s cured 20 n	nin. @ 153°C					
Tear measu	ired on Die /	A samples	o ===	~			
Compressio	on set meas	ured atter 22 I	nrs. @ 70°	C			
wooney me	easurea @ 1	32 0					

Table 20: Mineral Filler Loading in SBR 1500

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	, Mooney, t5/ML
MT N990 Ca	arbon Black						
25 phr	1.0	2.6	560	36	8.8	18	20/22
50"	1.4	4.3	650	40	15.0	20	19/25
75"	2.1	12.6	810	44	18.5	17	17/27
100 "	2.8	14.5	830	47	26.4	18	16/30
125 "	3.5	13.8	800	52	30.8	18	18/33
SRF N770 (	Carbon Blac	k					
25 phr	1.5	4.7	550	39	10.6	16	16/23
50"	3.4	9.4	590	45	24.6	17	14/27
75"	6.1	13.0	570	53	34.3	14	12/32
100 "	9.9	13.3	450	58	39.6	17	11/36
GPF N660 (	Carbon Blac	k					
25 phr	1.7	5.3	530	41	15.0	15	16/23
50"	4.3	12.8	650	47	26.4	16	14/28
75"	7.8	14.5	560	55	31.7	14	13/34
100 "	12.8	14.6	360	62	39.6	15	10/45
FEF N550 C	Carbon Blaci	k					
25 phr	2.0	6.5	560	40	16.7	18	15/23
50"	5.4	11.2	520	50	30.8	17	13/29
75"	10.3	14.3	430	56	35.2	15	11/37
100 "	15.1	15.9	330	66	42.2	15	9/50
HAF N330 (	Carbon Blac	k					
25 phr	1.9	6.8	550	41	17.6	18	14/25
50 "	4.7	16.3	620	48	37.0	20	11/31
75 "	10.8	18.6	460	61	40.5	18	9/43
100"	17.5	19.1	330	70	35.2	19	8/59
ISAF N220	Carbon Blac	:k					
25 phr	1.7	9.1	630	40	13.2	18	15/20
50 "	4.2	18.5	660	50	30.8	17	12/34
75"	10.6	19.9	480	63	38.7	18	10/47
100"	17.3	18.9	330	72	37.0	22	8/71
Base Com	pound	Ingredien	its			phr	
		Plioflex 171	120		1	38.00	
			P_2			2 00	
		Stearic Aci	-∠ 1			2.00	
		Zinc Ovide	4			5.00	
						1.50	
						1.60	
		Sulfur				2.40	
		Total			1	52.65	
Compounds	cured 15 m	in. @ 153°C					
Tear measu	red on Die A	samples					
Compressio	n set measu	ired after 22	hrs. @ 70°	С			
Mooney measured @ 132°C							

Table 21: Carbon Black Loading in SBR 1712 (37.5 parts oil extended)

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
Calcium Ca	arbonate Gro	ound					
25 phr	0.8	1.1	460	36	5.3	29	18/18
50 "	0.8	1.4	510	39	4.4	27	19/20
75"	0.8	1.8	600	41	5.3	33	20/22
100 "	0.8	1.6	520	42	6.2	36	20/22
125 "	0.7	1.9	660	42	6.2	40	21/24
DIXIE CLA	Y						
25 phr	0.9	1.6	530	38	6.2	26	19/18
50 [°] "	0.9	5.1	820	40	7.9	26	19/21
75"	1.1	7.4	880	44	7.9	42	21/23
100 "	13	8.0	910	47	10.6	46	22/26
125 "	1.6	8.6	900	52	16.7	49	23/33
Hi-Sil 233							
25 phr	10	21	540	36	70	22	18/22
50 "	1.3	8.6	790	45	17.6	26	20/30
75 "	1.0	11.2	840	48	23.8	34	20/44
100 "	1.0	10.6	850	61	20.0	50	19/90
100	1.0	10.0	050	01	50.7	50	10/09
MCNAMEE	CLAY	1.0	400	07		0.4	10/11
25 phr	1.0	1.2	430	37	5.3	31	18/14
50 "	1.0	2.0	650	41	5.3	31	18/17
75 "	1.2	1.1	870	45	9.7	36	19/20
100 "	1.3	9.6	930	47	14.4	42	20/21
150 "	1.5	9.6	950	51	15.0	48	20/25
Silene 732	D						
25 phr	0.9	3.5	640	338	7.9	15	15/21
50"	1.0	5.5	740	40	10.6	20	17/23
75"	1.2	9.4	800	46	15.8	26	19/28
100 "	1.6	8.0	770	52	22.9	27	19/39
Base Con	npound	Ingredien	ts			phr	
	,	Plioflex 171	20.		1	37 50	
			20 ⊃_2			2 00	
		Stearic Acid	-2			2.00	
		Zinc Ovide	4			5.00	
						1 50	
AGENTE STALITE S 1.50 ALTAY (MRTS) 1.60							
METHYL CLIMATE 0 15							
Sulfur 240							
		Total			1	52 15	
0					1	02.10	
Compound	s cured 15 n	11n. @ 153°C					
Comprossi		v samples	are @ 70°	c			
Moonov		ared after 22 f	iis. @ 70*	C			
wooney me	asureu @ 1	32 0					

Table 22: Mineral Filler Loading in SBR 1712 (37.5 parts oil extended)

### Plasticizers and Processing Aids in SBR

SBR compounds require plasticizers and processing aids to assist in breakdown, and to promote rapid incorporation of carbon black and mineral fillers. In addition to performing these functions, when the processing aids shown below are added at the start of the mix they assist in holding breakdown temperatures below the gel formation level and retard scorch in the subsequent processing operations.

The following comparison demonstrates the effectiveness of several processing aids in a cold SBR black reinforced compound.

Ingredients (phr)	Control	R	PL	LEEGEN	AP-2
Plioflex 1500C	100.00	100.00	100.00	100.00	100.00
Stearic Acid	2.00	2.00	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00	5.00	5.00
AGERITE STALITE S	1.50	1.50	1.50	1.50	1.50
N990 Carbon Black	120.00	120.00	120.00	120.00	120.00
N330 Carbon Black	10.00	10.00	10.00	10.00	10.00
AMAX	1.00	1.00	1.00	1.00	1.00
METHYL CUMATE	0.15	0.15	0.15	0.15	0.15
Sulfur	2.00	2.00	2.00	2.00	2.00
VANPLAST R		5.00			
VANPLAST PL			5.00		
LEEGEN				5.00	
VANFRE AP-2					5.00
Totals	241.65	246.65	246.65	246.65	246.65
Mooney Viscosity @ 100°C	85	75	72	76	73
Mooney Scorch @ 121°C					
Minimum Viscosity	67	56	55	56	56
Minutes to 5 pt. rise	24	26	27	26	27
Original Physicals, Press C	Cured 15 n	min. @ 153°C			
Hardness, Shore A	70	70	68	68	70
200% Mod., MPa	12.3	10.8	10.7	9.1	10.5
Tensile, MPa	14.1	14.0	14.1	12.7	14.0
Elongation, %	260	290	320	370	290
DuPont Spider Flow Mold,	6.4mm O	rifice, 10 Tons	Pressure		
Weight, g	12.5	13.8	13.4	13.4	14.8

Table 23: Plasticizers and Processing Aids for SBR

### **Cure Systems in SBR**

The cure systems for SBR are very similar to that of natural rubber, but often require higher levels of accelerators. Accelerators play an important role in the vulcanization of rubber, affecting scorch safety, rate of cure and the length and number of the crosslinks which form.

The different types of accelerators and the effect of the levels used are shown in Tables 24 thru 27.

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
Cured 30 min. @	153°C						
ALTAX (MBTS) CAPTAX (MBT) ZETAX (ZMBT) AMAX DURAX (CBS) MORFAX VANAX NS	5.4 3.0 2.3 10.2 11.2 12.3 11.9	15.2 11.9 10.7 18.5 18.4 19.0 15.5	690 900 920 540 480 470 370	57 52 60 60 61 62	57.2 58.1 56.3 37.8 34.3 29.0 28.2	32 42 46 19 17 17	24/37 27/37 32/37 54/37 34/39 32/39 38/40
Cured 10 min. @	171°C						
ALTAX (MBTS) CAPTAX (MBT) ZETAX (ZMBT) AMAX DURAX (CBS) MORFAX VANAX NS	6.1 3.7 2.9 9.3 10.0 10.9 11.3	16.6 13.0 12.3 17.7 18.1 20.2 18.0	700 820 870 540 500 520 440	56 54 52 58 60 60 59	51.0 59.0 51.9 35.2 31.7 26.4 28.2	46 61 65 33 29 28 29	
Base Compound	d I	ngredient	s			phr	
		Plioflex 1500 /ANPLAST /ANFRE AP Stearic Acid Zinc Oxide AGERITE S N990 Carbo N330 Carbo Sulfur Accelerator Total	DC R -2 TALITE S n Black n Black (as above	)		100.0 2.0 2.0 5.0 2.0 35.0 30.0 2.0 1.5 181.5	
Tear measured on Die A samples Compression set measured after 22 hrs. @ 70°C for the first series,							

Compression set measured after 22 hrs. @ 100°C for the second series

Mooney measured @ 132°C

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp Set, %	. Mooney, 5 t5/ML
Control	2.2	8.6	880	52	42.4	58	27/42
BISMATE	21.4	23.2	320	67	30.8	19	8/43
ETHYL CADMATE	16.3	24.0	440	63	44.9	15	11/42
METHYL CUMATE*	18.9	20.7	320	66	25.5	10	8/43
METHYL LEDATE	16.3	24.0	410	64	34.3	13	12/43
ETHYL SELENAC	17.9	23.7	380	64	37.0	15	10/43
SULFADS	14.1	25.2	480	63	46.6	17	7/43
ETHYL TELLURAC	20.6	23.2	330	67	31.7	18	15/43
ETHYL TUADS	14.7	23.6	430	63	45.8	15	15/42
METHYL TUADS	17.9	21.9	350	66	32.6	14	11/44
UNADS	17.2	23.7	400	66	37.8	13	15/43
BUTYL ZIMATE	10.5	24.5	580	60	44.0	21	17/44
ETHYL ZIMATE	13.6	23.2	460	62	39.6	14	15/43
METHYL ZIMATE	15.4	23.0	420	65	31.7	14	12/44
Base Compound	Ing	gredients	;			phr	
	Plic	oflex 1500	С			100.0	
	VA	NPLAST F	R			2.0	
	VA	NFRE AP-	2			2.0	
	Ste	aric Acid				5.0	
	Zin	c Oxide				5.0	
	AG	ERITE ST	ALITE S			1.5	
	N3	30 Carbon	Black			50.0	
	Sul	fur				20	
	AL	TAX (MBT	S)			1.0	
	Ulti	a Accelera	ator (as at	ove)		0.5	
	*(0	.35 for ME	THYL CUI	MATE		0.0	
		Total				169.0	*(168.85)
Compounds cured 2 Tear measured on D Compression set me Mooney measured @	:						

 Table 25: Ultras as Primary Accelerators in SBR 1500

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp Set, %	. Mooney, 5 t5/ML
Control	7.6	20.6	570	61	85.4	28	27/42
BISMATE	15.7	23.5	410	66	41.4	16	8/43
ETHYL CADMATE	21.1	24.4	500	64	38.7	19	11/42
METHYL CUMATE*	17.4	19.5	320	67	34.3	14	8/43
METHYL LEDATE	11.6	25.0	530	63	50.2	20	12/43
ETHYL SELENAC	13.4	26.1	510	64	50.2	20	10/43
SULFADS	11.4	24.9	530	62	47.5	22	7/43
ETHYL TELLURAC	14.8	24.6	440	65	40.5	19	15/43
ETHYL TUADS	12.8	23.7	470	64	37.8	20	15/42
METHYL TUADS	13.4	5.5	500	65	39.6	19	11/42
UNADS	12.5	24.6	500	63	39.6	20	15/43
BUTYL ZIMATE	11.2	23.0	510	64	54.6	23	17/44
ETHYL ZIMATE	12.0	25.3	530	64	62.5	22	15/43
METHYL ZIMATE	12.6	25.6	510	65	51.0	23	12/42
Base Compound	Ing	gredients	;			phr	
	Plic	oflex 1500	С		1	00.00	
	VA	NPLAST F	2			2.00	
	VA	NFRE AP-	2			2.00	
	Ste	aric Acid				2.00	
	Zin	c Oxide				5.00	
	AG	ERITE ST	ALITE S			1.50	
	N3	30 Carbon	Black			50.00	
	Su	fur				2 00	
	AL	TAX (MBT:	S)			2 00	
	Ult	a Acceler	e) ator (as al	ove)		0.15	
	*(0	10 for ME	THYL CUN	ATE)		0.10	
		Total			1	66.65	*(166.60)
Compounds cured ?	0 min @	153°C					
Toor monoured on Dio A complex							
Compression act measured after 22 bra @ 70°C							
Moonov monoured	asureu a		s. @ 10 C	,			
Mooney measured @ 132°C							

Table 26: Ultras as Secondary Accelerators in SBR 1500

	Black Filled Mineral Fille				
Ingredients (phr)	Sulfur Cured	EV	Sulfur Cured	EV	
Plioflex 1500C	70.00	70.00			
Plioflex 1502			70.00	70.00	
Polyisoprene (high <i>cis</i> )	30.00	30.00	30.00	30.00	
VANPLAST R	2.00	2.00	2.00	2.00	
VANFRE AP-2	2.00	2.00	2.00	2.00	
Stearic Acid	2.00	2.00	3.00	3.00	
Zinc Oxide	5.00	5.00	5.00	5.00	
AGERITE STALITE S	2.00	2.00			
AGERITE SUPERLITE SOLID			2.00	2.00	
Process Oil (high aromatic)	25.00	25.00			
Process Oil (naphthenic)			5.00	5.00	
Cumar resin			5.00	5.00	
Paraffin wax			1.00	1.00	
N330 Carbon Black	60.00	60.00			
N990 Carbon Black	20.00	20.00			
DIXIE CLAY			50.00	50.00	
Whiting (water ground)			50.00	50.00	
Hydrated silica			30.00	30.00	
Sulfur	2.50		2.10		
ALTAX MBTS	1.25				
AMAX				1.00	
ETHYL CADMATE		1.00		1.00	
METHYLTUADS	0.15	0.60			
ETHYLTUADS		0.40			
MORFAX			1.30	1.00	
DIDM		2.00			
Totals	221.90	222.00	258.40	258.00	
Mooney Scorch @ 121°C					
Minimum Viscosity	31	34	40	45	
Minutes to 5 pt. rise	31	20	31	23	
ODR @ 143℃					
t₅2, min.	3.2	2.8	3.0	4.2	
ť 90, min.	16	11	9	11	
Original Physicals, Press Cureo	d 20 min. @ 153°C	0			
Hardness, Shore A	61	60	51	54	
300% Modulus, MPa	11.3	11.0	2.0	1.8	
Tensile, MPa	16.9	16.5	8.4	9.4	
Elongation, %	450	440	960	830	
Compression Set. Method B. 7	0 hrs. @ 100°C				
%	42.4	12.2	46.5	28.8	
Physical Properties After Heat	Aging in Test Tube	s, 96 hrs.	@ 100°C		
Hardness, Pts. Change	+11	+6	+11	+1	
Tensile, % Change	-24	-8	-26	+6	
Elongation, % Change	-60	-20	-62	-13	

 Table 27: EV Systems vs. Sulfur Systems in SBR/Polyisoprene Blends

# Antioxidant Selection in SBR

While all SBR polymers contain some antioxidant as received, it is considered good compounding practice to include an antioxidant in each formula, particularly when compounding for heat resistance and heavy duty service.

Certain amine type antioxidants, like AGERITE SUPERFLEX SOLID G, are known to inhibit gel formulation in hot mixing, and are used in compounds to assure uniform extrusion and calendering.

Heat-aged physical properties in Table 28 and 29 show the advantages of using AGERITE and VANOX antioxidants.

		Tensile, MPa	Elong., %	Duro, Shore A
Original Physical Proper	ties. Press Cured	30 min. @ 153	3°C	
Control	,	17.8	330	68
AGERITE STALITE S		16.4	320	66
AGERITE SUPERFLEX	SOLID G	17.2	330	68
AGERITE RESIN D		16.9	320	68
AGERITE MA		16.1	310	68
VANOX NDBC		16.5	320	68
		Tensile,	Elong.,	Points
		%	%	Change
Retained Physical Prope	erties After Heat A	ging 48 hrs. @	100°C	
Control	·	77	55	+2
AGERITE STALITE S		94	72	+4
AGERITE SUPERFLEX	SOLID G	87	73	+2
AGERITE RESIN D		87	73	+2
AGERITE MA		97	74	+3
VANOX NDBC		92	72	+2
Base Compound	Ingredients		phr	
	Plioflex 1712C		137.5	
	VANFRE AP-2		2.0	
	Stearic Acid		2.0	
	Zinc Oxide		5.0	
	VANPLAST R		5.0	
	N330 Carbon Bla	ack	75.0	
	ALTAX (MBTS)		1.0	
	METHYL CUMA	TE	0.5	
	Sulfur		2.5	
	Antioxidant (as a	above)	2.0	
	Total		232.5	

# Table 28: Antioxidants in Carbon Black Filled SBR

		Tensile, MPa	Elong., %	Duro, Shore A			
Original Physical Properties, Press Cured 30 min. @ 153°C							
Control		13.0	760	60			
AGERITE SUPERLITE S	OLID G	12.1	770	60			
VANOX MBPC		12.3	780	60			
VANOX MTI		10.3	950	59			
VANOX ZMTI		9.8	920	59			
SONGNOX 3114		12.0	830	59			
					C	ЭE	
		Tensile,	Elong.,	Points	Brigh	ntness	
		%	%	Change	Orig.	24 hrs.	
Retained Physical Prope	rties After	Heat Aging	48 hrs. @	100°C			
Control		70	46	+10	20	12	
AGERITE SUPERLITE S	OLID G	67	58	+9	20	13	
VANOX MBPC		72	60	+8	21	12	
VANOX MTI		89	58	+9	19	12	
VANOX ZMTI		82	51	+11	19	12	
SONGNOX 3114		74	65	+7	20	10	
Base Compound	Ingredie	ents		F	bhr		
	Plioflex 1	5020		10	0.0		
	VANFRE	AP-2			2.0		
	Stearic A	cid			2.0		
	Zinc Oxio	le			5.0		
	VANPLA	ST R			2.0		
	DIXIE CL	.AY		8	0.0		
	Sulfur				2.5		
	ALTAX (N	MBTS)			1.5		
	METHYL	TUADS			0.5		
	Antioxida	int (as abov	e)		2.0		
	Total			19	7.5		
GE Brightness original a	nd after 24	I hrs. under	RS lamp				

Table 29: Antioxidants in Mineral Filled SBR

# BUTYL (IIR) and HALOBUTYL (BIIR & CIIR) Rubbers

# **Butyl Base Compounds**

Butyl rubbers, available in various degrees of unsaturation, are vulcanizable by three basic methods: accelerated sulfur vulcanization, crosslinking with dioxime related dinitroso compounds, and polymethylol-phenol resin cure. The lower unsaturation grades require stronger acceleration to cure at efficient production rates.

Processing aids, such as VANPLAST PL and VANFRE AP-2, are required to permit fast mixing. Antioxidants and protective waxes may be desirable in the high unsaturation, fast curing grades.

Typical base compounds are as follows:

Ingredients	Gum Compound	1	2
1. Elastomer	EXXON [™] Butyl 268	100.00	100.00
2. Processing Aid	VANFRE AP-2	2.00	2.00
3. Activators:			
Metal Oxide	Zinc Oxide	5.00	5.00
Fatty Acid	Stearic Acid	2.00	2.00
4. Accelerators:			
Thiuram	METHYL TUADS	1.25	1.00
Thiazole	CAPTAX (MBT)	1.00	0.50
5. Vulcanizing Agent	Sulfur	1.25	2.00
	Totals	112.50	112.50
Mooney Scorch @ 121°C			
Minimum Viscosity		46	45
Minutes to 5 pt. rise		45	46
Original Physicals, Press Cured 20 min. @	160°C		
Hardness, Shore A		34	34
300% Modulus, MPa		1.0	0.9
Tensile, MPa		2.4	2.8
Elongation, %		480	500

Butyl rubbers do not develop much strength with vulcanization and require the use of reinforcing fillers. Tables 30 and 31 show the effects of various loading levels of carbon black and mineral fillers.

	M300,	Tensile,	Elong.,	Duro,	Tear,	Comp.	Mooney,
	мРа	мРа	%	Shore A	KN/m	Set, %	t5/ML
MT N990 C	Carbon Black						
25 phr	2.1	4.0	420	40	9.7	15	18/46
50 "	2.9	6.1	530	48	15.8	16	16/48
75 "	3.6	5.4	540	54	16.7	17	14/52
100 "	3.9	4.4	490	62	20.2	18	12/58
125 "	3.9	4.2	460	66	19.4	18	11/63
SRF N770	Carbon Blac	k					
25 phr	3.2	10.8	550	46	19.4	16	15/56
50"	5.9	11.6	560	57	26.4	17	12/61
75"	8.3	10.0	460	66	41.4	17	11/74
100 "	9.4	9.9	320	74	45.8	21	9/87
GPF N660	Carbon Blac	k					
25 phr	3.5	12.7	570	47	15.0	15	14/55
50 "	6.6	11.0	570	59	33.4	16	12/64
75"	9.2	9.8	430	70	34.3	16	10/68
100 "	9.6	9.6	300	79	44.9	17	8/77
FEF N550	Carbon Blac	k					
25 phr	4.1	9.6	500	48	18.5	16	13/57
50 "	7.2	10.8	510	61	37.0	18	12/65
75 "	10.4	10.9	340	74	42.2	19	9/80
100 "		10.8	260	84	40.8	24	7/88
HAF N330	Carbon Blac	k					
25 phr	4 0	14.5	580	48	22.0	15	13/58
50 "	8.5	16.3	530	62	59.0	17	8/71
75 "	12.8	15.0	420	72	56.3	20	6/92
100 "		12.9	280	82	45.8	25	4/116
ISAE NOOD	Carbon Blac	r.					
25 nhr	3.4	16.6	630	46	25.5	15	11/59
50 "	8.7	17.3	530	61	67.8	20	10/78
75 "	13.5	16.6	400	75	74.8	24	
Base Con	npound	Inaredien	ts			phr	
		EXXON But	tvl 268	1		100.0	
			D_2			2.0	
		Stearic Acid	1			1.0	
		Zinc Oxide	4			2.0	
						1.0	
		CAPTAX (N	(BT)			0.5	
		Sulfur				2.0	
		Total				108.5	
Compounds cured 20 min. @ 171°C Tear measured on Die A samples							
Compression Mooney me	on set measu easured @ 1	ured after 22 h 32°C	nrs. @ 70°	С			

Table 30: Carbon Black Loading in Butyl Rubber

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML	
Calcium Car	rbonate (gro	ound)						
50 phr 75 " 100 "	1.1 1.0 1.0	4.3 4.2 3.6	550 570 550	43 46 47	4.4 4.4 4.4	48 53 59	22/42 24/42 23/43	
150 "	1.0	4.1	580	52	5.3	68	22/45	
DIXIE CLAY	·							
50 phr 75 "	2.0 2.3	17.2 14 7	820 770	45 48	10.6 13.2	50 61	8/50 7/56	
100 " 150 "	2.3 2.5	13.6 7.7	730 720	53 58	17.6 23.8	67 84	6/65 8/87	
Hi-Sil 233 25 phr	12	19.4	870	40	24.6	49	12/56	
50 "	1.6	11.9	870	49	35.2	80	11/105	
75  " 100 "	1.8 3.5	10.0 6.7	890 760	72 87	42.2 38.7	95 99		
McNAMEE (	CLAY							
50 phr	2.3	14.3	700	46	8.8	48	9/50	
75 " 100 "	2.4	12.4 11.5	720	51 55	13.2 15.0	58 66	8/56 7/62	
150 "	2.8	9.6	730	59	18.5	74	7/76	
Silene 762D	)							
25 phr	1.1	15.2	800	39	6.2	44	20/51	
50 "	1.5	15.8	840	46	15.0	55	15/64	
75 100 "	2.2	9.2	840 820	50 64	24.6 32.6	71		
Base Com	pound	Ingredien	ts			phr		
EXXON Butyl 268 VANFRE AP-2 Stearic Acid Zinc Oxide METHYL TUADS CAPTAX (MBT) Sulfur					100.0 2.0 1.0 5.0 1.0 0.5 2.0			
		Total				111.5		
Compounds Tear measur Compression Mooney mea	Compounds cured 20 min. @ 171°C Tear measured on Die A samples Compression set measured after 22 hrs. @ 70°C Mooney measured @ 132°C							

Table 31: Mineral Filler Loading in Butyl Rubber

# Process Aids in Butyl Rubber

The effectiveness of VANFRE AP-2 is illustrated by pictures of DuPont "Spider Mold" samples after molding and Mooney viscosity at both 121°C and 100°C.

	-	
Ingredients (phr)	Control	VANFRE AP-2
EXXON Butyl 365	100.0	100.0
Zinc Oxide	5.0	5.0
N550 Carbon Black	50.0	50.0
Silene 732D	50.0	50.0
METHYL TUADS	1.0	1.0
CAPTAX (MBT)	0.5	0.5
Sulfur	2.0	2.0
VANFRE AP-2		2.0
Total	208.5	210.5
Mooney Viscosity @ 100°C	99	85
Mooney Scorch @ 121°C		
Minimum Viscosity	71	56
Minutes to 5 pt. rise	16	19
ODR @ 171°C		
t₅2, min.	0.7	0.8
ť 90, min.	11.7	10.7
Original Physicals, Press Cured 20 min. @ 171°C		
Hardness, Shore A	76	76
300% Modulus, MPa	6.2	6.2
Tensile, MPa	8.1	7.8
Elongation, %	480	480
DuPont Spider Mold, 4.8mm Orifice, 30 Tons Pressu	ıre, Press Cui	red 10 min. @ 171°C

Table 32: VANFRE AP-2 in Butyl Rubber

Weight, g 17.8 19.5



### **Cure Systems in Butyl Rubber**

Butyl rubber's low levels of unsaturation require the use of ultra accelerators. Thiuram sulfides and dithiocarbamates are specifically used with elemental sulfur to provide acceptable cure times. Examples of various Vanderbilt accelerator systems for Butyl are shown in Table 33.

Compound	Α	В	С	D	Е	F
Ingredients (phr)						
EXXON Butyl 268	100.0	100.0	100.0	100.0	100.0	100.0
VANFRE AP-2	2.0	2.0	2.0	2.0	2.0	2.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0
Flexon 845	10.0	10.0	10.0	10.0	10.0	10.0
N330 Carbon Black	50.0	50.0	50.0	50.0	50.0	50.0
Sulfur	1.0	0.5	0.5		1.0	1.5
DTDM			1.0	1.5		
METHYL TUADS					1.5	0.5
ETHYL CADMATE	2.0	4.0	4.0	4.0	0.5	
ETHYL TELLURAC					1.5	1.0
ALTAX (MBTS)	0.5				1.0	
CAPTAX (MBT)						0.5
Totals	171.5	172.5	173.5	173.5	173.5	171.5
Mooney Scorch @ 121°C						
Minimum Viscosity	57	54	49	52	54	57
Minutes to 5 pt. rise	25	32	46	60+	23	14
ODR @ 171°C						
$t_2 2$ min	20	20	3.0	4 0	20	10
t' 90 min	11.0	7.0	9.0	8.0	9.0	13.0
Original Physicals Press Cured @ 171°	~		0.0	0.0	010	
Minutes Cured	, 15	10	10	10	10	15
Hardness Shore A	50	46	48	45	56	53
300% Modulus, MPa	4.6	28	34	19	49	55
Tensile MPa	15.8	14.5	15.1	14.3	15.2	16.4
Flongation %	690	770	730	820	650	660
Tear Die A kN/m	44.9	45.8	38.7	47.5	37.0	44 0
Commenced in Cost Mathead D 20 tons			00.1		00	
Compression Set, Method B, 22 hrs. @ 7	15 15	10	17	16	10	26
70	15	19	17	10	10	20

Table 33: Accelerator Systems for Butyl Rubber

Compound	G	н	I	J	К	L
Ingredients (phr)						
EXXON Butyl 268	100.0	100.0	100.0	100.0	100.0	100.0
VANFRE AP-2	2.0	2.0	2.0	2.0	2.0	2.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0	1.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0
Flexon 845	10.0	10.0	10.0	10.0	10.0	10.0
N330 Carbon Black	50.0	50.0	50.0	50.0	50.0	50.0
Sulfur	2.0	1.5	1.5	1.5	1.0	1.0
METHYL TUADS	0.5		1.0	0.7		
ETHYL TELLURAC	0.5	2.0		1.0	2.0	0.5
METHYL ZIMATE						1.5
ALTAX (MBTS)		1.0				
CAPTAX (MBT)	0.5		0.5	0.3	0.5	0.5
Totals	171.5	172.5	171.0	171.5	171.5	171.5
Mooney Scorch @ 121°C						
Minimum Viscosity	55	58	50	56	59	58
Minutes to 5 pt. rise	13	15	18	14	9	10
ODR @ 171°C						
t _s 2, min.	1.3	1.5	1.7	1.3	1.2	1.2
ť 90, min.	18	14	17	14	11	10
Original Physicals Press Cured @ 171°	2					
Minutes Cured	20	15	20	15	15	10
Hardness Shore A	55	55	54	53	51	52
300% Modulus MPa	6.4	56	60	56	48	46
Tensile MPa	16.8	16.0	16.4	16.1	15.7	15.8
Elongation. %	610	630	650	650	670	700
Tear Die A, kN/m	38.7	40.5	41.4	35.2	44.0	38.7
Compression Set Method B 22 hrs @	70°C					
%	30	25	21	22	14	20

 Table 33: Accelerator Systems for Butyl Rubber (continued)

#### Cure Systems in Halobutyl Rubbers

The halobutyl polymerization process is similar to butyl's, but with an added halogenation step to create either chlorobutyl or bromobutyl. Halobutyl rubber has broader vulcanization latitude than butyl due to the reactive functionality, so it may be covulcanized with general purpose high-unsaturation elastomers like NR, BR and SBR, while maintaining the mostly saturated backbone structure. When only zinc oxide is used to crosslink halobutyl rubber, dehydrohalogenation forms carbon-carbon bonds and gives a very stable heat and compression set resistant compound.

Bromobutyl rubber is generally faster curing than chlorobutyl and has a wider range of cure systems. Bromobutyl can be cured without zinc oxide, or by sulfur alone. It is also the only butyl rubber that can be crosslinked by peroxides and a suitable coagent.

Table 54. Accelerator Systems for Bromobuly Rubber								
Compound	1	2	3	4	5			
Ingredients (phr)								
EXXON Bromobutyl 2255	100.00	100.00	100.00	100.00	100.00			
VANWAX H SPECIAL	2.00	2.00	2.00	2.00	2.00			
Stearic Acid	1.00	1.00	1.00	1.00	1.00			
Zinc Oxide	3.00	3.00	3.00	3.00	3.00			
N330 Carbon Black	35.00	35.00	35.00	35.00	35.00			
N990 Carbon Black	25.00	25.00	25.00	25.00	25.00			
Magnesium Oxide	1.50		1.50					
ALTAX (MBTS)			1.00	1.25	1.25			
MORFAX	2.00	1.25	1.00					
SULFADS					0.60			
DTDM		1.00		1.25	0.30			
Totals	169.50	168.25	169.50	168.50	168.15			
Mooney Scorch @ 121°C								
Minimum Viscosity	59	58	61	60	62			
Minutes to 5 pt. rise	51	47	48	47	25			
Original Physicals. Press Cured 20 min. @	171°C							
Hardness. Shore A	50	49	51	49	51			
300% Modulus, MPa	6.4	6.9	5.6	6.4	4.9			
Tensile. MPa	13.0	14.3	12.5	14.4	12.8			
Elongation, %	560	520	620	600	670			
Compression Set. Method B. 22 hrs @ 70	O°C							
%	14	14	19	13	18			

Table 34 provides a number of standard cure systems for bromobutyl:

Table 34:	Accelerator	Systems	for	Bromobuty	I Rubbei
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## Antioxidants in Butyl Rubber

Due to the low levels of unsaturation in butyl rubber, antioxidants are often not required. Severe service conditions or highly loaded compounds may need the addition of antioxidants. Amine antioxidants can interfere with cure rate and cure state, and should be tested for each application. Cure system changes alone may improve heat resistance sufficiently in butyl rubber.

The use of antioxidants, along with an accelerator change, for improving the heat resistance in a chlorobutyl compound is demonstrated in Table 35.

I	<u> </u>				
Ingredients (phr)	No AO (TMTD)	No AO (MBTS+ ZDBC)	AGERITE STALITE S	AGERITE SUPER- LITE S	AGERITE SUPER- FLEX S
Chlorobutyl 1068	100 00	100 00	100 00	100 00	100 00
Stearic Acid	1 00	1 00	1 00	1 00	1 00
Zinc Oxide	5.00	5.00	5.00	5.00	5.00
Sunpar 2280	20.00	20.00	20.00	20.00	20.00
N660 Carbon Black	60.00	60.00	60.00	60.00	60.00
METHYL TUADS	0.20				
ALTAX (MBTS)		0.25	0.25	0.25	0.25
BUTYL ZIMATE		0.25	0.25	0.25	0.25
AGERITE STALITE S			1.00		
AGERITE SUPERLITE S				1.00	
AGERITE SUPERFLEX S					1.00
Totals	186.20	186.50	187.50	187.50	187.50
Original Physicals, Press Cur	ed 16 min.	@ 160°C			
Hardness. Shore A	44	44	42	42	44
300% Modulus, MPa	4.2	3.5	3.4	2.8	3.8
Tensile, MPa	9.2	8.6	8.1	7.9	8.5
Elongation, %	560	610	600	640	600
Retained Physical Properties	After Aging	in Test Tub	es, 72 hrs. @	∂ 149°C	
Hardness, Pts. Change	+4	0	+4	+3	+5
Tensile, %	34	56	77	77	91
Elongation, %	80	70	75	67	63
Retained Physical Properties	After Aging	in Test Tub	es, 24 hrs. @	0 177℃	
Hardness, Pts. Change		-11	-4	-4	0
Tensile, %		40	35	35	51
Elongation, %		75	80	75	70

Table 35:	Improving	<b>Heat Resistance</b>	in Chlorobut	yl Rubber
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## ETHYLENE-PROPYLENE RUBBER (EPDM, EPM)

### **Base Compounds**

Ethylene propylene diene (EPDM) rubber is a versatile class of polymers that are used in a wide variety of applications ranging from low cost consumer goods to high end performance hoses, belts and electrical insulation. EPDM has outstanding weather resistance, excellent physical properties and can maintain good processability and physicals with very high filler loading levels. The wide range of grades and end-use applications allow for many options in both compounding and processing.

EPDM elastomers are supplied in a number of grades which vary considerably in curing rates based on the level of the nonconjugated diene monomer. EPDM and EPM polymers may be compounded with considerable amounts of oil, carbon blacks and mineral fillers.

Antioxidants improve heat aging in Ethylene Propylene Rubbers and are particularly important in peroxide cures.

Ingredients	Gum Compound (phr)	EPDM	EPM
1. Elastomer		100.0	100.0
2. Processing Aid	VANFRE AP-2	2.0	2.0
3. Activators:			
Fatty Acid	Stearic Acid	1.5	1.5
Metal Oxide	Zinc Oxide	5.0	5.0
4. Accelerators:			
Thiazole	CAPTAX (MBT)	1.5	
Thiuram	METHYL TUADS	0.9	
Thiuram	ETHYL TUADS	0.6	
<ol><li>Vulcanizing Agent</li></ol>			
Sulfur	Sulfur	1.5	
Organic Peroxide	VAROX		6.0-8.0
Coagent	VANAX MBM		1.0-2.0
	Totals	113.0	115.5-118.5

Gum compounds suitable for developing commercial formulations are as follows:

# Cure Systems in EPDM

Terpolymers (EPDM) use organic accelerators or peroxides to develop suitable cure rates. Copolymer types (EPM) require organic peroxides or radiation for vulcanization.

Table 36: Accelerator Systems for EPDM							
Ingredients (phr)	l Ne	Fast-Curii on-Bloom	ng ling	Heat & Comp. Se Resistant			
Vistalon [™] 2504	100.0	100.0	100.0	100.0	100.0		
Zinc Oxide	5.0	5.0	5.0	5.0	5.0		
Stearic Acid	1.0	1.0	1.0	1.0			
VANFRE AP-2	2.0	2.0	2.0	2.0	2.0		
VANPLAST PL	5.0	5.0	5.0	5.0			
N550 Carbon Black	70.0	70.0	70.0	70.0	70.0		
N990 Carbon Black	60.0	60.0	60.0	60.0	60.0		
Sunpar 2280	35.0	35.0	35.0	35.0	35.0		
AGERITE STALITE S	1.5	1.5	1.5	1.5			
METHYL NICLATE®					1.5		
Sulfur	2.0	2.0	1.5	0.5			
SULFADS	0.8						
ETHYL TELLURAC	0.8						
METHYL TUADS	0.8	0.6	0.9	3.0			
CAPTAX (MBT)	1.5		1.5				
BUTYL ZIMATE		2.0		3.0			
ALTAX (MBTS)		1.0					
ETHYL TUADS			0.6				
METHYL ZIMATE				3.0			
DTDM				2.0			
VAROX DCP-40KE					8.0		
VANAX MBM					1.5		
Totals	285.4	285.1	284.0	291.0	283.0		
Mooney Scorch @ 121°C							
Minimum Viscosity	37	36	37	34	46		
Minutes to 5 pt. rise	6	11	11	24	13		
Original Physicals, Press Cured	1 15 min. (	@ 171℃					
Hardness, Shore A	73	72	74	70	70		
100% Modulus, MPa	5.8	5.7	4.6	3.7	5.4		
Tensile, MPa	12.3	11.8	10.5	10.1	12.5		
Elongation, %	230	270	280	350	180		
Compression Set. Method B. 70	) hrs. @ 1	100°C					
%	47	50	47	32	10		

### Peroxide Crosslinking in EPDM

Organic peroxides can be used to crosslink elastomers, but are especially useful in maximizing resistance to heat aging and compression set in EPDM compounds. Peroxides work by decomposing to form free radicals when heated. These radicals then couple to create carbon-carbon bonds across polymer chains. The carbon-carbon bonds are stronger than the sulfide crosslinks and therefore provide better retention of properties after heat aging.

The dialkyl peroxides, such as VAROX DBPH-50, are the most commonly used in EPDM crosslinking. Peroxyketals are faster curing due to their shorter reaction times, but they also are less efficient in saturated polymers.

The compounds in Table 37 show the use of three dialkyl peroxides and one peroxyketal (VAROX 231):

· · · · · · · · · · · · · · · · · · ·								
Ingredients (phr)	VAROX 802-40KE	VAROX DCP-40KE	VAROX DBPH-50	VAROX 231				
Vistalon 7500	50.00	50.00	50.00	50.00				
Vistalon 2504	50.00	50.00	50.00	50.00				
N660 Carbon Black	65.00	65.00	65.00	65.00				
N990 Carbon Black	35.00	35.00	35.00	35.00				
Sunpar 2280	25.00	25.00	25.00	25.00				
AGERITE RESIN D	2.00	2.00	2.00	2.00				
VANFRE AP-2	1.50	1.50	1.50	1.50				
VAROX 802-40KE	6.00							
VAROX DCP-40KE		8.00						
VAROX DBPH-50			6.00					
VAROX 231				3.25				
Totals	234.50	236.50	234.50	231.75				
MDR, 0.5° Arc		@ 177°C		@ 171°C				
M⊢ (dN•m)	16.1	13.6	14.5	7.5				
t _s 1, min.	0.7	0.6	0.8	0.4				
ť 90, min.	9.0	5.0	11.0	1.2				
Tan Delta @ M _H	0.08	0.10	0.08	0.21				
Original Physicals, Press Cured	l t' 90 + 2 min <u>.</u>	@177°C		@ 171°C				
Hardness, Shore A	65	61	65	56				
100% Modulus, MPa	3.0	2.2	2.5	1.3				
Tensile, MPa	15.4	13.5	14.4	6.5				
Elongation, %	316	346	341	553				
Compression Set, Method B, 22	? hrs. @ 150°	C						
%	21	19	22	50				

# Table 37: VAROX Organic Peroxides in EPDM

# **Process Aids in EPDM**

The addition of VANFRE AP-2 to this EPM insulation compound increased mold flow while having no effect on the electrical properties after soaking in water for eight weeks at  $80^{\circ}$ C.

Ingredients (phr)	Control	VANFRE AP-2			
Vistalon 404	100.0	100.0			
Zinc Oxide	5.0	5.0			
Red Lead	5.0	5.0			
SR-350	1.0	1.0			
SRF Carbon Black	10.0	10.0			
Burgess KE	110.0	110.0			
AGERITE MA	1.5	1.5			
VAROX DCP-40KE	7.0	7.0			
VANFRE AP-2		2.0			
Total	239.5	241.5			
Original Physicals, Press Cured 12 min. @ 171°C					
Hardness, Shore A	63	62			
200% Modulus, MPa	6.6	4.8			
Tensile Strength, MPa	8.1	6.5			
Elongation, %	280	360			
Dielectric Constant					
Dry	4.1	4.3			
Water @ 80°C	4.6	5.1			
After 8 wks. in Water @ 80°C	4.6	5.2			
DuPont Spider Mold. 4.8 mm Orifice. 40 Tons Pressu	ıre				
Weight, g	14.76	17.87			

Table 38: VANFRE AP-2 in an EPDM Insulation Compound



The addition of VANFRE AP-2 to this heavily loaded mineral filled EPDM compound increased mold flow with only a negligible effect on the basic physical properties.

Ingredients (phr)	Control	VANFRE AP-2
Vistalon 2504	50.0	50.0
Vistalon 3708	50.0	50.0
Stearic Acid	1.0	1.0
Zinc Oxide	5.0	5.0
AGERITE SUPERLITE SOLID	1.5	1.5
Flexon 580	55.0	55.0
Diethethylene glycol	5.0	5.0
DIXIE CLAY	100.0	100.0
Mistron Vapor	100.0	100.0
Calcium silicate	40.0	40.0
METHYL TUADS	4.0	4.0
Sulfur	2.0	2.0
VANFRE AP-2		4.0
Total	416.5	417.5
Mooney Viscosity @ 100°C	66	50
Mooney Scorch @ 132°C		
Minimum Viscosity	45	37
Minutes to 5 pt. rise	6	7
Original Physicals, Press Cured 20 min. @ 160°C		
Hardness, Shore A	73	73
200% Modulus, MPa	3.0	3.0
Tensile Strength, MPa	11.1	10.5
Elongation, %	640	650
DuPont Spider Mold, 6.4 mm Orifice, 15 Tons Pressu	re	
Weight, g	9.96	13.15

Table 39: VANFRE AP-2 in Mineral Filled EPDM



### Antioxidants in EPDM Rubber Compounds

In sulfur cured EPDM, it is often sufficient to use only primary antioxidants. However, peroxide curing does require special attention to antioxidant selection because many types of antioxidants can interfere with peroxide crosslinking. Primary antioxidants can donate hydrogen atoms, which compete with the polymer for peroxide radicals and lessen the state of cure. VANOX ZMTI is recommended for use in combination with primary antioxidants in peroxide curing because it exhibits minimal interference with the crosslinking mechanism. Tables 40 thru 42 demonstrate the application of antioxidants in EPDM.

		AGERITE	AGERITE	VANOX	VANOX
Ingredients (phr)	No AO	STALITE S	RESIN D	NDBC	ZMTI
Vistalon 2504	100.0	100.0	100.0	100.0	100.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
VANPLAST R	5.0	5.0	5.0	5.0	5.0
N990 Carbon Black	75.0	75.0	75.0	75.0	75.0
N550 Carbon Black	75.0	75.0	75.0	75.0	75.0
Sunpar 2280	70.0	70.0	70.0	70.0	70.0
CAPTAX (MBT)	1.5	1.5	1.5	1.5	1.5
METHYL TUADS	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5
AGERITE STALITE S		3.0			
AGERITE RESIN D			3.0		
VANOX NDBC				3.0	
VANOX ZMTI					3.0
Totals	335.5	338.5	338.5	338.5	338.5
Original Physicals, Press Cu	ired 10 mi	in. @ 171°C			
Hardness, Shore A	63	64	66	64	68
300% Modulus, MPa	6.7	6.0	5.7	5.7	5.4
Tensile, MPa	8.9	8.3	8.0	7.6	7.8
Elongation, %	430	450	460	420	490
Retained Physical Properties	s After Agi	ing in Test Tube	es, 72 hrs. @	150°C	
Hardness, Pts. Change	+8	+8	+9	+7	+6
Tensile, %	112	130	131	132	113
Elongation, %	35	44	37	50	45
Retained Physical Properties	s After Aqi	ing in Test Tube	es, 168 hrs. @	€ 150°C	
Hardness, Pts. Change	+13	+8	+10	+8	+9
Tensile, %	117	126	137	135	127
Elongation, %	28	35	30	43	35
Retained Physical Properties	s After Agi	ing in Test Tube	es, 240 hrs. @	0 150℃	
Hardness, Pts. Change	+16	+12	+15	+11	+11
Tensile, %	109	123	133	145	132
Elongation, %	26	31	24	43	31

# Table 40: Antioxidants in Sulfur Cured EPDM

As shown in Figure 7 and Table 41, when one half of the dosage of AGERITE RESIN D is replaced with VANOX ZMTI in a peroxide cured EPDM compound, the combination develops outstanding heat resistance @  $150^{\circ}C$ 



Figure 7: Antioxidants in Peroxide Cured EPDM

		AGERITE	VANOX	VANOX ZMTI +
Ingredients (phr)	No AO	<b>RESIN D</b>	ZMTI	AGERITE RESIN D
Vistalon 2504	100.00	100.00	100.00	100.00
VANFRE AP-2	2.50	2.50	2.50	2.50
Zinc Oxide	5.00	5.00	5.00	5.00
N990 Carbon Black	10.00	10.00	10.00	10.00
Translink 37	110.00	110.00	110.00	110.00
Sunpar 2280	15.00	15.00	15.00	15.00
Silane A-172	1.00	1.00	1.00	1.00
Red Lead	5.00	5.00	5.00	5.00
VAROX DCP-40KE	8.00	8.00	8.00	8.00
AGERITE RESIN D		1.50		0.75
VANOX ZMTI			1.50	0.75
Totals	256.50	258.00	258.00	258.00
Mooney Scorch @ 132°C				
Minimum Viscosity	26	28	27	26
Minutes to 5 pt. rise	9	13	9	12
Original Physicals, Press	Cured 10	min. @ 171°C		
Hardness, Shore A	62	62	65	63
300% Modulus, MPa	4.3	3.3	4.6	3.7
Tensile, MPa	6.2	7.1	5.6	6.2
Elongation, %	500	680	470	570
Retained Physical Properti	es After Ag	ing in Test Tub	es, 240 hrs. (	₪ 150°C
Hardness, Pts. Change	Brittle	+6	+3	+2
Tensile, %	Brittle	78	53	114
Elongation, %	Brittle	60	32	96

### Table 41: Antioxidants in a Peroxide Cured EPDM Wire & Cable Compound



Figure 8: Antioxidant Performance in a GP EPDM Compound Heat Aged @ 175°C

Table 42: Antioxidants in a Peroxide	Cured EPM/EPDM GP Compound
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		ACEDITE	VANOX	VANOX	VANOX ZMTI +	VANOX ZMTI +
Ingredients (phr)	No AO	RESIN D	CDPA	ZMTI	RESIN D	CDPA
Vistalon 706	70.0	70.0	70.0	70.0	70.0	70.0
Vistalon 7500	30.0	30.0	30.0	30.0	30.0	30.0
N550 Carbon Black	110.0	110.0	110.0	110.0	110.0	110.0
Paraffinic Oil	45.0	45.0	45.0	45.0	45.0	45.0
VAROX 802-40KE	6.0	6.0	6.0	6.0	6.0	6.0
VANAX MBM	1.0	1.0	1.0	1.0	1.0	1.0
VANOX ZMTI				2.0	2.0	2.0
VANOX CDPA			2.0			1.0
AGERITE RESIN D		2.0			1.0	
Totals	262.0	264.0	264.0	264.0	265.0	265.0
Original Physicals, Press	Cured t' 9	0 + 2 min. @	₽ 177°C			
Hardness, Shore A	68	69	65	70	69	68
100% Modulus, MPa	3.9	4.4	3.6	4.3	4.0	3.6
Tensile Strength, MPa	14.0	14.0	12.9	13.3	13.4	12.4
Elongation, %	287	304	306	272	302	283
Compression Set, Method	I B, 70 hrs	s. @ 150°C				
%	30	26	32	27	31	32
Retained Physical Proper	ties After J	Aging in Air,	70 hrs. @	175℃		
Tensile, %	53	68	63	78	88	82
Elongation, %	85	72	94	109	85	101
Retained Physical Proper	ties After J	Aging in Air,	168 hrs. @	₽ 150°C		
Tensile, %	73	83	78	97	96	93
Elongation, %	91	80	96	111	98	107

## **NEOPRENE RUBBER (CR)**

### Neoprene Base Compound

Neoprene is made from chloroprene monomers and may be a homopolymer or a mixture with other polymerizables to form polychloroprene. When properly compounded, Neoprene provides excellent resistance to degradation from heat aging, ozone, UV, abrasion, fire and chemicals.

Neoprene is generally sold as two main types: G type and W type. The G types are sulfur modified and can be cured with metal oxides alone. Zinc Oxide and magnesia function as the vulcanizing agent in polychloroprene. The W types require an additional accelerator in their base formulations to cure at acceptable speeds. Antioxidants are included in all Neoprene base compounds to assure good aging properties.

Ingredients	Gum Compound (phr)	G-type	W-type
1. Elastomer	Neoprene GNA	100.0	
	Neoprene W		100.0
2. Modifier	Stearic Acid	0.5	0.5
3. Vulcanization Retarder	ALTAX (MBTS)	0.5-1.0	0.5-1.0
4. Antioxidant	AGERITE STALITE S	2.0	2.0
5. Accelerators	VANAX CPA		1.5
	Thioureas		0.2-3.0
<ol><li>Vulcanizing Agents</li></ol>	Magnesia (High-Activity)	4.0	4.0
	Zinc Oxide	5.0	5.0
	Totals	112.0-112.5	113.7-117.0

The following are typical gum compounds of Neoprene:

While pure gum Neoprene vulcanizates exhibit good physical properties, fillers are used in practically all commercial formulations in order to provide the optimal balance of processing and physical properties. A comparison of properties obtained with various carbon blacks and mineral fillers in Neoprene W is shown in Tables 43 and 44.

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	
MT N990 Carbon Black							
25 phr	4.1	16.4	650	47	21.8	9	
50"	9.2	17.2	540	54	33.2	10	
75"	14.4	16.8	530	61	40.1	9	
100 "	16.1	16.4	320	66	35.7	9	
SRF N770 Ca	arbon Blaci	k					
25 phr	9.7	21.8	480	53	28.7	9	
50 "		25.7	280	67	24.4	7	
75"		25.8	200	75	28.7	8	
FEF N550 Ca	arbon Black	(					
25 phr	14.1	18.6	370	57	30.5	9	
50 "		26.4	230	70	28.7	9	
75"		22.6	120	85	21.8	10	
HAF N330 Ca	arbon Blaci	k					
25 phr	11.9	18.5	360	55	34.9	10	
50 "		24.7	220	70	26.1	12	
75"		22.7	120	84	22.6	12	
HAF N330/M	T N990 (eq	ual parts)					
25 phr	8.8	21.4	520	53	24.4	9	
50 "	19.6	22.9	350	61	34.9	10	
75"		24.3	230	74	38.3	11	
Base Comp	ound	Ingredien	ts		phr		

Table 43: Carbon Black Loading	j in Neoprene W
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Base Compound	Ingredients	phr
	Neoprene W	100.0
	VANFRE AP-2	2.0
	Stearic Acid	0.5
	Maglite D	4.0
	AGERITE STALITE S	2.0
	VANPLAST PL	5.0
	Zinc Oxide	5.0
	THIATE [®] EF-2	0.5
	Total	119.0
Compounds cured 20	min @ 153°C	

Compounds cured 20 min. @  $153^\circ\text{C}$  Tear strength measured on Die A samples

Compression set measured after 22 hrs. @ 100°C

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	
Calcium Carbonate (ground)							
35 phr	2.2	13.4	720	47	14.8	12	
75"	2.1	11.4	720	54	15.7	19	
110 "	2.2	8.8	700	60	17.6	24	
180 "	2.4	6.1	630	72	20.9	31	
DIXIE CLAY							
35 phr	4.5	17.2	830	52	38.3	34	
75 [°] "	6.3	15.8	790	60	48.8	51	
100 "	9.0	13.3	710	71	62.8	63	
180 "		12.9	220	82	42.0	69	
Hi-Sil 233							
25 phr	3.1	26.1	850	51	58.5	36	
50 "	6.7	19.3	800	81	91.6	76	
McNAMEE C	LAY						
35 phr	4.0	16.0	770	51	22.6	24	
75 "	5.0	14.2	770	60	32.2	34	
100 "	6.6	11.0	720	67	44.5	43	
180 "	8.0	8.0	420	80	60.3	50	
Silene 732D							
25 phr	3.9	16.5	740	53	31.3	29	
50"	5.8	13.9	740	67	54.1	48	
75"	9.4	12.6	580	80	86.4	71	
Base Comp	ound	Ingredien	ts		phr		
		Neoprene V	V		100.0		
		VANFRE AI	P-2		2.0		
		Stearic Acid	ł		0.5		
		Maglite D			4.0		
AGERITE STALITE S				2.0			
VANPLAST PL				2.0			
	Zinc Oxide				5.0		
THIATE EF-2				0.5			
		Total			116.0		
Compounds	cured 20 m	iin. @ 153°C					
Tear strength measured on Die A samples							
Compression set measured after 22 hrs. @ 100°C							

Table 44: Mineral Filler Loading in Neoprene W

# **Plasticizers and Process Aids in Neoprene**

As shown in Table 45, VANFRE AP-2 is an effective processing aid in this 70 durometer compound. VANFRE AP-2 developed a good state of cure, compression set, Mooney storage stability and excellent mold flow both before and after storage. No bloom was noted on the VANFRE AP-2 compounds after 4 weeks at room temperature.

Ingredients (phr)	Control	VANFRE AP-2
Neoprene W	100.0	100.0
Stearic Acid	0.5	0.5
Maglite D	4.0	4.0
AGERITE STALITE S	2.0	2.0
VANPLAST PL	5.0	5.0
N990 Carbon Black	100.0	100.0
Zinc Oxide	5.0	5.0
VANAX CPA	1.0	1.0
VANFRE AP-2		3.0
Totals	217.5	220.5
Mooney Scorch @ 121°C After 3 wks. Storage @	Room Temp.	
Minimum Viscosity	58	62
Minutes to 5 pt. rise	9	6
Original Physicals, Press Cured 30 min. @ 153°C		
Hardness, Shore A	69	69
200% Modulus, MPa	7.7	7.1
Tensile, MPa	12.3	12.0
Elongation, %	350	390
Compression Set. Method B. 70 hrs. @ 100°C		
%	19.4	25.4
Physical Properties After Heat Aging in Test Tubes,	96 hrs. @ 121	°C
Hardness, Pts. Change	+7	+6
Tensile, % Change	+2	-1
Elongation, % Change	-14	-21
DuPont Spider Mold, 6.4 mm Orifice, 20 Tons Pres	sure	
Press cured 20 min. @ 153°C, Weight, g	15.9	21.6
After one week storage @ 38°C, Weight, g	13.4	15.4

Table 45	VANERE	ΔP ₋ 2 in	Neonre	w one
Table 4J.		AF "4 III	neopre	211C VV



#### Cure Systems in Neoprene

The crosslinking of polychloroprenes is fundamentally different from the crosslinking of natural rubber because metal oxides and not sulfur are the vulcanizing agents required for cure. The generally accepted theory is that the metal oxide initiates the curing process by forming metal chloride, which then reacts with neighboring polymer chains.

Accelerators are very important in the curing of W type Neoprene. They affect both the rate of cure and the length and number of crosslinks that form. Thioureas are commonly used in Neoprene but give poor processing safety (scorch resistance). Sulfur can be used to increase dynamic properties. Thiurams are used to aid in retarding other cure systems. The studies in Tables 46 and 47 compare various Vanderbilt accelerator systems for Neoprene.

	VANAX	VANAX	UNADS,	THIATE
Ingredients (phr)	PML	CPA	DOTG	EF-2
Neoprene W	100.00	100.00	100.00	100.00
Stearic Acid	0.50	0.50	0.50	0.50
Maglite D	4.00	4.00	4.00	4.00
AGERITE STALITE S	2.00	2.00	2.00	2.00
VANPLAST PL	5.00	5.00	5.00	5.00
N990 Carbon Black	75.00	75.00	75.00	75.00
Zinc Oxide	5.00	5.00	5.00	5.00
VANAX PML	1.00			
VANAX CPA		1.50		
Sulfur			1.00	
UNADS			1.00	
VANAX DOTG			1.00	
THIATE EF-2				0.75
Totals	192.50	193.00	194.50	192.25
Mooney Scorch @ 121°C				
Minimum Viscosity	43	41	38	43
Minutes to 5 pt. rise	24	19	40	13
Original Physicals, Press Cured	20 min. @ 15	53°C		
Hardness, Shore A	64	55	57	61
200% Modulus, MPa	7.0	4.3	4.1	5.6
Tensile, MPa	13.8	13.4	13.0	14.3
Elongation, %	400	530	590	480
Tear Die A, kN/m	39.6	42.2	56.3	30.8
Compression Set, Method B, 70 h	nrs. @ 100°C			
%	27	27	59	13

Table 46: Accelerator Comp	oarison in Carbon	Black Filled Nec	prene W
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	VANAX	VANAX	UNADS,	THIATE
Ingredients (phr)	PML	CPA	DOTG	EF-2
Neoprene W	100.00	100.00	100.00	100.00
Stearic Acid	0.50	0.50	0.50	0.50
Maglite D	4.00	4.00	4.00	4.00
AGERITE SUPERLITE SOLID	2.00	2.00	2.00	2.00
VANPLAST PL	10.00	10.00	10.00	10.00
DIXIE CLAY	100.00	100.00	100.00	100.00
Zinc Oxide	5.00	5.00	5.00	5.00
VANAX PML	1.00			
VANAX CPA		1.50		
Sulfur			1.00	
UNADS			1.00	
VANAX DOTG			1.00	
THIATE EF-2				0.75
Totals	222.50	223.00	224.50	222.25
Mooney Scorch @ 121°C				
Minimum Viscosity	35	35	28	33
Minutes to 5 pt. rise	14	16	46	18
Original Physicals, Press Cured	30 min. @ 15	53°C		
Hardness, Shore A	64	61	62	65
200% Modulus, MPa	4.3	3.6	3.8	4.1
Tensile, MPa	13.1	12.8	15.2	13.8
Elongation, %	530	740	740	700
Tear Die A, kN/m	37.1	35.2	34.3	34.3
Compression Set, Method B, 70 h	nrs. @ 100°C			
%	67	67	70	53

Table 47: Accelerator Comparison in Mineral Filled Neoprene W

### Antioxidants in Neoprene

An amine antioxidant is standard in most formulations of both G types and W types of Neoprene. The Neoprene G types have inherently good strength and flex-fatigue resistance, while the Neoprene W types offer improved heat and compression set resistance. VANOX ZMTI, when used in addition to AGERITE STALITE S or AGERITE SUPERFLEX SOLID G will improve the heat and flex resistance of both G and W type Neoprene. The use of antioxidants in Neoprene GN and W types are compared in Tables 48 thru 51.

Ingredients (phr)	No AO	AGERITE STALITE S	AGERITE SUPERFLEX SOLID G
	100.0	100.0	100.0
	2.5	100.0	100.0
	2.5	2.5	2.5
Maglita D	4.0	0.5	0.5
Stoarie Acid	4.0	4.0	4.0
NOOD Carbon Black	75.0	75.0	75.0
Zipe Ovide	75.0	75.0	75.0
	5.0	2.0	5.0
		2.0	
AGERITE SUFERFLEX SOLID G			2.0
Totals	190.0	192.0	192.0
Mooney Scorch @ 121°C			
Minimum Viscosity	25	27	26
Minutes to 5 pt. rise	39	35	34
Original Physicals Press Cured 45	min @ 1539	<u>^</u>	
Hardness Shore A	64	63	64
200% Modulus MPa	1.8	4.8	10
Topsilo MPa	4.0	11.0	4.5 11 /
Flongation %	480	500	470
	400	500	470
Physical Properties After Heat Aging	in Test Tubes,	72 hrs. @ 121°C	
Hardness, Pts. Change	+13	+7	+6
Tensile, % Change	-9	+2	+2
Elongation, % Change	-69	-30	-23
Physical Properties After Heat Aging	in Test Tubes,	168 hrs. @ 121°C	
Hardness, Pts. Change	+23	+12	+11
Tensile, %	-7	+9	+9
Elongation, %	-87	-50	-43

# Table 48: Antioxidants in Neoprene GN

Ingredients (phr)	No AO	AGERITE STALITE S	AGERITE SUPERFLEX SOLID G
Neoprene W	100.0	100.0	100.0
Stearic Acid	0.5	0.5	0.5
Maglite D	4.0	4.0	4.0
Light Process Oil	5.0	5.0	5.0
VÄNPLAST PL	5.0	5.0	5.0
VANFRE AP-2	1.0	1.0	1.0
N770 Carbon Black	60.0	60.0	60.0
Zinc Oxide	5.0	5.0	5.0
VANAX CPA	1.5	1.5	1.5
AGERITE STALITE S		2.0	
AGERITE SUPERFLEX SOLID G			2.0
Totals	182.0	184.0	184.0
Mooney Scorch @ 121°C			
Minimum Viscosity	44	38	40
Minutes to 5 pt. rise	12	12	11
Original Physicals. Press Cured 30	min. @ 153°0	0	
Hardness, Shore A	66	65	65
200% Modulus, MPa	12.2	10.6	10.7
Tensile, MPa	19.0	19.2	18.7
Elongation, %	300	350	360
Tear Die A, kN/m	44.5	44.5	45.3
Compression Set, Method B, 70 hrs.	@ 100°C		
%	33	30	31
Physical Properties After Heat Aging	in Test Tubes,	72 hrs. @ 121°C	
Hardness, Pts. Change	+12	+5	+5
Tensile, % Change	-40	-12	-10
Elongation, % Change	-70	-11	-14
Physical Properties After Heat Aging	in Test Tubes,	168 hrs. @ 121°C	
Hardness, Pts. Change	+22	+9	+10
Tensile, %	-24	-11	-13
Elongation, %	-83	-20	-33

Table 49: Antioxidants in Neoprene W

Neoprine GN         100.0         100.0         100.0         100.0         100.0           Stearic Acid         2.0         2.0         2.0         2.0         2.0           Maglite D         4.0         4.0         4.0         4.0         4.0           N660 Carbon Black         45.0         45.0         45.0         45.0           Circo Light Oil         4.0         4.0         4.0         4.0           Zinc Oxide         5.0         5.0         5.0         5.0           VANAX CPA         1.0         1.0         1.0         1.0           VANOX ZMTI          3.0         2.0            AGERITE SUPERFLEX SOLID G           1.0         3.0           Totals         161.0         164.0         164.0         164.0           Mooney Scorch @ 121°C         Minimum Viscosity         21         23         21         19           Minutes to 5 pt. rise         9         5         5         8         Original Physicals, Press Cured 20 min. @ 160°C           Hardness, Shore A         70         73         70         68         200%         Modulus, MPa         9.2         9.0         9.2         7.7 </th <th>Ingredients (phr)</th> <th>No AO</th> <th>VANOX ZMTI</th> <th>VANOX ZMTI + AO</th> <th>AGERITE SUPERFLEX SOLID G</th>	Ingredients (phr)	No AO	VANOX ZMTI	VANOX ZMTI + AO	AGERITE SUPERFLEX SOLID G
Netopretie GN100.0100.0100.0100.0Stearic Acid2.02.02.02.0Maglite D4.04.04.04.04.0N660 Carbon Black45.045.045.045.0Circo Light Oil4.04.04.04.0Zinc Oxide5.05.05.05.0VANAX CPA1.01.01.01.0VANOX ZMTI3.02.0AGERITE SUPERFLEX SOLID G1.03.0Totals161.0164.0164.0164.0Mooney Scorch @ 121°C11232119Minimum Viscosity21232119Minutes to 5 pt. rise9558Original Physicals, Press Cured 20 min. @ 160°C18.017.6Hardness, Shore A70737068200% Modulus, MPa9.29.09.27.7Tensile, MPa18.518.018.017.6Elongation, %390480480420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°CHardness, Pts. Change+5+3+6+5Tensile, %96969999Elongation, %67<		100.0	100.0	100.0	100.0
Steam Ard2.02.02.02.02.0Maglite D4.04.04.04.04.0N660 Carbon Black45.045.045.045.0Circo Light Oil4.04.04.04.04.0Zinc Oxide5.05.05.05.0VANAX CPA1.01.01.01.0VANOX ZMTI3.02.0AGERITE SUPERFLEX SOLID G1.03.0Totals161.0164.0164.0164.0Money Scorch @ 121°C110100°C19Minutes to 5 pt. rise9558Original Physicals, Press Cured 20 min. @ 160°C18.017.6Hardness, Shore A70737068200% Modulus, MPa9.29.09.27.7Tensile, MPa18.518.018.017.6Elongation, %390480480420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°CHardness, Pts. Change+5+3+6+5Tensile, %96969999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°C <td< td=""><td>Stoarie Acid</td><td>2.0</td><td>2.0</td><td>2.0</td><td>2.0</td></td<>	Stoarie Acid	2.0	2.0	2.0	2.0
Magne D4.04.04.04.04.0N660 Carbon Black45.045.045.045.045.0Circo Light Oil4.04.04.04.04.0Zinc Oxide5.05.05.05.0VANAX CPA1.01.01.01.0VANOX ZMTI3.02.0AGERITE SUPERFLEX SOLID G1.03.0Totals161.0164.0164.0164.0Mooney Scorch @ 121°C11232119Minimum Viscosity21232119Minutes to 5 pt. rise9558Original Physicals, Press Cured 20 min.@ 160°C18.017.6Hardness, Shore A70737068200% Modulus, MPa9.29.09.27.7Tensile, MPa18.518.018.017.6Elongation, %390480480420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°CHardness, Pts. Change+5+3+6+5Tensile, %96969999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°C	Maglita D	2.0	2.0	2.0	2.0
Notice Calculation Black43.043.043.043.043.043.0Circo Light Oil4.04.04.04.0Zinc Oxide5.05.05.0VANAX CPA1.01.01.0VANOX ZMTI3.02.0AGERITE SUPERFLEX SOLID GAGERITE SUPERFLEX SOLID G103.03.0Totals161.0164.0164.0Mooney Scorch @ 121°CMinimum Viscosity212321199558Original Physicals, Press Cured 20 min. @ 160°CHardness, Shore A70737068200% Modulus, MPa9.29.09.27.7Tensile, MPa18.518.018.017.6Elongation, %390480480420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°CHardness, Pts. Change+5+3+6+5Tensile, %96969999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°CHardness, Pts. Change+10+7+7+10Tensile, %93 </td <td>NG60 Carbon Blook</td> <td>4.0</td> <td>4.0</td> <td>4.0</td> <td>4.0</td>	NG60 Carbon Blook	4.0	4.0	4.0	4.0
Child Light Onit4.04.04.04.04.04.04.0Zinc Oxide $5.0$ $5.0$ $5.0$ $5.0$ $5.0$ VANAX CPA $1.0$ $1.0$ $1.0$ $1.0$ $1.0$ VANOX ZMTI $3.0$ $2.0$ AGERITE SUPERFLEX SOLID G $1.0$ $3.0$ Totals $161.0$ $164.0$ $164.0$ $164.0$ Mooney Scorch @ $121^{\circ}$ C $1.0$ $3.0$ Minutes to 5 pt. rise $9$ $5$ $5$ $8$ Original Physicals, Press Cured 20 min.@ $160^{\circ}$ CHardness, Shore A $70$ $73$ $70$ $68$ $200\%$ Modulus, MPa $9.2$ $9.0$ $9.2$ $7.7$ Tensile, MPa $18.5$ $18.0$ $17.6$ Elongation, % $390$ $480$ $420$ DeMattia Flex FatigueKilocycles to $1.9  {\rm cm}$ $5$ $130$ $130$ $52$ Compression Set, Method B, 70 hrs. @ $100^{\circ}$ C $\%$ $59$ $71$ $66$ $62$ Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ $121^{\circ}$ CHardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, % $96$ $96$ $99$ $99$ Elongation, % $67$ $68$ $73$ $79$ Retained Physical Properties After Heat Aging in Test Tubes, $168  hrs.$ @ $121^{\circ}$ CHardness, Pts. Change $+10$ $+7$ $+7$ $+10$ <td>Circo Light Oil</td> <td>45.0</td> <td>45.0</td> <td>45.0</td> <td>45.0</td>	Circo Light Oil	45.0	45.0	45.0	45.0
Zille Oxide $3.0$ $3.0$ $3.0$ $3.0$ $3.0$ $5.0$ VANAX CPA $1.0$ $1.0$ $1.0$ $1.0$ VANOX ZMTI $3.0$ $2.0$ AGERITE SUPERFLEX SOLID G $$ $1.0$ $3.0$ Totals $161.0$ $164.0$ $164.0$ $164.0$ Mooney Scorch @ $121^{\circ}$ C $$ $$ Minimum Viscosity $21$ $23$ $21$ $19$ Minutes to 5 pt. rise $9$ $5$ $5$ $8$ Original Physicals, Press Cured 20 min. @ $160^{\circ}$ C $$ Hardness, Shore A $70$ $73$ $70$ $68$ $200^{\circ}$ Modulus, MPa $9.2$ $9.0$ $9.2$ $7.7$ Tensile, MPa $18.5$ $18.0$ $18.0$ $17.6$ Elongation, % $390$ $480$ $480$ $420$ DeMattia Flex FatigueKilocycles to $1.9$ cm $5$ $130$ $130$ $52$ Compression Set, Method B, 70 hrs. @ $100^{\circ}$ C $\%$ $59$ $71$ $66$ $62$ Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ $121^{\circ}$ CHardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, % $96$ $96$ $99$ $99$ Elongation, % $67$ $68$ $73$ $79$ Retained Physical Properties After Heat Aging in Test Tubes, $168$ hrs. @ $121^{\circ}$ CHardness, Pts. Change $+10$ $+7$ $+7$ $+10$ T	Zino Ovido	4.0	4.0	4.0	4.0
VANAX CFA       1.0       1.0       1.0       1.0       1.0       1.0       1.0         AGERITE SUPERFLEX SOLID G        3.0       2.0          AGERITE SUPERFLEX SOLID G         1.0       3.0         Totals       161.0       164.0       164.0       164.0         Mooney Scorch @ 121°C         1.0       3.0         Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ 160°C            Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue		1.0	5.0	5.0	5.0
AGERITE SUPERFLEX SOLID G         1.0       3.0         AGERITE SUPERFLEX SOLID G         1.0       3.0         Totals       161.0       164.0       164.0       164.0         Mooney Scorch @ 121°C         1.0       3.0         Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ 160°C            Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue          66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C         +-         Hardness, Pts. Change       +5       +3       +6       +5       +5         Tensile, %       96       96       99       99       99       Elongation, %       67       68       73       79         Retained Physical Properties After		1.0	2.0	1.0	1.0
AGERITE SUPERFLEX SOLID G         1.0       3.0         Totals       161.0       164.0       164.0       164.0         Mooney Scorch @ 121°C       Minimum Viscosity       21       23       21       19         Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ 160°C       Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7       7       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @ 100°C       %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C       14rdness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       121°C         Hardness, Pts. Change       <			3.0	2.0	
Totals161.0164.0164.0164.0Mooney Scorch @ 121°CMinimum Viscosity21232119Minutes to 5 pt. rise9558Original Physicals, Press Cured 20 min. @ 160°CHardness, Shore A70737068200% Modulus, MPa9.29.09.27.7Tensile, MPa18.518.018.017.6Elongation, %390480480420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C121°C121°CHardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, %9696999999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°C121°CHardness, Pts. Change $+10$ $+7$ $+7$ $+10$ Tensile, %93979997Elongation, %49556060	AGERITE SUPERFLEX SOLID G			1.0	3.0
Mooney Scorch @ 121°C         Minimum Viscosity       21       23       21       19         Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ 160°C       Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @ 100°C       %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C       121°C       14rdness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       99       99       121°C         Hardness, Pts. Change       +1       +5       +3       +6       +5       18 hrs. @ 121°C         Hardness, Pts. Change       +10       +7       +7       +10       99       99       99       99       99       99	Totals	161.0	164.0	164.0	164.0
Minimum Viscosity       21       23       21       19         Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ $160^{\circ}$ C       Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       5       130       130       52         Compression Set, Method B, 70 hrs. @ $100^{\circ}$ C       %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ $121^{\circ}$ C       Hardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, %       96       96       99       99       99       Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ $121^{\circ}$ C       Hardness, Pts. Change $+10$ $+7$ $+7$ $+10$ Tensile, %       93       97       99       97 $=97$ $=97$ $=97$ $=97$ $=97$ <td>Mooney Scorch @ 121°C</td> <td></td> <td></td> <td></td> <td></td>	Mooney Scorch @ 121°C				
Minutes to 5 pt. rise       9       5       5       8         Original Physicals, Press Cured 20 min. @ $160^{\circ}$ C       Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @ $100^{\circ}$ C       %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ $121^{\circ}$ C       Hardness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       99       99       99       99       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90       90	Minimum Viscosity	21	23	21	19
Original Physicals, Press Cured 20 min. @ $160^{\circ}$ C         Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue         Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @ $100^{\circ}$ C         %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ $121^{\circ}$ C         Hardness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99         Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ $121^{\circ}$ C         Hardness, Pts. Change       +10       +7       +7       +10         Tensile, %       93       97       99       97       97         Elongation, %       49       55       60       60	Minutes to 5 pt. rise	9	5	5	8
Hardness, Shore A       70       73       70       68         200% Modulus, MPa       9.2       9.0       9.2       7.7         Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @ 100°C       %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C       121°C       14rdness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       100°C       79         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C       121°C       14rdness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       121°C         Hardness, Pts. Change       +10       +7       +7       +10         Tensile, %       93       97       99       97       99       97         Elongation, %       49       55       60       60	Original Physicals, Press Cured 20 n	nin @ 16(	J°C		
10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10       10 <t< td=""><td>Hardness Shore A</td><td>70</td><td>73</td><td>70</td><td>68</td></t<>	Hardness Shore A	70	73	70	68
Tensile, MPa       18.5       18.0       18.0       17.6         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @       100°C $\%$ 59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @       121°C       Hardness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99       99       Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @       121°C       Hardness, Pts. Change       +10       +7       +7       +10         Tensile, %       93       97       99       97       97       99       97         Flopnation, %       67       68       60       60       60	200% Modulus MPa	92	90	92	77
Elongation, %       390       480       10.0       17.0         Elongation, %       390       480       480       420         DeMattia Flex Fatigue       Kilocycles to 1.9 cm       5       130       130       52         Compression Set, Method B, 70 hrs. @       100°C $\%$ 59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @       121°C       121°C         Hardness, Pts. Change       +5       +3       +6       +5         Tensile, %       96       96       99       99         Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @       121°C         Hardness, Pts. Change       +10       +7       +7         Flopmation       93       97       99       97         Elongation, %       49       55       60       60	Tensile MPa	18.5	18.0	18.0	17.6
Linguistin, $7^{0}$ 500400400420DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. @ 100°C $\%$ 59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°CHardness, Pts. Change+5+3+6+5Tensile, $\%$ 96969999Elongation, $\%$ 67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°CHardness, Pts. Change+10+7+7+10Tensile, $\%$ 93979997Elongation, $\%$ 49556060	Elongation %	300	480	480	420
DeMattia Flex FatigueKilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. (a) $100^{\circ}$ C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. (a) $121^{\circ}$ CHardness, Pts. Change+5+3+6+5Tensile, %969999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. (a) $121^{\circ}$ CHardness, Pts. Change+10+7+7+10Tensile, %93979997Elongation, %49556060	Elongation, 70	000	400	400	420
Kilocycles to 1.9 cm513013052Compression Set, Method B, 70 hrs. (a) $100^{\circ}$ C%59716662Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. (a) $121^{\circ}$ CHardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, %969999Elongation, %67687379Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. (a) $121^{\circ}$ CHardness, Pts. Change $+10$ $+7$ $+7$ $+10$ Tensile, %93979997Elongation, %49556060	DeMattia Flex Fatigue				
Compression Set, Method B, 70 hrs. (a) $100^{\circ}$ C         %       59       71       66       62         Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. (a) $121^{\circ}$ C         Hardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, %       96       96       99       99         Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, $168$ hrs. (a) $121^{\circ}$ C       Hardness, Pts. Change $+10$ $+7$ $+7$ $+10$ Tensile, %       93       97       99       97       97         Elongation, %       49       55       60       60	Kilocycles to 1.9 cm	5	130	130	52
%         59         71         66         62           Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C           Hardness, Pts. Change         +5         +3         +6         +5           Tensile, %         96         96         99         99           Elongation, %         67         68         73         79           Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°C         Hardness, Pts. Change         +10         +7         +7         +10           Tensile, %         93         97         99         97         55         60         60	Compression Set, Method B, 70 hrs.	@ 100°C			
Retained Physical Properties After Heat Aging in Test Tubes, 72 hrs. @ 121°C           Hardness, Pts. Change         +5         +3         +6         +5           Tensile, %         96         96         99         99           Elongation, %         67         68         73         79           Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°C         121°C           Hardness, Pts. Change         +10         +7         +7         +10           Tensile, %         93         97         99         97           Elongation, %         49         55         60         60	%	59	71	66	62
Hardness, Pts. Change $+5$ $+3$ $+6$ $+5$ Tensile, %       96       96       99       99         Elongation, %       67       68       73       79         Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs.       @ 121°C         Hardness, Pts. Change $+10$ $+7$ $+7$ $+10$ Tensile, %       93       97       99       97         Elongation, %       49       55       60       60	Retained Physical Properties After H	eat Aging	in Test Tube	es, 72 hrs. @ 12	21°C
Tensile, %         96         96         99         99           Elongation, %         67         68         73         79           Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs.         @ 121°C           Hardness, Pts. Change         +10         +7         +7         +10           Tensile, %         93         97         99         97           Elongation, %         49         55         60         60	Hardness, Pts. Change	+5	+3	+6	+5
Elongation, %         67         68         73         79           Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs.         @ 121°C           Hardness, Pts. Change         +10         +7         +7         +10           Tensile, %         93         97         99         97           Elongation, %         49         55         60         60	Tensile, %	96	96	99	99
Retained Physical Properties After Heat Aging in Test Tubes, 168 hrs. @ 121°CHardness, Pts. Change+10+7+7+10Tensile, %93979997Elongation %49556060	Elongation, %	67	68	73	79
Hardness, Pts. Change         +10         +7         +7         +10           Tensile, %         93         97         99         97           Elongation %         49         55         60         60	Retained Physical Properties After H	eat Aging	in Test Tube	es, 168 hrs. @	121℃
Tensile, %         93         97         99         97           Elongation %         49         55         60         60	Hardness, Pts. Change	+10	+7	+7	+10
Elongation % 49 55 60 60	Tensile, %	93	97	99	97
	Elongation, %	49	55	60	60

### Table 50: VANOX ZMTI in Neoprene GN

Since VANOX ZMTI contains zinc, it contributes to scorch in Neoprene compounds. As shown in Figure 9 and Table 51, the addition of 0.2 to 0.5 phr of a sulfenamide, such as DURAX (CBS), improves both scorch and flex resistance without affecting heat resistance.



Figure 9:	Improved Heat	& Flex Resistance	in Neoprene W
i igaio ei	In provou mout		

Ingredients (phr)	AGERITE STALITE S	AGERITE STALITE S + VANOX ZMTI	AGERITE STALITE S + VANOX ZMTI + DURAX (CBS)
Neoprene W	100.0	100.0	100.0
Stearic Acid	0.5	0.5	0.5
Maglite D	4.0	4.0	4.0
Naphthenic Oil	10.0	10.0	10.0
N990 Carbon Black	75.0	75.0	75.0
Zinc Oxide	5.0	5.0	5.0
VANAX CPA	1.5	1.5	1.5
AGERITE STALITE S	2.0	2.0	2.0
VANOX ZMTI		1.0	1.0
DURAX (CBS)			0.5
Totals	198.0	199.0	199.5
Original Physicals, Press Cured	l 20 min. @ 160°	C	
Hardness, Shore A	56	61	59
200% Modulus, MPa	4.1	5.0	4.6
Tensile, MPa	14.5	13.4	13.6
Elongation, %	470	460	470
DeMattia Flex Fatigue			
Kilocycles to 1.9 cm	11	88	504
Retained Physical Properties A	fter Heat Aging in	n Test Tubes, 168 h	rs. @ 121°C
Hardness, Pts. Change	+10	+5	+6
Tensile, %	80	84	89
Elongation, %	85	91	94

Table 51:	VANOX	ZMTI	Antioxidant	in	Neoprene	W
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#### ACRYLONITRILE-BUTADIENE RUBBER (NBR)

# Nitrile Gum Base

Nitrile rubbers are supplied with a range of acrylonitrile levels generally classified as high, medium and low. The sulfur dosage in a given formulation is based on the unsaturated (butadiene) portion of the elastomer.

Organic accelerators are used in compounding, along with zinc oxide and stearic acid activators.

While easier processing grades are available, ester type plasticizers are generally used in commercial compounds to aid in mixing and processing, and to improve low temperature properties of the finished product. Antioxidants are beneficial in some applications, particularly when designing compounds for service in hot air or oil.

Ingredients	Gum Compound	phr
1. Elastomer	Chemigum [®] N685	100.00
2. Process Aid	VANFRE AP-2	2.00
3. Activators		
Fatty Acid	Stearic Acid	1.50
Metal Oxide	Zinc Oxide	5.00
4. Plasticizers		
Ester	Dibutyl Phthalate	12.50
Hydrocarbon	Cumar Resin	12.50
5. Antioxidant	AGERITE STALITE S	1.50
6. Accelerator	ALTAX (MBTS)	1.50
7. Vulcanizing Agent	Sulfur (Spider Brand)	1.75
	Total	138.25
Original Physicals, Press Cured 20 min. @	2 154°C	
Hardness, Shore A		43
200% Modulus, MPa		1.2
Tensile, MPa		4.1
Elongation, %		640

A typical nitrile rubber gum compound is shown below:

Reinforcing or semi-reinforcing fillers, either carbon black or mineral fillers, are needed to obtain high strength (tensile and tear) in industrial products. Table 52 and Table 53 present examples of carbon black and mineral fillers in NBR.

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
MT N990 Ca	rbon Blac	k					
50 phr	2.4	13.4	750	52	33.4	54	41/34
100 "	4.9	12.4	730	63	45.8	55	33/40
150 "	6.8	11.6	650	65	48.4	56	25/56
SRF N770 C	arbon Bla	ck					
50 phr	6.0	14.8	590	57	37.8	49	32/41
75"	11.1	15.7	450	65	44.9	46	25/49
100 "	16.4	17.6	350	70	42.2	47	
FEF N550 C	arbon Bla	ck					
50 phr	9.0	18.3	550	60	49.3	44	34/39
75"	16.2	19.9	440	70	47.5	44	19/56
100 "		19.4	270	76	37.0	45	
HAF N330 C	arbon Bla	ck					
50 phr	9.2	18.7	510	59	41.4	53	22/45
75"	19.3	24.6	390	70	40.5	51	
SAF N110 C	arbon Blad	ck					
50 phr	9.0	20.6	540	66	40.5	50	27/56
75"	20.1	25.9	370	77	41.4	54	
Base Com	oound	Ingred	ients			phr	
		Chemig	um N689			100.00	
		VANFR	E AP-2			2.00	
		Stearic	Acid			1.50	
		Zinc Ox	ide			5.00	
		AGERI	FE STALIT	ES		1.50	
		Dibutyl	Phthalate			12.50	
		Cumar	Resin			12.50	
		ALTAX	ALTAX (MBTS)			1.50	
Sulfur (Spider Brand)					1.75		
		Total				138.25	
Compounds	cured 30 r	min. @ 154	Р°С				
Tear strength	n measure	d on Die A	samples				
Compression	Compression set measured after 70 hrs. @ 100°C						
Mooney mea	Mooney measured @ 121°C						

Table 52: Carbon Black Loading in Nitrile Rubber

	M300, MPa	Tensile, MPa	Elong., %	Duro, Shore A	Tear, kN/m	Comp. Set, %	Mooney, t5/ML
DIXIE CLAY	,						
50 phr	1.9	4.9	520	47	10.6	41	38/27
100 "	3.1	13.4	640	55	17.6	52	33/33
150 "	5.2	12.4	620	64	31.7	60	26/47
Hi-Sil 233							
50 phr	2.8	12.0	630	56	26.4	47	29/57
100 "	4.6	17.8	720	71	68.6	78	
150 "	9.3	17.0	570	93	81.0	96	
McNAMEE (	CLAY						
50 phr	2.1	6.1	530	49	10.6	38	38/27
100 "	2.8	9.4	620	55	15.8	50	36/34
150 "	3.5	10.0	650	62	22.0	56	33/39
Base Com	pound	Ingred	ients			phr	
		Chemia	um N689			100.00	
		VANER	E AP-2			2.00	
		Stearic	Acid		1.50		
		Zinc Ox	ide			5.00	
		AGERI	<b>FE STALIT</b>	ΈS		1.50	
		Dibutyl	Phthalate			12.50	
		Cumar	Resin			12.50	
		ALTAX	(MBTS)			1.50	
		METHY	'L TUADS			0.50	
		Sulfur				1.75	
		Tota				138.75	
Compounds cured 45 min. @ 154°C Tear strength measured on Die A samples Compression set measured after 70 hrs. @ 100°C Mooney measured @ 121°C							

Table 53	Mineral Fillers in Nitrile Rubber	

The viscosity results and the performance of VANFRE AP-2 in the DuPont Spider Mold prove it to be a very efficient processing aid in this 80 durometer nitrile compound.

Ingredients (phr)	Control	VANFRE AP-2
Chemigum N689	100.0	100.0
DOP	10.0	10.0
Stearic Acid	2.0	2.0
Zinc Oxide	5.0	5.0
AGERITE STALITE S	1.0	1.0
N550 Carbon Black	70.0	70.0
N770 Carbon Black	30.0	30.0
DURAX (CBS)	1.0	1.0
METHYL TUADS	0.9	0.9
Sulfur	1.5	1.5
VANFRE AP-2		3.0
Totals	221.4	224.4
Mooney Scorch @ 121°C		
Minimum Viscosity	103	83
Minutes to 5 pt. rise	8	9
Original Physicals, Press Cured 10 min. @ 166°C		
Hardness, Shore A	81	81
100% Modulus, MPa	13.0	11.4
Tensile, MPa	18.3	18.0
Elongation, %	150	160
DuPont Spider Mold, 4.8 mm Orifice, 30 Tons Pres Press Cured 10 min. @ 166°C	sure	
Weight, g	12.3	18.5

# Table 54: VANFRE AP-2 in an 80 Shore A NBR Compound



## Cure Systems in NBR

The sulfur cure systems of NBR are very similar to that of natural rubber but nitrile can also be peroxide cured. The following examples show various Vanderbilt accelerator systems for NBR.

Compound	Α	В	С	D	E
Ingredients (phr)					
Nipol [®] 1042	100.00	100.00	100.00	100.00	100.00
VANFRE AP-2	2.50	2.50	2.50	2.50	2.50
Stearic Acid	2.00	2.00	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00	5.00	5.00
AGERITE STALITE S	1.50	1.50	1.50	1.50	1.50
Dioctyl Phthalate	10.00	10.00	10.00	10.00	10.00
N550 Carbon Black	70.00	70.00	70.00	70.00	70.00
N770 Carbon Black	30.00	30.00	30.00	30.00	30.00
Sulfur	1.50	1.50	1.50	1.50	1.75
ALTAX (MBTS)			1.50		1.50
CAPTAX (MBT)	1.50				
DURAX (CBS)		1.50		1.50	
METHYL TUADS		1.00			0.10
UNADS			0.50	0.50	
METHYL ZIMATE	1.50				
Totals	225.50	225.00	224.50	224.50	224.35
Mooney Scorch @ 121°C					
Minimum Viscosity	88	85	84	86	83
Minutes to 5 pt. rise	5	11	15	14	18
Original Physicals, Press Cured 10 min.	@ 166°C				
Hardness, Shore A	78	78	77	77	75
100% Modulus, MPa	13.2	16.3	13.6	12.3	11.0
Tensile, MPa	17.9	18.1	17.5	17.4	17.6
Elongation, %	140	120	140	140	160
Tear Die A, kN/m	25.5	24.6	26.4	22.9	26.4
Compression Set, Method B, 70 hrs. @	100°C				
%	11	8	20	21	33

Table 55: Accelerator Comparison in Nitrile Rubber

Compound	F	G	Н	I	J
Ingredients (phr)				•	
Nipol 1042	100.00	100.00	100.00	100.00	100.00
VANFRE AP-2	2.50	2.50	2.50	2.50	2.50
Stearic Acid	2.00	2.00	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00	5.00	5.00
AGERITE STALITE S	1.50	1.50	1.50	1.50	1.50
Dioctyl Phthalate	10.00	10.00	10.00	10.00	10.00
N550 Carbon Black	70.00	70.00	70.00	70.00	70.00
N770 Carbon Black	30.00	30.00	30.00	30.00	30.00
Sulfur	0.50	0.25	0.20		
DURAX (CBS)	1.00	1.50			
MORFAX				1.50	2.50
SULFADS		1.50			
METHYL TUADS	2.00		1.50	1.00	2.00
DTDM			1.50	2.00	1.00
Totals	224.50	224.25	224.20	225.50	226.50
Mooney Scorch @ 121°C					
Minimum Viscosity	86	96	89	82	80
Minutes to 5 pt. rise	13	5	10	18	13
Original Physicals, Press Cured 10 min.	@ 166°C				
Hardness, Shore A	74	75	77	76	76
100% Modulus, MPa	10.7	9.9	11.9	12.8	13.3
Tensile, MPa	17.9	17.8	18.8	22.4	21.6
Elongation, %	150	170	160	180	160
Tear Die A, kN/m	19.4	22.9	22.9	21.1	16.7
Compression Set, Method B, 70 hrs. @ 1	00°C				
%	11	21	13	15	11

 Table 55: Accelerator Comparison in Nitrile Rubber (continued)

	Black Filled		Mineral Fi	lled
Ingredients (phr)	Sulfur Cured	EV	Sulfur Cured	EV
Chemigum N685	100.00	100.00	100.00	100.00
VANFRE AP-2	2.00	2.00	2.00	2.00
Stearic Acid	1.50	1.50	1.50	1.50
Zinc Oxide	5.00		5.00	5.00
AGERITE STALITE S	2.00	2.00	2.00	2.00
Paraplex G-25	5.00	5.00	10.00	10.00
N550 Carbon Black	30.00	30.00		
N990 Carbon Black	30.00	30.00		
DIXIE CLAY			30.00	30.00
Hydrated Silica			30.00	30.00
Maglite D		10.00		5.00
Sulfur	1.50		2.00	
ALTAX (MBTS)	1.50		1.50	2.00
DURAX (CBS)		1.75		
ETHYL CADMATE				2.00
METHYL TUADS		1.38		
ETHYL TUADS		0.92		
UNADS	0.15		0.15	
DTDM		1.10		2.00
Totals	178.65	185.65	184.15	191.50
Mooney Scorch @ 121°C				
Minimum Viscosity	39	48	41	62
Minutes to 5 pt. rise	39	31	60+	16
ODR @ 171°C				
t₅2, min.	1.7	1.7	2.3	1.3
ť 90, min.	3.7	9.0	4.8	4.8
Original Physicals, Press Cu	red 10 min. @ 10	0°C		
Hardness, Shore A	64	65	64	65
300% Modulus, MPa	5.4	5.5	2.1	2.8
Tensile, MPa	14.6	12.4	10.6	13.9
Elongation, %	530	400	750	680
Compression Set. Method B.	. 70 hrs. @ 100°C	;		
%	30	17	62	31
Physical Properties After Hea	at Aging in Test Tu	ubes, 70 hr.	s. @ 149°C	
Hardness, Pts. Change	+13	+9	+20	+7
Tensile, % Change	-42	-17	-56	-24
Elongation, % Change	-85	-48	-83	-12

Table 56: Efficient Vulcanization (EV) vs. Sulfur-Cure Systems in NBR

# Antioxidants in NBR

Nitrile compounds require antioxidants to combat degradation caused by high temperatures due to the unsaturation in their polymer backbone. These antioxidants may also require some extraction resistance since NBR compounds are often used in oils and solvents. VANOX ZMTI is the recommended antioxidant for heat stability in nitrile rubber. It can be used alone or in combination with AGERITE STALITE S, AGERITE SUPERFLEX, or VANOX CDPA with good results, as shown in the next few studies.

Table 57: Antioxidants in Nitrile Rubber					
Ingredients (phr)	AGERITE RESIN D	AGERITE STALITE S	VANOX ZMTI	VANOX MTI	
Chemigum N689	100.00	100.00	100.00	100.00	
Stearic Acid	1.00	1.00	1.00	1.00	
Zinc Oxide	5.00	5.00	5.00	5.00	
Dioctyl Phthalate	10.00	10.00	10.00	10.00	
N770 Carbon Black	75.00	75.00	75.00	75.00	
Sulfur	1.75	1.75	1.75	1.75	
ALTAX (MBTS)	1.50	1.50	1.50	1.50	
METHYL TUADS	0.10	0.10	0.10	0.10	
AGERITE RESIN D	2.00				
AGERITE STALITE S		2.00			
VANOX ZMTI			2.00		
VANOX MTI				2.00	
Totals	196.35	196.35	196.35	196.35	
Mooney Scorch @ 121°C					
Minimum Viscosity	63	57	64	68	
Minutes to 5 pt. rise	13	17	9	7	
Original Physicals, Press Cured 5 m	nin. @ 166°C				
Hardness, Shore A	65	66	66	66	
200% Modulus, MPa	10.5	11.1	10.7	10.9	
Tensile, MPa	18.6	18.6	18.1	18.4	
Elongation, %	360	350	350	350	
Physical Properties After Heat Aging	g in Test Tubes	, 70 hrs. @ 12	1°C		
Hardness, Pts. Change	+6	+6	+5	+5	
Tensile, % Change	+3	+14	+18	+16	
Elongation, % Change	-28	-20	-9	-6	



Figure 10: VANOX ZMTI Antioxidant in EV-Cured NBR

				'	
Ingredients (phr)	No AO	VANOX CDPA	VANOX CDPA + VANOX ZMTI	VANOX CDPA + VANOX ZMTI	VANOX ZMTI
Ninal DN 2220	70.0	70.0	70.0	70.0	70.0
	70.0	70.0	70.0	70.0	70.0
NIPOI DN 3335	30.0	30.0	30.0	30.0	30.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0
N774 Carbon Black	65.0	65.0	65.0	65.0	65.0
DOP	5.0	5.0	5.0	5.0	5.0
METHYL TUADS	3.0	3.0	3.0	3.0	3.0
VANOX CDPA		3.0	2.0	1.0	
VANOX ZMTI			1.0	2.0	3.0
Totals	179.0	182.0	182.0	182.0	182.0
Original Physicals, Press Cured t' 90	) + 2 min. (	@ 171℃			
Hardness, Shore A	59	60	60	60	60
200% Modulus, MPa	5.5	5.1	4.4	4.1	4.5
Tensile Strength, MPa	16.1	16.0	16.2	15.7	16.5
Elongation, %	566	582	735	722	704
Compression Set, Method B, 70 hrs.	. @ 121°C				
%	48	49	54	57	61
Retained Physical Properties After A	ging in Air,	70 hrs. @	150°C		
Hardness, Pts. Change	+28	+17	+18	+17	+28
Tensile Strength, MPa	4.8	17.4	18.9	18.2	5.1
Elongation, %	Brittle	154	193	185	Brittle

## Table 58: VANOX ZMTI in Efficient Vulcanization (EV) Cured NBR

Ingredients (phr)	AGERITE RESIN D	AGERITE STALITE S	METHYL NICLATE	VANOX ZMTI
Chemigum N689	100.0	100.0	100.0	100.0
Paraplex G25	10.0	10.0	10.0	10.0
N990 Carbon Black	65.0	65.0	65.0	65.0
N550 Carbon Black	35.0	35.0	35.0	35.0
VAROX DCP-40KE	4.0	4.0	4.0	4.0
AGERITE RESIN D	1.5			
AGERITE STALITE S		1.5		
METHYL NICLATE			1.5	
VANOX ZMTI				1.5
Totals	215.5	215.5	215.5	215.5
Mooney Scorch @ 121°C				
Minimum Viscosity	80	72	73	72
Minutes to 5 pt. rise	7	7	6	7
Original Physicals, Press Cured 20 n	nin. @ 160°C			
Hardness, Shore A	68	66	67	67
100% Modulus, MPa	2.9	3.1	3.4	3.2
Tensile, MPa	13.6	13.8	13.7	13.9
Elongation, %	350	310	310	320
Compression Set, Method B, 70 hrs.	@ 121°C			
%	31	34	34	36
Physical Properties After Heat Aging	in Test Tubes	, 70 hrs. @ 12	1°C	
Hardness, Pts. Change	+6	+6	+6	+8
Tensile, % Change	-7	-4	-5	+3
Elongation, % Change	-9	-23	-19	-9

 Table 59: Antioxidants in Peroxide Cured Nitrile

Ingredients (phr)	AGERITE RESIN D + VANOX ZMTI	AGERITE STALITE S + VANOX ZMTI	METHYL NICLATE + VANOX ZMTI
	100.00	100.00	100.00
Derenley C25	100.00	100.00	100.00
NOOD Carbon Plack	10.00	65.00	10.00
N990 Calboli Black	05.00	05.00	05.00
	35.00	35.00	35.00
	4.00	4.00	4.00
AGERITE RESIN D	0.75		
AGERITE STALITE S		0.75	
METHYL NICLATE			0.75
VANOX ZMTI	0.75	0.75	0.75
Totals	215.50	215.50	215.50
Moonev Scorch @ 121°C			
Minimum Viscosity	72	68	71
Minutes to 5 pt. rise	7	8	6
Original Physicals, Press Cured 2	0 min. @ 160°C		
Hardness, Shore A	67	68	68
100% Modulus, MPa	2.9	3.0	2.9
Tensile, MPa	13.4	13.3	13.6
Elongation, %	350	320	340
Compression Set, Method B, 70 h	rs. @ 121°C		
%	37	36	41
Physical Properties After Heat Agi	ng in Test Tubes, 72	? hrs. @ 121°C	
Hardness, Pts. Change	+8	+5	+5
Tensile, % Change	+1	+3	-1
Elongation, % Change	-9	-9	-21

 Table 59: Antioxidants in Peroxide Cured Nitrile (continued)



Figure 11: VANOX ZMTI Antioxidant in a Peroxide Cured NBR

Table 60. Antioxidants and Flex Resistance in Feroxide Cured NBR					
Ingredients (phr)	No AO	VANOX CDPA	VANOX CDPA + VANOX ZMTI	VANOX ZMTI + VANOX CDPA	VANOX ZMTI
Nipol DN 4555	100.0	100.0	100.0	100.0	100.0
Zinc Oxide	5.0	5.0	5.0	5.0	5.0
Stearic Acid	1.0	1.0	1.0	1.0	1.0
N774 Carbon Black	90.0	90.0	90.0	90.0	90.0
DOP	15.0	15.0	15.0	15.0	15.0
VAROX DCP-40KE	3.0	3.0	3.0	3.0	3.0
VANOX CDPA		3.0	2.0	1.0	
VANOX ZMTI			1.0	2.0	3.0
Totals	214.0	217.0	217.0	217.0	217.0
Original Physicals, Press C	ured t' 90 +	2 min. @ 1	71°C		
Hardness, Shore A	72	69	68	71	73
200% Modulus, MPa	14.8	12.5	11.8	13.4	14.3
Tensile Strength, MPa	17.3	16.3	16.2	16.6	17.2
Elongation, %	292	336	358	337	309
DeMattia Flex Fatigue					
Kilocycles to 1.9 cm	85	700	600	400	150
Compression Set, Method I	3, 70 hrs. @	⊉ 121°C			
%	35	40	39	37	37

Table 60: Antioxidants and	Flex	Resistance in	Peroxide	Cured NBR
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## Antioxidants in HNBR

HNBR rubber is nitrile rubber which has been hydrogenated to reduce the number of carbon-carbon double bonds. The saturation improves the heat and ozone resistance of nitrile in HNBR. All HNBR rubber can be peroxide cured to provide the most heat resistant cure system. Table 61 shows the results of an antioxidant study in peroxide cured HNBR.

		VANOX	VANOX CDPA		
Ingredients (phr)	No AO	CDPA	+ VANOX ZMTI		
Zetpol 2020	100.0	100.0	100.0		
Zinc Oxide	5.0	5.0	5.0		
Stearic Acid	0.5	0.5	0.5		
N330 Carbon Black	20.0	20.0	20.0		
N990 Carbon Black	45.0	45.0	45.0		
VANOX CDPA		1.5	1.5		
VANOX ZMTI			1.5		
VAROX DCP-40KE	8.0	8.0	8.0		
Totals	178.5	180.0	181.5		
Mooney Scorch @ 121°C					
Minimum Viscosity	59	51	53		
Minutes to 5 pt. rise	18	23	28		
Original Physicals, Press Cured t'	90 + 2 min. @ 1	71°C			
Hardness, Shore A	69	66	66		
200% Modulus, MPa	22.9	15.4	14.9		
Tensile, MPa	24.0	23.2	23.0		
Elongation, %	232	306	330		
Compression Set, Method B, 70 hrs. @ 150°C					
%	22	28	32		
Retained Physical Properties After Heat Aging in Air, 70 hrs. @ 175°C					
Hardness, Pts. Change	+18	+14	+14		
Tensile, %	26	37	66		
Elongation, %	1	13	26		
Retained Physical Properties After Heat Aging in Air, 168 hrs. @ 150°C					
Hardness, Pts. Change	+13	+11	+13		
Tensile, %	57	106	106		
Elongation, %	25	55	58		

Table	61:	VANOX	CDPA	in	HNBR
I GOIO	•••		SPIA		



# CHAPTER 5 Laboratory Testing and Factory Processing

#### **PROCESSABILITY TESTS and CUREMETERS**

#### by John A. Sezna

Rubber Testing Consultants Akron, OH

The testing of rubber is generally divided into two categories: processability and cured physical properties. Processability testing is usually conducted on materials at the intermediate stages of rubber product fabrication. Cured physical properties are measured on either finished rubber products, or on specially cured specimens that may also have been subject to a conditioning step simulating the service life of the rubber. Many of the typical cured physical property tests are described in the chapter following this one.

Processability is a very general term which relates to the ability to successfully plasticize, mix, form and vulcanize rubber compounds without process interruptions. For practical purposes, processability test measurements are divided into viscous and elastic properties during shear flow, and changes in those properties during the vulcanization reaction. All rubbers are viscoelastic, which means that they exhibit both viscous and elastic properties. The relative viscous and elastic responses of a rubber under process conditions determine its processability. Vulcanization is the chemical reaction in which crosslinks are formed between polymer chains that convert a compound from a predominantly viscous material to a predominantly elastic material. Vulcanization (cure) reactions vary according to both time and temperature, and significantly influence the physical properties of the cured rubber. Cured rubber compounds are also viscoelastic, so physical properties of rubber compounds are measured by both static and dynamic mechanical tests designed to simulate the service conditions imposed on finished rubber products.

The viscous and elastic properties of uncured rubbers vary according to deformation, rates of deformation and process history. Vulcanization is a reaction that varies with time, temperature and heat history. Cured rubber properties vary significantly according to deformation, rates of deformation and service experience. Given all these sources of variation, an infinite number of tests could be imagined that measure rubber physical properties. Fortunately, a consensus has been reached in the industry on methods of measuring these properties, based on national and international standards. In this discussion, tests accepted by ASTM (American Society of Testing and Materials) and by ISO (International Standards Organization), are referenced where appropriate. Many commonly used rubber tests are described in this section. Following the description of each test, the author has given his comments on its advantages and disadvantages. These comments are editorial, not factual, and should be treated as opinions based on experience.

#### **Rubber Viscoelastic Properties**

Rubber is a material that responds to deformation both as a liquid and as a solid. Materials possessing this combination of properties are called viscoelastic.

A typical viscous response for unvulcanized rubber is illustrated in Figure 1. In this example, the flow resistance (shear stress, $\tau$ ) of two rubber compounds is plotted for a range of flow shear rates ( $\dot{\gamma}$ ) typical of rubber processes.



Figure 1: Typical Rubber Shear Stress vs. Shear Rate Response

The shear stress versus the shear rate responses shown in Figure 1 are often straight lines when plotted on a log-log scale. Most rubber compounds exhibit this behavior for much of the range of shear rates typical of rubber processing. These materials conform to the *Power Law* model of flow:

$$\tau = k \dot{\gamma}'$$

where *k* is the shear stress when the shear rate equals 1 sec⁻¹, and *n* is the slope of the log shear stress/log shear rate line.

For any liquid, the ratio of shear stress to shear rate defines its viscosity,  $\eta,$  as:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

Because rubber shear stress increases more slowly than an increase in the shear rate, the viscosity of rubber decreases with increased shear rate, as shown in Figure 2. This behavior is called shear-thinning. Most rubber processes take advantage of this property by processing at high shear rates. Note that the differences between the two compounds observed at low shear rates are reversed at high shear rates. This illustrates the importance of measuring viscous properties at processing shear rates in order to accurately predict processability.





The Power Law equation for viscosity is:

$$\eta = k\dot{\gamma}^{n-1}$$

Rubber elasticity is also rate dependent. Figure 3 shows typical changes in uncured rubber viscosity and elastic modulus versus shear rate. As the shear rate increases, the viscosity decreases and the elastic modulus increases. The increase in elastic modulus with an increase in shear rate varies widely with elastomer types. Some polymers, like Natural Rubber and Nitrile elastomers, have very high elastic modulus at high shear rates. This property is usually called "nerve". Compounds with high elastic properties may require additional work or shearing energy to reduce both viscous and elastic properties. Work-reduced viscoelasticity often recovers some or all of its stiffness after a rest period. An alternative to using shear energy to reduce elastic properties is the use of chemical peptizing agents, as discussed in the compounding sections of this book.



#### Figure 3: Typical Rubber Viscous and Elastic Responses to Shear Flow

Most physical tests conducted in the rubber laboratory measure viscoelastic properties under specific conditions, which can be related to processing or the end use of rubber products. Compounders must take into consideration the relationship between the test and the processing conditions before interpreting test results.

## Plastometers

#### Williams Plastometer

The Williams Plastometer^{1,2} was used extensively in factory processing before the development of tests like the Mooney viscometer and the Rheometer. It is still a common test in the silicone rubber industry. The test is a parallel plate compression of a rubber button followed by a recovery period. It is described in detail in ASTM Standard Test D 926. The test fixture, shown in Figure 4, is placed in an oven and maintained at the desired test temperature (usually 70°C or 100°C). Test specimens are cylindrical, with a volume of 2 cm³ (approximately 16 mm diameter by 10 mm high). Consistent sample volume is critical for good test precision. After pre-heating a specimen for 15 minutes, it is placed between the parallel plates and compressed under a 49 newton force (using a 5 kg mass for the upper plate plus an added weight). An indicator gauge monitors sample height during the test. The specimen is compressed for a fixed interval, usually 3, 5 or 10 minutes, depending on the rubber stiffness.



There are two Williams Plastometer test methods:

*Method A* of the test measures the final compressed thickness,  $h_1$ , in hundredths of a mm, and converts it to "Plasticity", P:

$$P = 100 \cdot h_1$$

After compression, samples are immediately removed from the plastometer and allowed to cool at 23°C for one minute. The increased height after cooling,  $h_2$ , in hundredths of a mm, is used to calculate the recovery,  $R_A$ :

$$R_A = 100(h_2 - h_1)$$

Figure 4: Williams Parallel Plate Plastometer Photo courtesy of Qualitest, Inc.

*Method B* of the Williams Plastometer test calls for the specimen to be compressed to a height of 5 mm for 30 seconds, followed by a recovery without load, at the test temperature for 5 minutes. The height after the recovery,  $h_3$ , measured in hundredths of a mm, is used to calculate method B recovery,  $R_B$ :

$$R_B = 100(h_3 - 5)$$

The Williams Plastometer test is slow, labor intensive, and has poor precision, according to the ASTM D 926 precision statement.³ In recent years, this test has been conducted mostly on materials with low viscosity and stiffness, such as silicone rubbers. These materials are often messy and difficult to run in the Mooney Viscometer, and for them the Williams Plastometer remains a primary processability test. Other materials could also benefit from stress relaxation tests like the Williams Plastometer, as will be seen in the discussion of other test options.

#### Wallace Rapid Plastimeter

The Wallace Rapid Plastimeter, as shown in Figure 5, is a modified parallel plate compression test, most commonly used for natural rubber. This test was developed to meet the need for a low cost, rapid test that could be used by rubber plantations to check their product quality. The test is standardized as ASTM Standard Test D 3194 and ISO 2007. Its application to natural rubber is based on the change in plasticity after oxidative aging. In the test, 0.40 cm³ cylindrical pellets with a height of 3.4 mm are pre-heated for 10 seconds in the Plastimeter, followed by a 98 newton compression for 15 seconds, and immediately followed by a release of the load. The compression is performed at 100°C. As with the Williams Plastometer, the Wallace Plasticity is the final compressed height, in hundredths of a mm, times 100. Since the test aims at measuring the difference plasticity before and after aging, three samples are tested unaged and three are aged for 30 minutes at 140°C before testing. The Plasticity Retention Index, or PRI, is calculated as the ratio of Plasticity values before and after aging:

$$PRI = \left(\frac{Aged \ Plasticity}{Unaged \ Plasticity}\right) \times 100$$

The Wallace Rapid Plastimeter PRI test is convenient and inexpensive, but has poor precision, according to ASTM D 3194.⁴ One of the main reasons may be the sample preparation step, since its repeatability precision is much better than its reproducibility (lab to lab) precision. This test is widely used for natural rubber, but seldom for other rubbers.



Figure 5: Wallace Rapid Plastimeter MK IV Photo courtesy of GENEQ Inc., an authorized Wallace Instrument distributor

## Defo Test

The Defo test is also based on a parallel plate test, but it uses a more sophisticated loading and unloading cycle and a more detailed data analysis to measure viscoelastic properties over a range of shear rates. The test was originally German Standard DIN 53514. After further development, the test was approved as ASTM Standard Test D 6049 in 1996. To perform the complex analysis with acceptable precision, samples must be uniform with no air bubbles. This requires a special vacuum compaction device for raw polymer samples and/or a heated mold for unvulcanized rubber compounds. The sample preparation step requires 10 to 15 minutes of molding, followed by 10 minutes of vacuum compaction. Prepared samples must rest another 30 minutes before testing. Once the samples have been properly formed into cylinders 30 mm in diameter and 13 mm high, they are heated and inserted between the parallel plates, with sandpaper inserted between the plates and the sample. Normal test temperature is 105°C. The principle of the Defo test compression/recovery cycle is illustrated in Figure 6. Specimens are alternately compressed and allowed to recover. The compression cycle is selected so that the compression time for the first load and release cycle  $(t_{\tau})$  is between 10 and 80 seconds. Common forces are 40 N, 100 N and 160 N. If multiple forces are to be applied, one test piece is used for each force setting. Each test on a single specimen consists of two loading cycles.





The Defo test is the basis for a number of calculations which are related to the viscous and elastic properties of the rubber sample. For example, shear rate is *proportional* to  $1/dt_1$ . From this, viscosity is *proportional* to:

*Viscosity*  $\propto F \times dt_1$ 

in units of Ns. Based on multiple forces applied to multiple samples of the same rubber, the Power Law flow model slope (n) is estimated by linear regression:

$$n = \frac{\Delta \log(F \times dt_1)}{\Delta \log(F \times dt_2)}$$

Elasticity is reported as elastic recovery DE in units of 0.1 mm, based on the recovery height  $h_2$  (from a compressed height of 7 mm) after a recovery time equal to the compression time  $t_T$ . The elastic recovery in mm is:

$$DE = \frac{\left(h_2 - 7\right)}{0.1}$$

Other parameters measured from the Defo Test include the changes in viscosity and elasticity between the first to the second cycles.

The Defo test is a potentially powerful test for the measurement of the viscoelastic properties of rubber.⁵ Its limitations include a lengthy sample preparation step, which prevents its routine use for production control, and the

indirect measurement of rheological properties, which requires the conversion of results by correlations to true rheological values. Also, the requirement that multiple samples be tested to measure the shear stress/shear rate relationship introduces the potential of additional error.

All of the plastometer tests described in this section are stress relaxation tests using parallel plates to compress the samples. Variations of these tests have been produced over the years by many manufacturers employing similar concepts, but the three mentioned above are still available and in current use. Stress relaxation tests can also be conducted using viscometers, torsional shear testers, and capillary rheometers. These will be discussed in the sections describing those devices.

#### **Torque Rheometers**

Torque rheometers are based on measurement of the torque required to drive a variety of test heads, typically miniature versions of production mixers and extruders. Mostly tabletop units, they designed to study all types of rubber and plastic materials under shear stress, shear rate and temperature conditions resembling production. The production processes simulated include mixing, kneading, extrusion, calendering, and extrusion. C. W. Brabender[®] and Thermo Scientific (Haake Rheocord) are the primary manufacturers of torque rheometers.

The test heads can be quickly interchanged. Temperature control is provided by circulating oil, water, air, or by electric heaters. Cure tests and capillary rheometer tests can be conducted using an extruder fixture to feed the capillary die. Older models used a torque arm dynamometer to measure torque, with the torque arm directly linked to a chart recorder. A modern torque rheometer, the C. W. Brabender Intelli-Torque Plasti-Corder[®], is shown in Figure 7, use a torque transducer and electronic data analysis. Both types of instruments are still found in use in rubber laboratories.



Figure 7: Intelli-Torque Plasti-Corder with Mixer/Measuring Head Attachment

Photo courtesy of C.W. Brabender Instruments, Inc.

Torque measurements during mixing are the equivalent of power measurements on the drive system of a mixer or other rubber process equipment. Power traces during mixing are extremely useful in studying the breakdown in rubber viscosity and the efficiency of incorporation of fillers and plasticizers. In this way, torque rheometers can be used as an aid in improving the efficiency of a mixing study.

While torque rheometers are extremely versatile research tools for studying a wide range of rubber processes, they have limitations when scaling up to larger volumes, and in test precision. The scale up of mixing volumes, for example, must take into account the fact that smaller mixers tend to have more intensive shear, relative to the volume of rubber being mixed, than larger mixers. Also, larger mixers have different heat transfer rates than smaller mixers. The issue of torque rheometer precision is mostly related to temperature control. Torque rheometers have temperature variability that ranges from the excellent control of testers with small samples under tightly controlled shear conditions, to the wider range of conditions that can occur in large, manually controlled processes like mixing. The most useful role for torque rheometers may be in research and development work relating to processability, where they function as small-scale models of the production process.

## Laboratory Extruders

Torque rheometers and laboratory size mixers can be used as small-scale models for production sized extruder processes. These instruments can support

compound studies evaluating extrudability, edge tearing tendencies, die swell reaction, and capillary rheometry. Extrudability studies are conducted using a special die to check for edge tearing, called a Garvey Die, or using an actual extruded product profile. Extrusion studies to measure die swell commonly use a circular die cross section, either as part of a capillary flow test, or as a simple measurement of die swell. Capillary flow is measured with special dies mounted on either a piston or a screw laboratory extruder.

The Garvey Die extrudability test uses a special die (depicted in Figure 8), with very small radius edges contrasting with a concentrated central flow region, and is defined in ASTM D 2230.



Figure 8: Profile of Garvey Die for Extrudability Test

The basis of the test is a comparison of the differences in flow rates between the central portion and the extreme edges. This difference in flow rate puts the edges under tension, and if the rubber has a tendency to tear, the edges will appear rough or torn. A subjective rating, as demonstrated in Figure 9, requires the compounder to visually compare the extrudate to a series of photos representing a range of extrusion quality, from smooth surfaces and edges with no tears, to a very rough surface extrusion with severely torn edges. The extruder operator can vary the temperature and screw speed until an ideal extrusion quality is achieved with a reference compound. The operator then runs the same conditions with the experimental compound for comparison.



Figure 9: Lab Extrusion Test Specimens

The Garvey Die extrudability test is very subjective and can be influenced significantly by operator technique. Also, the Garvey Die extrusion test does not always predict the extrusion quality achieved using another die and extruder configuration.

## **Extrusion Die Swell**

Extrusion die swell is difficult to measure because any contact with the extrudate influences measurements, and because die swell is both rate-and-time-dependent. The term "die swell" is sometimes confusing, because the same phenomenon is also called "extrusion shrinkage". Going thru a circular die opening, the extrudate swells in diameter and shrinks in length after it leaves the die. This is an elastic response of the material that is being accelerated through the die. The rubber wants to return to its pre-extrusion shape; the longer it is held in a new shape, the less die swell is observed. Die swell increases with extrusion stresses, and since shear stress increases with shear rate, die swell usually increases with rate. Die swell can be reduced by post extrusion tension.

Techniques to measure die swell directly have been developed using screw type laboratory extruders and a circular die with a tapered entrance angle. The temperature and screw speed are adjusted until the desired output flow rate is achieved in steady flow. The extrudate is marked twice to produce an easily handled specimen length. The extrudate is cut at the extruder head and placed on a bench top to cool. The original length and a cooled length are measured. Ideally, the bench top should be a non-stick surface so that the extrudate is free to swell in diameter as it shrinks in length. This method is highly dependent on operator technique, and has poor precision.

Piston extruders, in the form of capillary rheometers, can also extrude a circular cross section. The rheometers are often oriented vertically so that the

extrudate falls downward. Many of these instruments accommodate an optical die swell measuring device beneath the die. The external factors that affect die swell are temperature and gravitational forces. Because capillary dies tend to be small in diameter, the extrudate cools faster than for a production extrudate. Longer extrudates generate higher gravitation forces. Gravity can place enough tension on soft rubber extrudate to give it a negative die swell. If the extrudate is constrained, the material tends to form a coil, causing an oscillating die swell reading. Capillary rheometer mounted die swell measurements provide improved precision over manual methods, but the amount of die swell measured is usually different than observed in production.

For circular cross section extrudates, die swell is calculated from the die opening diameter ( $D_0$ ) and the swelled extrudate diameter ( $D_f$ ):

Percent Die Swell = 
$$\frac{(D_f - D_0)}{D_0} \times 100$$

Shrinkage is calculated from a change in length:

Percent Shrinkage = 
$$\frac{\left(L_0 - L_f\right)}{L_0} \times 100$$

Because the extrudate volume remains constant for a circular cross section, volume equals L x ( $\pi$  D²/4), die swell is related to shrinkage:

$$\frac{L_f}{L_0} = \left(\frac{D_o}{D_f}\right)^2$$

Shrinkage is easier to calculate for non-circular cross sections.



Figure 10: Die Swell as Rubber Leaves an Extruder Die

## Laboratory Mold Flow

The DuPont "spider" mold, as shown in Figure 11, is a useful comparison test for evaluating compound flow characteristics under transfer or injection molding conditions.



Figure 11: Vanderbilt DuPont Spider Mold

In the spider mold the compound enters the cavity in the center and flows into four grooves. Two grooves, for evaluation of the compound flow characteristics, are nine inches long with 1/4 in. and 1/8 in. diameter semi-circular cross-sections. The other two grooves are 3/8 in. diameter semi-circular cross-sections and each contains a sharp 315° corner before joining in the "knit section" of the cavity. This area has a 1/4 in. by 1/8 in. rectangular cross-section so that tensile specimens can be taken from this area to measure the effects compounding ingredients or mold release agents have on compound "knitting".

The two flow grooves and the knit section are vented. Hash marks at  $\frac{1}{4}$  in. intervals along the side of these grooves fill with compound and provide easy determination of flow. Experience has shown that two to three inches of flow in the 1/8 in. diameter grooves is the minimum required for filling the tensile bar in the knit section.

#### **Capillary Rheometers**

Capillary rheometers are tube flow measurement devices that are uniquely suited to measure high shear rate rubber flow properties.^{6,7} They are much better at testing filled rubber compounds than unfilled raw polymers. Capillary rheometer testing for rubber is standardized under ASTM D 5099, but this method represents a compromise among different types of instruments, and many compounders select alternate test conditions.

Capillary rheometers are also used to measure thermoplastic flow, but the testing parameters for rubber are different than those for thermoplastics. Thermoplastics require short heating times to reach the melt temperature, which is usually higher than rubber processing temperatures. As a result, capillary rheometers designed for thermoplastics generally have a small 9.5 mm (3/8")

diameter barrel for rapid heating. Rubber starts as a high viscosity melt at room temperature, so a larger barrel diameter allows for easier loading and adequate heating times at rubber process temperatures. Larger barrel diameters also accommodate sticky rubber compounds with a minimum of trapped air pockets. Capillary rheometers designed specifically for rubber have barrel diameters of 12.5 mm (1/2") or 19 mm (3/4").

A second consideration in capillary rheometer design is the location where the barrel pressure is measured. For many thermoplastics, the pressure drop along the barrel length is small compared to the capillary die pressure drop, and pressure is often calculated based on the piston force. For rubber, this is not the case. Capillary rheometers used to test rubber must either measure the barrel pressure at the die entrance (which requires a barrel diameter of 9.5 mm or greater), or at the pressure drop along the barrel length, which means that the piston position must be used. Finally, the viscosity of thermoplastic melts is generally lower than rubber viscosity, requiring higher barrel pressures to test most rubbers.

Figure 12 is a schematic diagram of a capillary rheometer. The piston has a diameter of 2R, moving a velocity V, and resisted by a force F. The pressure at the piston tip,  $P_0$ , is greater than the pressure at the die entrance,  $P_E$ . The pressure drop at the entrance to the die equals ( $P_E - P_c$ ). The pressure drop along the capillary length equals the pressure at the beginning of the capillary tube ( $P_c$ ) minus the exit pressure ( $P_e$ ). The exit pressure is often assumed to be zero. Important dimensions include the die diameter (2r), and the die length, not including the entrance zone (L). Apparent shear rate is calculated from the volume flow rate and the die diameter. Apparent shear stress is calculated from the die entrance pressure ( $P_E$ ) and the die L/D ratio.



Figure 12: Capillary Rheometer Test Schematic

Capillary rheometer tests produce results as apparent shear stress versus apparent shear rate. This means that the test results must be corrected to obtain the true values, which usually requires two or more tests with capillary dies at different L/D ratios. Some capillary rheometers produce corrected results with one test by using multiple barrels and dies. The capillary rheometer apparent shear rate is based on a simple calculation that assumes constant viscosity at all shear rates (Newtonian flow), and laminar flow (parallel stream lines). The shear rate is equal to the difference in velocity between layers divided by the distance between the layers. This is commonly listed in units of reciprocal seconds (S⁻¹, or 1/sec). For a capillary die, the formula for apparent shear rate is:

Apparent Shear Rate, 
$$\dot{\gamma}_a = \frac{32(Volume \ Flow \ Rate)}{\pi \ (Die \ Diameter)^3}$$

As the above equation indicates, a small change in die diameter can change the shear rate much more than a simple increase in volume flow rate.

Apparent shear stress is calculated using the die entrance pressure and the surface of the capillary wall where the stress is distributed. The calculation for apparent shear stress in a capillary die is:

Apparent Shear Stress, 
$$\tau_A = \frac{P_E}{4 (Die L/D)}$$

Apparent viscosity equals the ratio of apparent shear stress and apparent shear rate:

Apparent Viscosity, 
$$\eta_A = \frac{\gamma_A}{\tau_A}$$

In order to apply capillary rheometer data to other processes, the apparent values must be corrected to determine the true values of shear rate, shear stress, and viscosity. The correction of shear stress is called the Bagley Correction. To make this correction, a minimum of two tests, each with a die with a different L/D ratio, but at the same shear rate, must be run. The results of these tests typically resemble those in Figure 13.



In Figure 13, the pressure at zero L/D is the pressure drop from the die

entrance to the beginning of the straight portion. This can correlate with any converging flow pressure drop. The L/D axis intercept is the magnitude of the Bagley Correction, an added L/D value to calculate true shear stress:

True Shear Stress, 
$$\tau = \frac{P_E}{4 ((Die L/D) + Bagley Correction)}$$

The Rabinowitsch shear rate correction uses the slope of the Power Law model of apparent shear stress versus apparent shear rate. As discussed earlier, the slope is n from the Power Law model, and the Rabinowitsch correction for shear rate is:

True Shear Rate, 
$$\dot{\gamma} = \dot{\gamma}_A \left(\frac{3n+1}{4n}\right)$$

and corrected viscosity is:

True Viscosity, 
$$\eta = \frac{True \ Shear \ Stress, \tau}{True \ Shear \ Rate, \gamma}$$

The magnitude of correction shifts is illustrated by the example in Figure 14.



Figure 14: Example Data Shifts for Capillary Rheometer Corrections

Capillary rheometers are excellent models of high shear rate flow, and measure viscosity accurately. The flow behavior they measure correlates both in theory and in practice with many rubber processes, including mixing, calendering, extrusion, and injection molding.^{8, 9, 10, 11, 12, 13} They require the manual loading of samples, and multiple tests are required if different dies, test temperatures,

or an extremely wide set of test conditions are to be evaluated. The loading and cleaning of a capillary rheometer barrel can be difficult with some rubber samples. While capillary rheometers are an excellent development tool, they have not been accepted as a common production control test in the rubber industry as they have in the thermoplastic industry.



Figure 15: Example of Rubber Viscoelastic Behavior in an Unsealed Cone-plate Rheometer

# **Rotational Rheometers/Viscometers**

Viscometers for rubber must accommodate viscoelastic behavior, which is rubber's tendency to move to a lower state of stress, due to its elasticity when a rotational shear stress is applied. If rubber is deformed in an unsealed test cavity, there is a limit to the shear rates that can be applied before the material flows out of the test area. For example, if a cone and plate configuration is used for the test, increasing the rotational speed creates a normal, or axial, force which moves the rubber away from the center and up the sides of the cone. At a limiting speed, the unsealed cone and plate configuration will be unable to test the rubber. Unsealed cone and plate rheological testers measure the normal force required to directly measure viscoelastic properties. These devices are excellent for the low shear rate measurement of viscous and elastic properties of rubber. Because the normal force is small compared to the torsional forces for rubber, the sample must be carefully prepared before testing. The lengthy sample preparation required by unsealed cavity test configurations has limited the use for rubber production testing.



Figure 16: Mooney Viscometer Test Configuration

The Mooney Viscometer¹⁴ is a sealed cavity rotating shear viscometer designed to measure the "shearing viscosity" of rubber in Mooney Units (M). It is not a true rheometer, because it does not measure a fundamental rheological property of rubber. The shearing action is performed by a flat, serrated disk rotating inside a shallow, sealed, heated test cavity. Torgue is converted to Mooney Units so that 8.30 N·m (73.5 lbf·in) equals 100 M. Normal rotational speed is 2 cycles per minute, but other speeds have been used. The shear rate is zero at the disk center, and approximately 1.5 s⁻¹ at the disk edge. The sealed cavity is split into two dies, with either radial grooves or serrations cut into the surfaces to minimize slippage. Test samples should be 25 cm³ in volume, split approximately evenly between a lower piece with a hole to accommodate the rotor stem and an upper piece which is placed above the rotor. When the test cavity is closed the rubber is confined under high pressure. Significant pressure variations can cause significant variations in test results. Two rotors are supplied with each instrument. The large rotor (38.1 mm, or 1.50" in diameter) is commonly used for all viscosity measurements unless the 200 M maximum torque is reached, in which case the smaller rotor (30.48 mm, or 1.20" in diameter) is used.

ASTM Standard Test D 1646 describes three different test modes for the Mooney Viscometer: Viscosity, Stress Relaxation, and Scorch. ISO Standard 249 includes the viscosity and scorch methods. Another special test for non-pigmented SBR using the Mooney Viscometer is ASTM D 3346, sometimes referred to as the "Delta Mooney" test.

The Mooney viscosity test normally consists of a 1 minute pre-heat with a stationary disk, followed by 4 or 8 minutes of disk rotation. The torque at the end of the test interval is reported in Mooney units. Common test temperatures for viscosity are 100°C and 125°C. An example of a typical test reported result is: 50 – UML 1+4(100°C), where 50 – is the viscosity number, U indicates the rubber was unmassed (not milled before testing), M indicates Mooney, L indicates large rotor (S for small rotor), 1 is the pre-heat interval in minutes, 4 is the disk rotation time in minutes after preheat that the reading is taken, and 100°C is the test temperature. The Mooney viscosity test is one of the most common

processability tests reported in the rubber industry, however it is often unable to predict any but the simplest of processability differences between materials, because it only measures a low shear rate viscosity that may not relate well to high shear rate processing.

Mooney Stress Relaxation (SR) was added to the ASTM D 1646 Standard as a test to be run immediately following a viscosity test, to provide more information about rubber viscoelasticity and polymer structure. As noted in the earlier discussion of stress relaxation tests, sample preparation significantly affects test precision. In the Mooney SR test, the Mooney viscosity test is the preparation step, thus improving test precision. The test is run by suddenly stopping disk rotation and recording the decay of torque with time. It is only available on Mooney viscometers manufactured since 1987, and cannot be added to an older viscometer because the test results will have poor precision. Several different data points are used with the SR test, some better than others for different materials. The data points include time to 80% decay from the Mooney viscosity; percent decay at 30 seconds; slope of a Power Law decay model; intercept of a power law decay model; and area under the stress relaxation curve, in M-s units.



Figure 17: Typical Mooney Viscosity Test Curve Followed by a Stress Relaxation Test

The interpretation of the stress relaxation test for viscoelasticity can be summarized by looking at a plot of Log Mooney torque versus Log decay time, as shown in Figure 17. If the test material were completely elastic, the torque would never decay, and the graph would show a horizontal line equal to the viscosity test torque. If the material were completely viscous, the torque would drop to zero as soon as the disk rotation stopped. With rubber, we see a decay curve in between the two extremes - the faster the decay, the less elastic the rubber. Many rubbers exhibit a Power Law type of decay, which would be a straight line in the graph below. The equation for Power Law decay is: The Mooney SR test adds significantly to the sensitivity of the Mooney viscosity test. The Mooney viscosity test is sensitive primarily to the Average Molecular Weight of polymers, or to the low shear rate viscosity of rubber compounds. Mooney SR is sensitive to polymer variables like Molecular Weight Distribution, Chain Branching, and Gel Content. For compounds, it is also sensitive to plasticizer levels, filler type, filler distribution, and the presence of scorch. From the standpoint of processability, both the Mooney viscosity and the SR decay slope can be used to compare the processability of different batches.^{15, 16}



Figure 18: Log-Log Plot of Mooney Stress Relaxation Test Responses

The Mooney Scorch test is typically run on fully compounded rubber at the high end of the range of processing temperatures, for example, 135°C for fast curing compounds, and 150°C for slow curing compounds. This test is sometimes combined with a viscosity test by some compounders to try to take advantage of both tests. The key data points for Mooney scorch are Minimum Viscosity; T5 and T35 (the time it takes for the torque to rise 5 and 35 units with a large rotor); or T3 and T18 (the time it takes for the torque to rise 3 and 18 units with a small rotor). The cure rate index is reported as  $\Delta tL = t35 - t5$  for the large rotor, and  $\Delta tS = t18 - t3$  for the small rotor.



Figure 19: Alpha Technologies MV 2000 Mooney Viscometer Photo courtesy of Alpha Technologies



Figure 20: The Rheometrics Dynamic Spectrometer Photo courtesy of TA Instruments, ARES-G2 Rheometer

Modern Mooney viscometers have incorporated design features like improved temperature control and test conditions that significantly improve precision. The improvement primarily relates to long-term repeatability on the same instrument and reproducibility between instruments. The addition of the SR test and computer-based data collection have increased the value of this test.

The Mooney Viscometer has long been a common test in the rubber industry because it is easy to run, easy to interpret, and less expensive than other tests. While the SR test has enhanced the usefulness of the Mooney Viscometer for process flow properties, it does not always detect variations in rubber that can significantly affect processability. Improvements in the capability of the curemeter have led to a decline in the use of the Mooney scorch test.

## **Oscillating Shear Rheometers**

Dynamic Mechanical Rheological Testers (DMRTs), like the Rheometrics Dynamic Spectrometer shown in Figure 20. are rotational rheometers capable of testing rubber samples in both oscillating shear and torsion. Uncured specimens are tested in a Cone-Plate configuration, with the edges sealed only by the test material. One of the two surfaces provides axial deflection in a sinusoidal oscillation. Because of the unsealed configuration, of rubber test conditions are somewhat limited.

DMRTs simultaneously measure the viscous and elastic properties of a rubber sample, thereby distinguishing the effects on processability of molecular weight, molecular weight distribution, and branching. These instruments can measure viscoelastic properties that affect the processability of rubber compounds, as well as the increase in stiffness from the vulcanization reaction.

From the DMRT values for torque, angular position, and test temperature changes over time, viscosity  $\eta^*$ , complex shear modulus G^{*}, elastic shear modulus G', viscous shear modulus G", the dissipation factor tan  $\delta$ , and the stress relaxation modulus G(t) can be automatically

calculated (Figures 21 and 22). Also, from the DMRT graphs of the modulus versus temperature, the glass transition temperature and other transitions can be measured. High strain resolution at strains as low as 0.001% enables the characterization of variables such as loading levels and filler dispersion.

Samples tested in torsion are generally vulcanized and adhered to plates. A heat chamber surrounds the plates and test specimen. The force generated by sample expansion is monitored and automatically adjusted to a preset value to compensate for thermal expansion.

The advantage of a DMRT is that it provides information relating production processability to the rubber's intrinsic rheological properties, but unsealed test configurations are limited to low strains and may be unable to test during the complete vulcanization reaction without rotor slippage at high torque levels. DMRTs sometimes require a higher level of operator skill level than is needed for other production tests like the Mooney Viscometer and curemeter.



Figure 21: Dynamic Test Data for Unvulcanized Rubber


Figure 22: Dynamic Test Data for Vulcanized Rubber

### Curemeters

Curemeters are DMRTs primarily designed to measure the change in rubber stiffness resulting from the vulcanization, or cure reaction. To prevent rotor slippage at the higher torques, which often occurs when the cure nears completion, curemeters constrain samples under pressure with a sealed test cavity. This allows the operator the freedom to quickly load, run and reload the instrument. The Mooney Viscometer cannot measure the complete cure reaction because its rotor turns continuously. The curemeter applies a moderate oscillating strain so that the rubber is in contact with the test surfaces during the entire the cure reaction. The test is very popular with rubber producers because in one rapid test, rubber properties are measured before, during, and after cure. Another benefit is that small variations in the formulation or work history of a compound often show up as shifts in the curemeter torque curve.

#### Oscillating Disk Rheometer (ODR)

The Oscillating Disk Rheometer (ODR), introduced in the 1960s, was the first curemeter design to gain wide acceptance in the rubber industry. It consists of a bi-conical oscillating disk imbedded in a heated, sealed test cavity. The disk oscillates either at  $\pm$  1°, 3°, or 5° of arc, or at  $\pm$  14%, 42%, or 70% strain, with a frequency of 1.67 Hz (100 cpm). The test is standardized in ASTM D 2084 and ISO 3417. Standard test conditions call for 1° arc, 1.67 Hz, and 160°C. Most compounders select the temperature and arc that best suit their requirements of

efficiency and sensitivity.

Three types of S shaped curves can be expected from curemeter tests, as shown in Figure 23. One curve type reaches a plateau when the cure reaction is completed. This curve is typical of SBR compounds. A second type is a curve that reaches a maximum and then decreases with further heating. The decrease in torque is called "reversion", and it represents a reaction in which cross-links are broken with further heating, leading to lower torques. The reversion reaction is typical of Natural Rubber compounds. A third type of cure curve rises initially at a rapid rate, then proceeds to decrease as the curve continues to rise. This is called a "marching modulus" curve. Marching modulus curves occur in many different cure systems and polymers. ASTM data points include:

- M_L Minimum torque
- M_{HF} Maximum torque at point where curve plateaus
- M_{HR} Maximum torque of a reverting curve
- M_H Highest torque during test when no plateau or maximum is reached
- $t_s 1$  Minutes to rise 1 torque unit above  $M_L$  (used with 1° arc)
- $t_s 2$  Minutes to rise 2 torque units above  $M_L$  (used with 3° arc)
- $t_x$  Minutes to x% of  $M_H$ ,  $t_x$  = minutes to (x  $M_H$ )/100 torque
- + t'_x Minutes to x% of torque increase, t'_x = minutes to M_L+ x(M_H M_L)/100 torque
- PCR Maximum cure rate, PCR = Peak slope of cure curve, torque units/minute



Time

Figure 23: Typical Oscillating Disk Rheometer Data Points

# Moving Die Rheometer (MDR)

Rotorless curemeters like the Alpha Technologies MDR 2000® moving die

rheometer were introduced in the 1980s. In a rotorless curemeter, the lower die oscillates instead of a rotor. Rotorless curemeter tests are standardized in ASTM D 5289 and ISO 6502. Standard test conditions call for a frequency of 1.67 Hz (100 cpm), oscillating strains of  $\pm$  0.5°, 1°, or 3° of arc ( $\pm$  7%, 14% or 42% strain in the MDR 2000), and a 160°C temperature.

Rotorless curemeters offer several advantages over ODRs.¹⁷ Their advantages include rapid temperature recovery for a more isothermal test, and the ability to place film between the sample and the dies for easy sample removal. The MDR 2000 adds the advantages of a custom temperature control system, a sealed test cavity, and separation of the oscillating lower die from torgue measurement in the upper die. Custom temperature control provides more repeatable, rapid temperature recovery for improved test precision. A sealed test cavity holds samples under pressure to minimize slipping. Separation of the drive and torque measurements allows the MDR to accurately measure viscous and elastic torgues, as well as the phase shift from the applied strain. These improved rheometer design features greatly improve test precision and sensitivity. In a rotorless curemeter, the surface area attached to the torque transducer is less than that of the ODR rotor surface area. As a result, MDRs produce lower torques and faster cure times than ODRs.18 Better repeatability, and the elimination of ODR drawbacks such as erratic, slow temperature recovery and torgue losses during a test, gives MDR users greater sensitivity to the variation of rubber compounds. Many former ODR users have converted to rotorless curemeters.



Figure 24: Alpha Technologies MDR 2000 Test Configuration

The MDR 2000's separation of torque measurements from the lower die oscillation allows the measurement of both viscous and elastic torque. ODRs and rotorless curemeters that measure torque linked with applied strain can only report elastic torque with precision. In the MDR, the oscillating die applies a sinusoidal shear strain. Rubber samples typically resist the strain with a sinusoidal complex torque (S*) that is out of phase with the strain cycle by an angle  $\delta$ . S* torque divides into an in-phase elastic torque (S') and a viscous torque (S") that is 90° out of phase with the strain cycle. MDR test results are plotted as changes in S' and S" and in the tangent of the phase angle (Tan  $\delta$ ) with

time. Tan  $\delta$  is calculated as the ratio of Peak S″/Peak S' at any point in time.

Typical MDR data points include those used with ODR tests plus:

- S" @ML Viscous torque (S") when S' elastic torque reaches minimum
- Tan  $\delta$  @ML S"/S' when S' elastic torque reaches minimum
- S" @MH Viscous torque (S") when S' elastic torque reaches maximum
- Tan  $\delta$  @ML  $\,$  S"/S' when S' elastic torque reaches maximum



Figure 25: Components of an Oscillating Rheometer Torque Signal



Figure 26: Typical Rotorless Curemeter Data Points

# Sponge Compound Curemeters

Several rubber curemeters have been designed which measure both the vulcanization and blow reactions typical of cellular rubber compounds. For many

years, an instrument called the Monsanto Cone Rheometer was the standard instrument used for this test. It used a double cone test cavity with a pressurized seal to enclose and heat the sample. A pressure transducer on the surface of the outer die measured pressure increases due to the blow reaction. The inner cone oscillated through an arc, and a torque transducer produced a torque curve, indicating the progress of the vulcanization reaction. When properly adjusted, the Cone Rheometer produced repeatable measures of both reactions. Unfortunately, the setting of pressure conditions required some experience on the part of the operator. If the sample was enclosed under too high a pressure, the blow reaction might not be detected. If the sample was held under too low a pressure, the test cavity seal might be lost. These operating difficulties limited the use of the Cone Rheometer, and this instrument was discontinued.

Rotorless curemeters can measure both the blow and cure reactions if the rubber sample is held under the proper pressure. Unsealed rotorless curemeters rely on the uncured rubber to form a seal at the edges of the test cavity. When these instruments are equipped with a pressure transducer, they measure both the blow and cure reactions in a single test. This self-sealing system does not work well for all sponge compounds.

Sealed rotorless curemeters like the MDR 2000 do not rely on the rubber compound to seal the test cavity. In fact, these instruments are designed to generate high cavity pressures to minimize slippage. In order to measure the low pressures generated by sponge compound blow reactions, samples tested in sealed die systems must under-fill the test cavity.¹⁹ In many cases, a specimen that fills 75% test cavity allows precise, simultaneous measurement of both the blow and cure reactions for sponge rubber compounds. The primary requirement for the operator is to prepare specimens within a narrow weight tolerance of  $\pm$  0.1g. Film can be used to allow the easy removal of test specimens without sacrificing test sensitivity.

Sponge rubber compounds are a special case for curemeter testing, because of the conflict between the need for high cavity pressures to measure the cure reaction, and the need for low cavity pressures to measure the blow reaction. In most sponge rubber compounds, the timing and the intensity of both reactions are critical to consistent product quality. If the blow reaction is too early, the cell structure will be open cell, when closed cell may be desired. If the blow reaction is too late or less intense than desired, the cured rubber may be too dense. The MDR 2000 provides the efficiency of measuring both reactions in a single test.

#### **RPA 2000**

The Alpha Technologies RPA 2000 Rubber Process Analyzer is a DMRT with the MDR 2000 sealed test cavity design. This combination allows for the easy loading and unloading of rubber samples, plus a wider range of test conditions than are available with some DMRTs. The RPA can vary test conditions over a wide range:

Test Condition	SI Unit	Curemeter Units	Limits of Freq., Strain
Frequency	0.03 to 33 Hz	2 to 2000 cpm	cpm x° arc <u>&lt;</u> 2,047
Strain	± 0.7 to 1256%	± 0.05 to 90° arc	Hz x % Strain <u>&lt;</u> 462
Temperature	40 to 230°C	104 to 446°F	Max. Shear Rate = 30 s ⁻¹

Although the shear rate limitation appears low for most rubber processes, the results of experiments developed by Cox and Mertz indicate that RPA frequency in radians per second is equivalent to capillary shear rates in s⁻¹. This correlation allows the RPA to measure rubber flow properties up to 209 rad./s, which is equivalent to 209 s⁻¹ in many cases. Test temperatures can be rapidly changed during a test by using a low mass heater and forced air cooling. RPA tests and test sequences can easily be programmed using menu driven software. Test condition flexibility allows the RPA to test a single rubber sample for key properties before, during, and after cure.

RPA processability tests are standardized in ASTM D 6204. This test method calls for a pre-heat at very low strain (0.5 Hz,  $\pm$  2.8% strain), followed by a frequency sequence of 0.1, 2, and 20 Hz at  $\pm$  7% strain. The pre-heat time for raw polymers is 4 or 8 minutes, and 2 minutes for rubber compounds. Processability test temperatures are 100 or 125°C, or typical processing temperatures. This test is quicker and easier than a Mooney viscometer test with stress relaxation, and reveals more information about the processability of either raw polymers or rubber compounds. As with the MDR 2000, RPA 2000 tests can also be automated. A second stage RPA processability test, running a strain sweep after the frequency sequence, is under discussion in ASTM. High strain sweeps are useful for detecting variations in Natural Rubber and Nitrile elastomers that a frequency sweep may not detect.





#### Figure 27: Typical Sealed Torsion Shear Rotorless Curemeter

Operated as a curemeter, the RPA runs cure tests as efficiently as the MDR, according to ASTM Standard D 5289 or ISO 6502. The RPA can also change temperatures up or down at rates as high as 1°C/second to match actual cure temperature profiles. In some cases, variable temperature cure tests are more sensitive to compound variations than isothermal tests.

Once a rubber sample has been cured in the RPA test cavity, the temperature can be lowered by as much as 100°C below the cure temperature. At lower temperatures, the RPA can apply dynamic strain and frequency conditions to measure dynamic properties according to ASTM D 5992. The ability to test

specimens that have been cured in the same instrument is more efficient than curing special parts to be tested in dedicated dynamic testers.

Rotorless shear rheometers like the RPA 2000 combine the test condition versatility of a DMRT with the robust user friendly test configuration of a rotorless curemeter. The result is an instrument uniquely suited to characterize the processability and vulcanization reactions of the uncured rubber, and also to measure cured rubber dynamic properties in a test sequence performed on a single sample.²⁰ RPA tests correlate with many standard rubber tests that supplement curemeter tests. As a result, instruments like the RPA may reduce the testing burden for many laboratories, while increasing the quality and timeliness of test data for production control.

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### VULCANIZATE PHYSICAL PROPERTY MEASUREMENTS

#### by John A. Sezna

Rubber Testing Consultants Akron, OH

This chapter lists many common physical property tests used to measure the performance characteristics of vulcanized rubber and thermoplastic elastomers. Many common tests are documented as ASTM¹ and ISO² Standards. New physical property tests are constantly being evaluated to more accurately predict service performance. The tests described in this chapter are not intended to be all-inclusive, but are provided for reference purposes.

### **Tension Tests**

ASTM Standard Test D 412 and ISO 37 both describe procedures for determining the tensile properties of vulcanized rubber and thermoplastic elastomers. Tensile properties are widely used as a rapid means of measuring the general quality of a rubber compound. Tension tests are simple, quickly performed, and are commonly used in laboratory comparisons. The precision of tension tests may be deficient in some cases, due to the presence of poorly dispersed ingredients or flaws in the molded sample. The following properties are typically measured in tensile tests:

*Modulus* - The term modulus, or stress, is used to express the amount of force per unit of original cross-section area required to stretch the test piece to a given elongation. It expresses resistance to extension, or stiffness of the rubber. Typical elongation values used to determine modulus are 100% and 300%. Modulus is expressed in Pascals (MPa) or pounds per square inch (psi).

*Tensile Strength* - This is defined as the force per unit original cross-section area applied at the time of rupture of the dumbbell shaped test specimen. The precision of tensile strength tests is usually less than that for modulus. Tensile rupture is often precipitated by the presence of poorly dispersed ingredients or flaws in the molded sample. Tensile strength values are not normally distributed, and are sometimes used as pass/fail criteria to measure rubber quality. As with modulus, tensile strength is expressed in Pascals or pounds per square inch.

*Elongation* - The term elongation is used to describe the ability of rubber to stretch without breaking. In the case of a tensile test to failure, the term "ultimate elongation" refers to the length of the test piece at the time of rupture. Elongation is expressed as a percent of the original length of the test piece.

Tension Set - When vulcanized rubber is stretched and released, it does not return to its exact original length, but remains longer than it was before stretching. The increase in length, expressed as a percent of the original length, is defined as tension set, or permanent set. It depends on the amount and time of deformation.



Figure 1: Vanderbilt Rubber Lab Tensile Tester

Preparation of Tension Test Samples - Elastomeric compounds evaluated in developing data for Vanderbilt publications are prepared in accordance with procedures outlined in ASTM Standard Practice D 3183 "Rubber – Preparation of Pieces for Test Purposes from Products" and Standard Test Methods D 3184 through D 3192, covering the mixing, conditioning and curing of compounds for common polymers.

Mixing equipment includes 20 cm x 40 cm (8" x 16") open roll mills having friction ratios and roll travel speeds conforming to ASTM standards, a size B Banbury[®] internal mixer with two-speed motor and air pressure operated ram, and a 1 meter (40") open roll mill for masterbatching and larger scale compounding operations.

The molds used to press cure test slabs are constructed as shown in Figure 2. Neutral soap solution mold lubricant or cellophane may be used to facilitate easy stripping and rapid quenching after curing. Press platen temperatures are frequently checked with iron-constantan or copper-constantan thermocouples to ensure that consistent vulcanizing conditions are maintained.



Figure 2: Design of Four Cavity Compression Mold

Dumbbell test pieces are cut with water-lubricated dies, generally conforming to the dimensions shown in Figure 3. Exceptions are made when the test piece does not allow for testing to failure. For example, with high elongation rubbers, a smaller die with a center cross section 3.1 mm (1/8") wide and a center gauge length 12.5 mm (1/2") long is used to allow the sample to break within the crosshead travel limits of the tensile tester. Smaller test pieces may also be used when testing in an environmental chamber with a limited test travel range. For materials with low elongation ranges, a wider test piece may be used. Great care should be taken to keep the cutting dies sharp and in conformance to specified dimensions. If a test piece is not cut by a single stroke, or if the cut surface is not smooth, premature failures can occur, reducing the measured tensile strength. For elongation measurements, visual or optical measurement benchmarks may be applied to test pieces. These marks are applied with parallel steel blades, using a stamp pad with contrasting marking medium, or special tape strips may be applied. When tensile testers with contact extensometers are used, there is no need to apply bench marks to test pieces.



Figure 3: Design of Dumbbell Die for Cutting Test Pieces

*Evaluation of Tension Test Results* - If automatic recording equipment is not available, the following manual procedure may be used to calculate stress-strain data:

- Record the force in Newtons (pounds force) required to obtain the desired elongations (for example, at 100%, 300% and on to failure).
- From force and measurements of the original cross-section, stress (tensile) values can be calculated and recorded as:

Stress, in Pa (psi) =  $\frac{\text{force, in Newtons (pounds force)}}{\text{width x thickness in meters (inches)}}$ 

 For example, a dumbbell test piece cut with a 12.5 mm (0.25") wide die having a median thickness of 2.0 mm (0.079") and a break force of 365 N (82 lbf) has a tensile strength of:

> <u>365 N</u> 6.35 mm x 2.03 mm = 28.3 MPa (4100 psi)

(Note: a Pascal equals the stress of one Newton per square meter. Rubber stresses are typically measured in mega Pascals, and stated in MPa units.)

• The stress at 100% and 300% elongation may be calculated in the same manner, using the forces at these elongations.

*Tear Resistance* - Tear resistance in rubber may be described as the resistance to growth of a nick or cut when tension is applied in a transverse direction. It is commonly expressed in units of Newtons per meter (pounds per inch). ASTM Standard Test Method D 624 and ISO 34 describe several tear test configurations, each measuring a different characteristic of this property:

*Nicked Crescent Tear* - These test specimens, defined in ASTM D 624 as Type A and B, are razor-nicked on the inside curve of a crescent shape. As the specimens are pulled in a direction perpendicular to the "nick", the tear is

expected to grow in the direction of the original cut. This configuration is designed to measure tear propagation tendencies in a cured rubber compound. Due to the variation in "nicks" and in test pieces, this test has poor precision compared to other tear tests.

 $90^{\circ}$  Tear - Defined as ASTM D 624 Die C Tear, this specimen has a  $90^{\circ}$  angle that is pulled at a  $45^{\circ}$  angle from the apex of the angle in the center of the test piece length. This type of specimen fails suddenly, and is designed to measure the tendency of a cured rubber compound to initiate a tear at a stress concentration point. This is the tear test normally used by the R.T. Vanderbilt Company Rubber Laboratory.



Tolerance ± 0.05mm (0.002[°])

### Figure 4: Design of ASTM D 624, Die C Tear Sample

*Trouser Tear* – Cut in the shape of a pair of trousers from a flat sheet, this test specimen is clamped in a tensile tester so that one leg of the trouser shape is pulled in each direction. This test is intended to measure tear propagation in the direction of the trouser legs. The difficulty with this test is that the tear does not always follow the expected path.

*CP Trouser Tear* – Also intended to measure tear propagation, Controlled Path (CP) Trouser Tear specimens consist of molded bars of rubber with a thin sheet of the rubber molded between them. The test piece is initially cut between and parallel to the molded bars, and pulled like a trouser tear specimen. The purpose of the molded bars is to force the tear to follow a path along the axis of the tensile pull. Also, unlike the simple trouser tear test, the legs of the bar are less likely to elongate at the forces necessary to propagate the tear.

Note that no correlation of results has been established from one type of tear test to another. This indicates the difficulty of using laboratory tear test results to predict tear in service where additional loading conditions may occur.

### Hardness

Hardness is a property of rubber that indicates resistance to indentation, and is expressed as a number referring to the scale of the instrument by which it is measured. It is an important property, frequently used in rubber specifications along with tensile properties. There is a modest correlation between hardness and tensile modulus, but it is important that hardness not be used as a replacement for tensile modulus results.

ASTM Standard Test Methods D 531, D 1415, D 2240, and ISO 48 describe hardness testing procedures using the most widely accepted methods. D 2240 describes the construction and uses of several hardness measuring instruments which use calibrated springs, rather than a dead weight, as the means for estimating a hand-applied force on the indentor foot acting through a presser foot. The Durometer hardness scale runs from zero for full extension to 100 for zero extension of the indentor.

*Durometers* - Durometers, as illustrated in Figure 5, are used in routine hardness testing. This type of instrument is provided with several arbitrary scales. The Shore A Durometer is used for soft rubber testing, and the Shore D Durometer is used for harder products. IRHD hardness scales are specified by ASTM D 1415 and by ISO 48. The IRHD scale is similar but not equivalent to the Shore A scale. The relationship between Shore A and IRHD hardness is significantly affected by differences in the shape of the indentor and the applied force.



Figure 5: Hardness Testers P&J Plastometer photo courtesy of Shore Instrument Co.

Pusey and Jones Plastometer - This hardness measuring device and its operation are described in ASTM Standard Test Method D 531. It is widely used to measure the hardness of rubber covered rolls, particularly those used in the

paper industry. This instrument operates on the dead weight principle, with a 3.2 mm (0.125") diameter indentor foot actuated by a 1 kg (2.2 lb.) load. Hardness readings, taken after 1 minute, are recorded on a scale graduated in hundredths of a millimeter.

# Abrasion Resistance

This property may be defined as the resistance to wearing away through rubbing or impact in service. Many laboratory tests have been developed to measure abrasion by modeling different conditions of wear. Most of these tests have poor precision and poor correlation with service wear.

*NBS Abrader* - ASTM Standard Test D 1630 and ISO 4649 describes the apparatus for the National Bureau of Standards Abrader and the instructions for its use. This test is widely used by shoe sole and heel manufacturers to meet specifications and to indicate relative abrasion resistance.

The NBS Abrader has three pivoted and weighted arms that press test pieces against a 40 grit, No.1½ garnet abrasive paper. The abrasive is held on a 50 mm (6") diameter rubber covered drum rotating at 45 revolutions per minute. Dial gauges mounted on a hinged bridge indicate wear in 0.025 mm (0.001") increments. A compressed air line keeps the abrasive surface clear.

Three test specimens measuring  $25 \times 25 \text{ mm} (1 \times 1'')$  and approximately 2.5 mm (0.1'') thick are run in parallel to obtain the average number of revolutions required to wear away 2.5 mm (0.1'') of thickness. A standard compound is used to provide a relative value for comparison to other test results. The number of revolutions required to abrade the test material as compared to the standard compound is expressed as a ratio, using an index of 100 for the latter.



Figure 6: National Bureau of Standards Abrader Photo courtesy of Advanced Rubber Testing Technologies

*Pico Abrader* - In this test, described in ASTM Standard Test Method D 2228, a pair of tungsten carbide knives of specified geometry and sharpness is used to abrade the surface of a disk-shaped molded rubber specimen. The knives are

lowered onto the rotating specimen at a specific force, and a dusting powder is used to keep the knives from gumming up. Abrasion is measured by volume loss based on the change in specimen weight. Calibration compounds are mixed and molded as reference standards. If the expected abrasion levels occur with the reference compounds, then the Pico Abrader is considered to be calibrated. The Pico abrasion test is intended to predict abrasion similar to tire tread wear, but its correlation with actual tire wear is poor.

### Flex Fatigue Resistance

The ability of rubber products to withstand flexure under dynamic loading conditions is related to service conditions, and the tendency for initiation and propagation of cracks. The growth of these cracks under repeated deformation can lead to catastrophic failure. This process is known as fatigue. Fatigue failure in rubber originates at minute flaws where stress is concentrated. There are two distinct causes of crack formation in rubber: ozone scission and mechanical-oxidative rupture. The effects of these causes can be reduced through compounding for maximum fatigue resistance to give longer service life, or to allow more severe operation conditions.

Rubber articles such as tires, belts and soles are subject to repeated flexing which may gradually bring about failure. This may be due to ply separation between reinforced layers in tires and belts, crack growth in the rubber itself, or a rupture as in a tire blowout. Various specialized tests have been devised and used to test molded rubber samples or finished assemblies by subjecting them to simulated service conditions. ASTM and ISO Standard test methods cover many of these tests, including the Scott Flexing Machine for the testing of separation tendencies in rubber-fabric combinations (ASTM D 430); the DuPont Flexing Machine for ply separation tests or to test for failure due to surface cracking (ASTM D430); the DeMattia Flexing Machine for surface cracking or crack growth due to repeated bending or extension (ASTM D 430 and D 813, ISO 1132 and 133); the Ross Flexing Machine to test for cracking of shoe sole materials (ASTM D 1052); and the Fatigue to Failure Tester, which provides a combined measure of crack initiation and crack growth (ASTM D 4482). The results of each method are representative only of the test configuration, and may not correlate with other tests or with service life under different conditions.

*DeMattia Flex Machine* - The DeMattia test uses test pieces that are molded strips 25 mm (1") wide by 6.35 mm (0.25") thick by 150 mm (6") long, with a semi-cylindrical transverse groove of a 2.39 mm (0.94") radius. The machine is adjusted for a maximum travel of the moving grips of 100 mm (4"). During each stroke of the DeMattia machine the grips approach each other to a distance of 19 mm (0.75") and separate to a distance of 75.9 mm (2.99"). The circular groove is oriented so that it becomes the outside surface of the bent specimen. This configuration concentrates the bending strain at the bottom of the molded groove.

During a test, a DeMattia test piece is repeatedly bent to a doubled position, maximizing the strain in the groove. This is intended to simulate the flexing

of a groove in a tire tread. The usual flexing speed is 300 cycles per minute. After a suitable number of cycles, depending on the compound, the test piece is examined and rated according to the degree of cracking, by comparison to a photograph of standard specimens graded from 0 (no cracking) to 10 (completely cracked through). Flexing may be continued for subsequent inspections and ratings, or until the test pieces have cracked through – in which case the flexures to failure are recorded. The photo in Figure 7 shows the standard specimens.

The DeMattia flexing mechanism may be enclosed in an insulated chamber for non-ambient temperature tests, and for testing in gasses other than air. When flex-testing SBR compounds in the DeMattia machine, it is customary to nick the test piece before flexing to measure crack growth. ASTM Standard Test Method D 813 describes this procedure. The end point of this test is generally taken as the number of cycles necessary to promote growth of the nick from an initial cut of 2.5 mm (0.10") to a crack 19.0 mm (0.75") wide.



Figure 7: DeMattia Flex Machine Photos courtesy of GIBITRE Instrument s.r.l. Dergano, Italy

Ross Flex Machine – As described in ASTM D 1052, this test is performed by bending up to six pairs of test pieces 25 mm (1") wide by 150 mm (6") long to a 90° angle at a rate of 100 flexures per minute. Test piece thickness may vary from 3.1 mm to 12.5 mm (0.25-0.5"), but comparisons should be made only with samples of equal thickness. One end of each test piece is firmly clamped, while the other end is held between two rollers. The top roller is adjustable to allow the test piece to slide freely during flexing. Between the clamped end and the rollers is a rounded edge over which the test piece flexes. The weight of the top roller is the only pressure exerted on the test piece during a test.



### Figure 8: Ross Flex Machine

Photo courtesy of Advanced Rubber Testing Technologies

Prior to testing, a perforation is made in each test piece with a 2.5 mm (0.1") wide chisel point awl, in the center at a point 63.5 mm (2.5") from the attached end of the strip and perpendicular to its length. When attaching the test piece in the machine, the perforation must be set at the exact point of maximum flex at the 90 degree angle. As the test progresses, the increase in the width of the initial surface perforation is measured in 2.5 mm (0.1") increments. Failure of the test piece is indicated when the perforation's growth has extended the full width of the strip, regardless of its depth.

*Fatigue-to-Failure Tester* - The testing machine provides a combined measure of crack initiation and crack growth. A photograph of the tester is shown in Figure 9. The test method, described in ASTM D 4482, subjects dumbbell shaped test pieces to a repeated strain cycle as the bars holding the test specimens are displaced by rotating cams. A PC controls the cycling process and counts cycles on each specimen until failure. The count values are saved to a disk file every 100 strokes so that the data will not be lost in case of a momentary power failure.



Figure 9: Fatigue-to-Failure Tester Photos courtesy of United Testing Systems

The maximum strain imposed in the Fatigue-to-Failure test can be varied over a wide range by changing cams on the instrument. The fatigue properties of vulcanized compounds may be compared directly at equal strain, or the results may be converted to equal strain energy conditions. Figures 10a and 10b illustrate typical results for Natural Rubber and SBR black-filled compounds as a function of the extension ratio and strain energy, respectively.

Strain energy values are calculated by plotting the stress-strain curve for a pre-fatigued sample and integrating the area under the curve up to the extension used for fatigue testing. Comparison at equal strain energy compensates for differences between materials with differing modulus values.

During a test cycle, the samples are subjected to increasing strain at uniform acceleration for a quarter of a cycle, after which the strain is relaxed for a quarter of a cycle. Samples are held at zero strain for half of a cycle. Testing continues until all samples fail by separating into two parts. Since rubber samples under fatigue loading fail at a frequency corresponding to a statistical distribution of results, a minimum of 6 test pieces should be tested for each material and each test condition. Fatigue-to-Failure testers are designed to test 24 or more samples under one or more strain conditions to accommodate the need for a statistically valid set of test results.

A study by Vickery, et al³, observed that the degree of mixing has a strong influence on fatigue results, and also demonstrated that the Monsanto Fatigue to Failure Tester gave better reproducibility than the DeMattia test method.



#### **Dynamic Properties**

Vulcanized rubber and thermoplastic elastomers have both elastic and viscous responses to deformation. A number of tests have been devised to measure both of these responses to dynamic loading conditions. ASTM Standard Guide D 5992 describes the theory and practice of measuring the response of rubber to dynamic loading conditions.

*Resilience* - Resilience is defined by ASTM D 1566 as the ratio of energy output to energy input during the rapid recovery of a deformed specimen. In cured rubber testing, this is often measured with a rebound test or a cyclic loading test. Several types of rebound testers have been devised, and many are still in use.

Goodyear Healey Rebound Tester - ASTM Standard Test Method D 1054 describes the Goodyear Healey Rebound Pendulum Test. This test uses a freely falling pendulum hammer dropped from a fixed height to impact a rubber cylinder. The height of the pendulum after rebounding from the impact is recorded. Since the energy of impact and rebound are both proportional to the height of the pendulum, the percentage rebound is used to measure resilience:

Rebound =  $\frac{1 - \cos(\text{angle of rebound})}{1 - \cos(\text{original angle})} \times 100$ 

Two specimens, 12.5 mm (0.5") high by 41 mm (1.6") in diameter, should be tested, taking the average of the fourth, fifth and sixth impacts on each specimen. If temperature dependence is to be studied, the specimens should be conditioned prior to testing. While this test is labor intensive, and may require the preparation of several specimens, the simplicity of the test is appealing.

Resilience by Vertical Rebound (Bayshore) – ASTM Standard Test Method D 2632 determines impact resilience of solid rubber from measurement of the vertical rebound of a dropped mass. Resilience is calculated as the ratio of rebound height to drop height of a metal plunger of prescribed mass and shape which is allowed to fall on the rubber specimen.

The height of the drop point and the resilience scale above the base of the instrument is adjustable so that the drop height is always  $400 \pm 1$ mm above the specimen surface. The resilience scale is marked in 100 equally space divisions. The descent of the plunger and its ensuing ascent (rebound) is guided by a vertical rod (plunger guide).

The standard test specimen may be molded or cut from a slab of rubber at a thickness of  $12.5 \pm 0.5$  mm, and have a minimum distance of 14 mm from the point of the plunger to the edge of the specimen.

Three test specimens are taken from the same sample, and six test determinations are made on each specimen. The first three test determinations are not recorded, as they condition and stabilize the specimen.

Since the instrument scale is divided in 100 equal parts, the test determination is equal to the resilience value in percent. The 4th, 5th and 6th test determinations from a specimen are used to calculate the test result from the specimen. The test results are averaged to the nearest whole number, which is the resilience value of the specimen. The median may also be used.



Figure 11: Rebound Testers

Goodrich Flexometer (Heat Buildup) - The Goodrich Flexometer, as described in ASTM Standard Test Method D 623 (Method A), is used to measure the increase in heat due to cyclic deformation under load. Rubber cylinders, 25 mm (1") high and 17.5 mm (0.7") in diameter, are either cut from cured rubber or molded for testing. As illustrated in Figure 12, the test specimen is positioned between heated, insulated anvils. The lower platen rests on a pivot arm that has a weight attached to one end so that a load of 0.7 to 2.1 MPa (100 to 300 psi) is applied. The top anvil is connected to an adjustable eccentric that drives a vertical oscillation at 30 Hz (1800 rpm). The stroke of the oscillation may be varied, but the recommended strokes are 4.45 mm (0.175"), 5.71 mm (0.225"), and 6.35 mm (0.25"). The bottom anvil has a thermocouple that monitors the temperature of the base of the specimen. An optionally available oven may be placed around the specimen to increase the test temperature.



Figure 12: Goodrich Flexometer Photo courtesy of Ektron Tek Company (Model EKT 2002 GF)

Under severe loading conditions, some materials will fail by "blow out". A "blow out" occurs when rubber degrades due to heat buildup and internal gasses are formed which destroy the integrity of the sample when the gas pocket collapses. The main factor is the amount of time before "blow out". Under less severe conditions, the key data is the temperature rise after 25 minutes of testing, when a thermal equilibrium is usually reached.

In older models of the Goodrich Flexometer, the pivot arm rested on a knife edge, and temperature and time were monitored by chart recorders. Newer models use a more precise bearing pivot, and electronically measure temperature, elastic and viscous forces, and the phase shift in force response. The viscoelastic response measurements allow a more precise measure of dynamic properties, which may be applied to other loading conditions. The

heat buildup and blow out measurements are more difficult to apply to service conditions, because they are only representative of the individual test.

Yerzley Oscillograph - The Yerzley Oscillograph is a laboratory device designed to measure the mechanical properties of rubber under small strains. It is described in ASTM Standard Test Method D 945. In this test, specimens are loaded by an unbalanced lever and the resultant deflections are recorded. This enables calculation of static modulus at any stage of a loading sequence. Creep and recovery rates can also be obtained. Since the lever is supported by a knife edge, specimens can be impact loaded, and the free vibration response measured. The free vibration test allows the calculation of dynamic modulus, a resilience index, an oscillation frequency, and a measurement of stored energy. Specimens may be loaded in compression or in shear configurations.

This test is primarily used for materials that deform approximately 20% under compressive stresses below 2 MPa (290 psi), or shear stresses below 1 MPa (145 psi). As a result, Yerzley free vibration tests measure small forces and displacements, and are more suited to the research laboratory where the instrument can be isolated from ambient vibrations.

Dynamic Mechanical Testers (DMTs) - A number of instruments have been designed to measure the dynamic properties of cured rubber parts. Many of these devices were custom made fixtures that test under simulated service conditions. For testing cured laboratory specimens, standard configurations have been adopted by many manufacturers, although specimen sizes vary somewhat between instrument types. ASTM Standard Guide D 5992 describes the various test configurations and test results available for dynamic testing.

Typical laboratory DMT tests may involve the application of a cyclic strain or load to a cured rubber cylinder. A typical loading uses a 29 mm diameter by 12.5 mm thick cured rubber specimen which is pre-loaded prior to the application of a cyclic compressive strain. As long as the specimen is kept under compression throughout the test, it is not necessary to bond the specimen to the loading surfaces. Other test configurations require more complicated preparation to test the sample under conditions of under oscillating shear, under tension/ compression, or under bending. Figure 13 below illustrates the typical force response to a sinusoidal cyclic loading condition in a DMT test.



Figure 13: Typical Rubber Force Response to Cyclic Strain

Laboratory testing with DMTs usually requires preparation of a cured specimen, which must be conditioned for a minimum of 16 hours before testing. This delay complicates routine measurement of rubber compound dynamic properties by DMTs.

Rubber Process Analyzer - The RPA 2000 Rubber Process Analyzer is a special type of DMT that cures a specimen in the instrument, using a rotorless curemeter test configuration. After cure, the RPA can lower the temperature rapidly to measure cured dynamic properties. The sample is loaded in a oscillating shear configuration which measures elastic and viscous torques (S' and S"), elastic and viscous shear modulus (G' and G"), as well as the tangent of the loss angle (Tan  $\delta$ ) due to damping. Typical test conditions involve strain steps up to 100% and frequency steps up to 30 Hz. Eliminating the need to separately cure test specimens makes the RPA a more practical test for monitoring dynamic property variations of rubber compounds for both research and production control.

#### Low Temperature Properties

All elastomers become progressively stiffer as they are cooled. Stiffening due to thermal cooling is known as "second order transition". "First order transition" is stiffening due to crystallization, or molecular alignment. These two stages of stiffening can adversely affect the ability of an elastomer to function properly. Certain compounding ingredients can be added or avoided to change low temperature characteristics. Unfortunately, some ingredients, such as ester plasticizers, increase the rate of crystallization for many elastomers while lowering the brittle point temperature. Heating or flexing destroys thermally induced crystallinity, and the rubber returns to normal. The brittle point, measured by ASTM Standard Test Method D 746, is the temperature at which a specimen becomes brittle and will shatter on sudden bending or impact. Since the brittle point is not a sharply defined point, the ASTM test defines it as the temperature at which 50% of the specimens fail the specified test. Both the rubber thickness and the rate of loading affect the brittle point. Brittleness temperature has no direct relationship to stiffness.

Elastomers are far superior to plastics in low temperature performance. Some elastomers have to be compounded especially for low temperature applications. Others, such as EPDM, polybutadiene and silicone, have good low temperature flexibility and brittle point temperatures as low as -51°C to -73°C for EPDM and -90°C to -105°C for polybutadiene and silicones. Elastomers will continue to seal and/or flex in many low temperature applications where other materials soon fail.

A number of standard tests have been devised to measure the low temperature performance of rubber compounds and of cured rubber parts. The following table lists several ASTM standards designed to test the low temperature characteristics of elastomers:

ASTM		
Designation*	Title	Measurement
D 746	Brittleness Temperature of Plastics and Elastomers by Impact (Solenoid Impact)	Brittleness
D 1043	Stiffness Properties of Plastics as a Function of Temperature by Means of a Torsion Test (Clash-Berg)	Modulus of Rigidity
D 1329	Evaluating Rubber Property – Retraction at Lower Temperature (TR Test)	Elongation values as specimen thaws
D 1053	Stiffening at low Temperatures: Flexible Polymers and Coated Fabrics	Stiffening (Twist) Resistance

Table 1:	ASTM	Standards	for	Low	Tem	perature	Testing
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*Order of popularity and general importance

### Aging Properties and Tests

Laboratory tests that predict the potential life of rubber products follow the general procedure of exposing the vulcanizate to deteriorating environments under static or dynamic conditions. The environmental conditions used in the laboratory are often more severe than those actually encountered in service. These are described as "accelerated" aging tests, since they intend to measure in a short time the changes in properties that take place over extended periods under actual service conditions. The correlation of results between accelerated and natural aging is difficult in many cases. Accelerated tests do, however, show trends, and are widely used as a guide in compounding studies and rubber product specifications.

Heat is one of the primary conditions that cause rubber deterioration. The presence of oxygen serves to accelerate heat-induced aging effects. A number

of heat aging tests have been devised to identify these effects.

*Compression Set* - Rubber is often used in sealing applications where a compressive load is applied. If the rubber loses its resilience and no longer resists the compressive displacement with the same force, the seal created by the compression of the rubber may be compromised. In the Compression Set Test, defined in ASTM Standard Test D 395 and in ISO 815, a constant load (Method A of ASTM D 395) or constant deflection (Method B of ASTM D 395) is applied to compress a cylindrical button. The constant displacement method is the most widely used. The test specimens are either 29 mm in diameter by 12.5 mm thick, or 13 mm in diameter by 6 mm thick. Typical aging conditions are 22 hours at 70°C, or 70 hours at 100°C. Customer specifications may require more severe test conditions. Compression set is calculated as a percentage of the original specimen's thickness.



Figure 14: Vanderbilt Rubber Lab Compression Set test equipment

Oven Aging – Acceptable test methods and ovens for rubber aging are described in ASTM Standard Test Method D 573. The oven aging procedure calls for heating dumbbell test specimens in preheated air at atmospheric pressure which circulates freely around the test piece. The most widely used aging temperature is 70°C (158°F), although some product specifications call for oven aging at temperatures up to 121°C (250°F) for unsaturated rubbers. Increased temperatures cause deterioration at a rapid rate, which does not necessarily follow the same chemical laws of reaction predicted by time-temperature relations at lower temperatures. Higher test temperatures are useful for comparing specific properties of some synthetic rubber compounds. Aging intervals frequently used are 2, 4, 7 and 14 days. Ovens for accelerated aging tests offer the advantages

of easy operation, flexibility in the choice of temperatures, and the ability to test a large number of specimens. The main disadvantage is that contamination of test specimens may occur due to migration of sulfur or protective materials when compounds with different formulations are aged simultaneously.

Separate ovens are used for aging tests of rubbers specially compounded for heat resistance with sulfurless cure systems. An oven aging method which uses individual cans, perforated at the bottom to permit free air circulation, and exhausting through a common manifold fitted with a blower, is also used. This arrangement permits the simultaneous aging of dissimilar compounds without contamination.

Tensile properties are typically compared before and after heat aging. The aging effect is usually stated as a percentage change in the measured property, along with a description of the aging conditions.

Test Tube Aging - ASTM Standard Test Method D 865 describes a "test tube" method for heat aging that has received wide acceptance. This procedure eliminates the possibility of contamination between different rubbers containing volatile ingredients. Individual test tube aging units are constructed as depicted in Figure 15 with vent tubes to permit free circulation of air and the removal of volatile components. Three dumbbell specimens from the same compound are typically suspended in each test tube. Glassware used in this manner can be easily cleaned after each test. Special electrically heated aluminum blocks that hold a number of test tubes are used for the Test Tube Aging test.



Figure 15: Vanderbilt Test Tube Heat Aging equipment

Oxygen Pressure Aging - Originally described as the "Oxygen Bomb" test when introduced by Brierer and Davis in 1924, this aging method combines the deteriorating effects of high pressure oxygen and heat. The test is described in ASTM Standard Test D 572. An oxygen pressure of 2.1 MPa (300 psi) and a temperature of 70°C (158°F) are the most frequently used test conditions. To

evaluate rubbers specially compounded for heat resistance, the temperature is typically increased to 80°C (176°F). Rubber compounds tested by oxygen pressure aging degrade much more rapidly than when subjected to heat aging alone.



Figure 16: Vanderbilt Rubber Lab Oxygen Bomb Equipment

*Air Pressure Aging* - ASTM Standard Test Method D 454 describes an accelerated aging test in which rubbers are exposed to 550 kPa (80 psi) of air pressure and a temperature of 127°C (260°F) for short periods of time. This procedure, introduced by the U. S. Rubber Company (now Chemtura, Inc.) was originally known as the air bomb test. It is the most drastic of the accelerated aging tests, with significant deterioration taking place in a matter of hours, compared to days for oxygen pressure aging.

### Natural vs. Accelerated Aging

The relative effects of natural and accelerated aging on the physical properties of natural rubber tread-type compound in Table 2 are compared in Figure 16. The graphs shown are reproduced from a paper titled "Correlation of Room Temperature Shelf Aging with Accelerated Aging", presented by the Vanderbilt Laboratory at a meeting of the Rubber Division of the American Chemical Society (New York, Sept. 1954). An updated compound used for comparison is listed below:

Ingredient	phr
SMR-L	100.0
Stearic Acid	2.0
Zinc Oxide	5.0
N990 MT Carbon Black	35.0
N330 HAF Carbon Black	30.0
AGERITE [®] STALITE [®] S	1.5
VANPLAST® R	2.0
VANFRE® AP-2	2.0
Sulfur	3.0
ALTAX [®] (MBTS)	1.0
Total	181.5

Table 2: Natural Rubber Tread-Type Compound

In 1931, a series of compounds were mixed at R.T. Vanderbilt Company, Inc. to obtain data for publication purposes. At intervals during the next 22 years, the physical properties of these stocks were determined. The tensile strength and elongation test results gave a fairly uniform decrease in property retention, while the modulus showed a rapid increase followed by a gradual decline. In order to compare the updated compound a new set of aging tests were run to determine the relative performance of air aging in test tubes versus oven air aging. The observed trend from this study was also added to the graphs.

Among the accelerated aging tests, the oven air aging procedure provided the closest correlation to shelf life aging effects. This is determined from the overall similarity of the graphs plotting physical property changes from natural aging and aging in air at 70°C. In general, one day of oven aging corresponds to one year of natural or shelf aging for natural rubber.

The important thing in all technical development and control is to choose an aging test which most nearly approaches service conditions, and to guard against the shortcomings of even the best of tests. For some rubber products, the oven test may correlate to natural aging or represent heat deterioration at elevated use temperatures. The convenience of the oven air aging tests then justifies its use. The more closely service conditions are simulated, the more meaningful the tests become.







Figure 17: Comparison of Normal and Accelerated Aging

### Weather Resistance

Describing rubbers as "weather resistant" implies that they will withstand prolonged outdoor exposure without deteriorating to a point where they are no longer fit for service. Outdoor exposure on the roof of a plant or laboratory, or on test farms where the ambient atmosphere is favorable to rapid deterioration, is one of the oldest aging tests applied to rubbers, and is still widely practiced.



Figure 18: Effects of Weathering on Inadequately Protected Rubbers Photo courtesy of Bell Telephone Laboratories (Lucent)

Methods for mounting prepared samples and exposing them to obtain information on their weather resistance are described in ASTM Standard Test Methods D 518, which uses looped flat strips, and D 1171, which uses triangular molded, extruded, or sponge strips mounted over mandrels. The purpose of both tests is to bend the sample so that the exposed surfaces are stressed uniformly.

The Goodrich Flex Machine, as shown in Figure 19, is used for outdoor dynamic testing for weather resistant rubber compound development.



Figure 19: Vanderbilt Outdoor Dynamic Testing Wheel

As a result of intensive research, the so-called "weather components" that contribute to the aging of rubbers and other organic materials have been isolated.

It is now generally agreed that in addition to heat, oxygen and moisture, light and ozone are major contributing factors in the atmospheric aging of rubbers. Light consisting of wave lengths between 200 and 500 nm (2000 and 2500 Angstroms), and ozone in dilute concentrations ranging up to 100 parts per 100 million of air in extreme cases, are critical agents of aging. Accelerated exposure tests using these destructive forces are used to obtain valuable information for weather resistant compound design.

Accelerated Light Exposure Tests - Light consisting of wavelengths in the ultraviolet spectral band may deteriorate rubbers by discoloring white or light colored products to an objectionable degree, or developing a brittle surface layer which crazes upon flexing. Light-susceptible rubbers will undergo these alterations when exposed in an unstressed condition. Tendencies to discolor through exposure to light can be compared in a laboratory by using a Weather-Ometer. In principle, this test involves the exposure of samples to a standard ultraviolet light source under controlled conditions.



Figure 20: Vanderbilt Rubber Lab Weather-Ometer

ASTM Standard Test Method D 1148 describes a light discoloration test using sunlight bulbs as the source of ultraviolet radiation to expose samples under prescribed conditions. A modification of this test, described in ASTM D 925, is used to study the discoloration of organic finishes on metal parts, caused by the exposure to sunlight of rubber parts with which they come into contact. ASTM D 750 describes equipment and procedures for exposing samples to calibrated light sources for accelerated aging tests.

Accelerated Ozone Cracking Tests - Ozone is the atmospheric compound

which is responsible for the cracking of rubber products under conditions of stress or strain. Ozone concentrations have been found to vary from 0 to 100 parts per hundred million (pphm) around the world. The severity of cracking is modulus dependent and a direct function of ozone concentration. The strain at which maximum ozone damage occurs is lower for rubbers that crystallize on stretching, such as polyisoprene. Ozone cracking does not occur in saturated polymers, and the extent of ozone damage increases with the degree of main chain unsaturation.

The Vanderbilt Rubber Laboratory uses a Mast Keystone Model 700-10 Ozone Test Chamber to compare the resistance of stressed rubbers to deterioration in a controlled ozonized atmosphere. Ozone concentration is maintained at 50-100 pphm of air, as indicated in ASTM D 1149. Additional ASTM test methods for ozone resistance include D 518, D 1171, and D 3395. A Mast Model 727-3 Ozone Meter (Ultraviolet Absorption Technique) coupled to a strip chart recorder provides a continuous record of ozone concentration 24 hours a day throughout an entire test period.

ASTM Standard Test Method D 518, Method B describes the preparation of bent loop test specimens used by the Vanderbilt Rubber Laboratory for ozone tests. These test specimens are cut from cured laboratory test slabs having a thickness ranging from 1.9 mm (0.075") to 2.5 mm (0.100") so that the grain is in the lengthwise direction. The rectangular test specimens are 25 mm (1") wide by 150 mm (6") long. Duplicate test specimens should be run.

The test samples are mounted between wooden blocks in a bent loop position, and the basic screening test consists of 24 hours' exposure at 50 pphm of ozone in air at 50°C. Samples are then examined under a 7 power magnifying glass, and are rated from 0 to 10. The 0 rating indicates no cracking, and 10 indicates severe cracking or broken specimens. The frequency and depth of cracks are also noted. It may be necessary to extend the exposure period or raise the test temperature in some cases to establish a basis for comparison.

Ozone present in high concentrations (150 parts per million or higher, as opposed to a few parts per hundred million) exerts a much faster cutting action on stressed rubbers. Such concentrations are encountered when electrical energy flows from a conductor of high potential into the surrounding air. High voltage is generally accompanied by a faint glow, or corona, and has the ability to convert the oxygen in the surrounding air to ozone.



Figure 21: Vanderbilt Rubber Lab Ozone Chamber

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### RUBBER PROCESSING and RUBBER PROCESSING MACHINERY

### by Michael A. Melotto*, with updates by Frank Borzenski

Farrel Corporation Ansonia, CT *Deceased

### **Trends In Rubber Processing**

With the beginning of the 21st century, the most notable advancements in the rubber industry can be found in better quality rubber products and improved efficiency in the methods by which they are produced. Competition, government safety demands, and the need to reduce manufacturing costs each have contributed to these improvements. The rubber industry has been notorious for its conservative attitude when it comes to modernization. This reflects to some extent upon the high cost of capital equipment. Automation is no longer a vulgar word to management or direct labor employees who are both aware of the need to improve and become more competitive. Computers have contributed significantly to many of these improvements. Not only is machinery capable of being automatically controlled, but the manufacturers of machinery and rubber product raw materials have also benefited from computerization.

Implementation of controls over the safe use of raw materials has been exercised by the presence of Material Safety Data Sheets in every mixing facility. Concern for operator's safety is ever present in this respect, as well as with the latest requirements that have been placed upon machinery manufacturers to make their equipment safer. Items such as body bars on mills, special cages on laboratory mills and explicit safety tags that have been placed on mixing machines are examples of these improvements.

Mixing and forming machinery used in the manufacture of rubber products appears to be the same today, as it was seventy-five to eighty years ago. Mills, internal batch mixers, extruders, and calendars, are still the fundamental devices used to mix and process rubber compounds. Continuous mixers and twin-screw extruders are the latest innovations to be used in a limited degree for mixing rubber compounds. Their main limitation relates to the fact that materials to be mixed in these machines must be available in free flowing forms, capable of being delivered from continuous feeders. From outward design appearances, two-roll mills and internal mixers used for mixing and processing rubber compounds, have the same basic appearances and provide the same services that historically have been required of them. Unlike the proverbial "rose is a rose", rubber processing machines have undergone major changes and bear little similarity to their original designs. Likewise the rubber tire of today is still round and black, but markedly outperforms earlier designs. In order to provide the quality levels required of modern rubber products, machinery has undergone and continues to under-go improvements. Improvements have been designed not only to improve efficiency and product quality, but also to provide greater endurance and resistance to wear.
The mill room of today, following materials handling devices, usually consists of mills and batch mixers, as depicted in Figure 1. A mill performs the function of rubber preparation and warm–up for successive processing, and may be used as a batch-handling device under a batch mixer, and in some instances can be ideal for mixing a single batch of a specialty compound. The batch mixer is usually the workhorse of the mill room. This mixer can provide the requirements of long runs and is capable of automated operation. In order to fully utilize the capabilities of rubber processing machinery, one must understand the purpose for its design and the optimum method of operation. It has been said and still holds true, that rubber quality begins in the mill room. If quality is not achieved with satisfactory mixing machinery, quality raw materials, and good mixing procedures, subsequent processing and fabrication procedures will suffer. Down stream equipment will rarely correct poorly mixed rubber compounds.



Figure 1: Typical Mill Room Layout

# RUBBER COMPOUND MIXING

# **Elastomer Mastication**

The first step in the compounding process involves the mastication or breakdown of the polymer. This step is necessary to render the polymer receptive to the fillers and other ingredients of the formulation. With some low viscosity polymers, little or no pre-mastication may be necessary. Natural rubber is especially sensitive to mastication as this process can significantly reduce Mooney viscosity of the polymer, depending upon time and temperature of the masticating process. Synthetic polymers have relatively stabile viscosities within their functional temperature range; therefore mastication simply prepares them to be better receptive to fillers, as well as provides uniform homogenization when a compound contains two or more polymers. The function of mastication can be accomplished on an open two-roll, or in internal mixers such as the Banbury[®] Mixer (a tangential type batch mixer) or the Intermix[®] (an Intermeshing type batch mixer).

Natural Rubber usage, having been increased by the development of the radial tire, still enjoys much demand. Among its many unique characteristics, are the wide variations in viscosity that exist from lot to lot. Many improvements have been made at the rubber plantations, which now provide controlled viscosity grades of natural rubber as well as standard grades containing far less impurities than earlier forms. Although the Ribbed Smoked Sheet (RSS) grade is still available, most users prefer the SR grades, which are, supplied plastic wrapped and are the same size and weight as most synthetic rubber bales.

Natural rubber may be premasticated on open mills, but the common practice is to use an internal mixer. Mastication may be accomplished in several ways. A separate premastication step may be used in which the entire lot of natural rubber is broken down and prepared for the next phase of mixing. It is found that a small amount of carbon black, such as 10-20 phr, will aid in the breakdown process. Another method, which is very popular, is premastication of the polymer with a special plasticizing agent such as VANPLAST[®] R, prior to the addition of the remaining compounding ingredients. This method, rather than being a separate mixing step, is accomplished in the first step of the mixing cycle. Care must be exercised in the mastication process to insure the unique properties of the polymer are not compromised in the interest of trying to maximize productivity.

A major point in the process of breaking down natural rubber, regarding subsequent stages of processing, is that there will be a certain degree of elastic recovery as the material cools down. Values of viscosity measured directly after processing will not necessarily reflect starting point values in the next step in the process.

*Synthetic Rubbers* are produced in a wide variety of types and grades. Thermoplastic elastomers, and blends of rubber and thermoplastics, further add to this class. Besides their chemical and physical differences, they differ from natural rubber mainly in their viscosity uniformity and stability. Premastication is usually only necessary when compounds contain a blend of polymers. In this case, premastication will provide a matrix which will be more receptive to uniform incorporation of the subsequent compounding ingredients.

The processing of synthetic elastomers usually begins in the internal mixer. Operating conditions, such as rotor speed, ram pressure, and most significantly, mixer temperature, must be selected to achieve the best results. Although these polymers can usually tolerate higher temperature levels than natural rubber, it is generally not necessary to approach these levels for effective mixing. Higher mixer speeds are also normally used in mixing synthetic rubber compounds. Consideration must be given to the possibility of excessive polymer temperature being reached, at which point crosslinking or "gelling" and thermal degradation of the polymer can take place. Careful mixing procedures will avoid this. Chemicals may also be added to the compound to minimize this possibility.

Both synthetic and natural rubber compounds may achieve shorter mixing cycles by the use of chemical plasticizers. However, care must be exercised to assure that using these chemicals will not alter the polymer structure and adversely effect end product properties.

#### Masterbatching

Masterbatching refers to the incorporation of most of the compound ingredients into the rubber, omitting the active chemicals constituting the curing or crosslinking system. By omitting the curing system, the masterbatch may be mixed intensively without fear of exceeding the reaction temperature of these chemicals. Masterbatching is sometimes done in two stages where high loadings of carbon black and other fillers must be incorporated. The ultimate objective in masterbatching is the incorporation of all of these fillers. Dispersion is accomplished by those actions that soften and prepare the polymer to accept the fillers, as well as to subject the fillers to high shear forces which break apart filler agglomerates, providing for effective dispersion. The level of dispersion of the various ingredients into the rubber affects the final viscosity of the compound. The two objectives of masterbatching are maximum filler dispersion and achieving proper final viscosity.

In addition to carbon black, other difficult to disperse chemicals, such as zinc oxide, can be prepared as masterbatches. These masterbatches are not the same as the two-stage mixing process. In the case of the specific chemical masterbatch, a concentrated batch is prepared which will permit greater shear and better dispersion during the mixing process. The masterbatch (also referred to as a pre-dispersion) may then be added to the compound during a typical mixing cycle, resulting in more rapid incorporation of the required chemical.

#### Re-mill

"Re-mill" refers to additional mixing steps conducted for the purpose of improving dispersion and/or reducing viscosity of the masterbatch. The re-mill has more frequently been used with high carbon black, low oil compounds common to the high performance tires of today. Without re-mills, some of these compounds are virtually impossible to process and fabricate. Efforts to reduce re-mills continue in the form of additives, processing aids and more sophisticated fabricating techniques which permit processing rubber compounds of much higher viscosities than ever before.

#### **Finish Mixing**

The "finish" mixing step of the rubber compound involves the addition of

curatives and crosslinking agents. Rather than the high shear associated with carbon black dispersion, these chemicals require optimum distribution within the rubber compound to ensure uniform vulcanized properties. This step is also constrained by temperature limitations to prevent premature crosslinking. Blends and masterbatches of curative systems are sometimes used to enhance dispersion and the rate of incorporation, increasing overall productivity. Some mechanical goods rubber compounds are capable of being mixed in a single pass, thereby eliminating finish mixing as a separate pass.

Since finish mixing must be accomplished at temperatures rarely exceeding 120°C, internal mixing machines will usually run much slower than masterbatching cycles. In some large mixing facilities certain machines are assigned masterbatching tasks, while others only perform finish mixing operations. In instances where a single mixer must be used for both tasks, the machine must be designed with multiple or variable speed capability. Regardless of mixer, absolute control is required of machine metal temperature, machine operating parameters, materials, and mixing procedures to assure reproducibly uniform, high quality compounds.

# **RUBBER COMPOUND MIXING & FORMING MACHINERY**

## The Two-Roll Rubber Mill

The two-roll rubber mill was the first practical rubber mixing machine. Typical original designs were as follows:

- · Two rolls counter rotating toward the center
- · Both rolls water-cooled
- · Roll speeds geared to a friction ratio of 1.25:1.00
- · Adjustable roll gap
- · Safety Mill Stop safety cable over top of rolls
- · Power provided by single speed AC motor

Reviewing these elements of design shows they all have been altered and improved in the modern rubber mill. Since thousands of mills have been manufactured, many fitting the above description still remain operating around the world. Modern mills still have two counter rotating rolls, which are sized in roll diameters and lengths according to production requirements. Roll cooling is much more sophisticated, with drilled roll cooling as opposed to the original design of bored roll cooling. Friction ratios are now designed lower, in the order of 1.10:1.00, and can be adjusted with the use of variable speed motors or hydraulic drives. Safety is significantly improved with the implementation of body bars and quick opening hydraulically adjustable rolls. A two-roll is shown in Figure 2.



Figure 2: 84 Inch Two-Roll Mill with Stock Blender

Design improvements have minimized and eliminated many of the problems associated with mill mixing. However, even if the best procedure for mixing a specific compound was developed, one may still face the problems of sticking to the roll surface, rubber stock moving to the wrong roll, and too rapid a temperature rise. Rubber will typically travel to the faster or warmer roll. The compound can usually be kept on the operator's side by using roll speed control. Using a lower friction ratio and installing or adjusting the higher roll speed on the operator's side, or on the stock removal side, will usually eliminate this problem. In addition, the use of drilled roll temperature control will maintain a roll surface temperature constant within a few degrees variation from end to end of the roll. Drilled roll temperature control eliminates the problem of wide variations in roll temperatures which cause rubber sticking in some spots and good release in others. The combination of roll speed and roll fiction control, along with roll temperature control, will contribute to maintaining lower compound temperatures on the mill. Experiments have proven lower roll speeds will result in lower stock temperature on the mill, without affecting productivity. A reduction in roll friction ratio or a reduction in total roll speed will vield lower compound temperatures on the mill. Compound temperature is directly related to the sum of the speeds of the two rolls.

These equipment improvements, although costly, provide benefits in quality, productivity, and reduction of scrap. For many years, rubber industry experts have claimed mills would eventually be eliminated, but they have not. Mills still remain the lowest cost investment in mixing machinery and may be the best choice for a new or small company. With all of the benefits described, the uses of mills for mixing rubber still have a major fault. This fault lies in the fact that mills are labor intensive, and yield variable results because the judgment for mixing techniques is in the hands of the operator. Procedures for adding ingredients, cutting, blending, and finishing are judgment calls by the operator, and typically don't occur in the same sequence for every batch.

The selection of the correct batch size for mixing on a specific size mill is also very important. Often a batch weight that is too large for the size of mill available results in excessive material loss and inconsistent quality. However mills used as batch-off or drop-mills below internal batch mixers will handle larger volumes of rubber, since their only requirement is to sheet the rubber prior to entry into the festoon cooling system. In this case it is imperative that the operator pass the entire discharged batch through the mill once, before sheeting off, in order to reduce its heat history and maintain a uniform product.

Although their usage has been minimized following developments of internal mixers with better mixing efficiency, two-roll rubber mills still have their niche in the rubber industry. Rather than possibly contaminate a more sophisticated mixing machine for a single specialty batch, the mill is ideal alternative. Due to simplicity of design mills can be cleaned quite easily, in spite of their relatively messy mode of operation. The major applications for two-roll rubber mills continues to be as batch-off devices below internal mixers, and as warm-up preparation devices for extruders and calenders.

#### The Internal Batch Mixer

The rapid growth of the automobile industry early in the 20th century increased the demands for greater quantities of tire rubber compounds. The two-roll rubber mill was incapable of meeting these needs, being labor intensive and characterized by long mixing cycles. The first intensive internal batch mixer was introduced in 1916, and named the Banbury® Mixer after its inventor, Fernley H. Banbury. The design of this mixer consisted of two counter rotating rotors in a chamber. A plunger called a ram was provided above the chamber to drive the rubber into the mixing chamber. The chamber and rotors were designed for water-cooling, and the mixing chamber could open at the conclusion of the mixing cycle to discharge the batch to a two-roll mill for sheeting and removal. The first Banbury Mixer had a 72 liter chamber capacity, and the first design was so successful that it was followed in size by a 620 liter chamber capacity. The Banbury Mixer revolutionized the rubber industry. Mixing cycles for rubber compounds were reduced from the traditional mill cycles of greater than thirty minutes to less than ten minutes. Losses of raw materials, typical of the tworoll mill were significantly reduced. While the Banbury Mixer is a registered trademark of the Farrel Corporation, other manufacturers of similar mixers exist today; their machines are often referred to as Banbury mixers.

When the Banbury Mixer was introduced natural rubber was the only rubber polymer available. Formula ingredients were relatively simple, consisting of rubber, carbon black, oil, and a simple curing system. The original mixer design was relatively simple. Many inventions and improvements have followed, in keeping with the needs of the rubber industry, not only to address the requirements of new polymers and raw materials, but also for improvements in productivity and quality.

Another concept in internal batch mixer design contains interlocking rotors. This design was invented and introduced in 1934 by Francis Shaw, Ltd., and

named the Shaw Intermix[®]. The Intermix design was not immediately popular with the tire industry since it required lower fill factors, longer mixing cycles, and used more energy. The Intermix differed from the Banbury in that its primary mixing occurs between the two rotors, similar to a two-roll mill, whereas the Banbury primarily mixes between the rotating rotors and the chamber sides.

The Shaw Intermix gained, and continues to maintain, popularity with producers of technical rubber goods compounds primarily due to its ability to mix rubber compounds at lower temperatures, which is attributed to its greater mixer surface area to batch volume. This feature permits the introduction of curing ingredients in a single mixing cycle. In most cases this feature represents a cost reduction, since technical goods rubber manufacturers provide a greater variety of compounds than tire manufacturers, and in many cases the multiple pass mixing procedure could be reduced to one pass. Mechanical goods rubber compounds are typically short runs of many unique formulations.

As mentioned earlier, internal batch mixers have matured through many unique innovations since their origin. The following describes many of the innovations which have taken place on the major elements of these mixers. Figures 3 and 4 show the F-270 Banbury Mixer and the K6a Intermix internal batch mixer.



Figure 3: F-270 Banbury Mixer



Figure 4: K6a Intermix

# Rotors Rotors Rotors Construction Rotors Rotors Rotors Discharge Door

#### **Elements of Internal Batch Mixers**

Figure 5: Principal Components of Internal Batch Mixer

Ram – The ram in a tangential rotor mixer consists of a "V" bottom design, whereas the ram in an interlocking rotor mixer is curved, continuing the curved surface of the mixing chamber. The purpose of this device is to drive rubber and other raw materials into the mixing chamber. Earlier design rams had flat bottoms. The newest design for the ram is a "Keel Bottom Weight". This acts as a mixing dam to move material efficiently throughout the mixing chamber. The new weight, combined with new rotor designs, permits larger batch sizes and can result in improved compound quality.

Clearances of the ram to throat of the hopper are critical, permitting the removal of air and generated gases and vapors. The clearances cannot be too great or they will allow material to spew out of the mixing chamber during mixing. Control of the up and down movement of the ram has traditionally been provided by air. Current options permit hydraulic control, which eliminates the requirement of an air compressor. The traditional "tell-tail" rod, which indicates the position of the ram on the batch, can now be replaced with an electronic ram position indicator, which is commonly referred to as an "RPI". The RPI can remotely display ram position on a meter or PLC screen.

Mixing Chamber - The mixing chamber has two steel sides connected by end frames. Drilled passages connected in a serpentine pattern are designed in the sides for precise temperature control of the mixing surfaces. Sides are treated with special hard surfacing materials to resist wear. Alloys of unique wear resistance coatings are also available to address highly abrasive or corrosive compounds. After application of hard surfacing, the sides are ground or machined smooth to insure optimum heat transfer and to facilitate cleaning and efficient mixing. Sides may contain as many as four openings to permit installation of fluid injection nozzles for directing fluid ingredients of the compound directly into the mixing chamber. With the Intermix, heating and cooling circuits are provided in the rotor end plates, weight, and door top as standard. Intermix batch circulation patterns drive materials toward the end frames and up the rotor end plates. Rubber circulation in the Banbury mixer, depending on rotor type, is generally toward the center of the mixer and directed away from the end frames. Therefore cooling of the rotor end plates in these locations is not as critical, but is available if required.

*Rotors* – Both the Banbury and Intermix have two counter rotating rotors. The Banbury rotors are tangential and can operate at frictional or even speeds within the mixing chamber.

Banbury rotor design directs the compounds in the mixing chamber in numerous directions to achieve incorporation and blending of ingredients. Rotor tips are flat and manufactured to precise widths and clearances to optimize dispersion of the compound ingredients. The original rotor design introduced for the Banbury Mixer was a two-wing style. A four-wing type introduced later, is more intensive, and became popular in the tire industry for providing shorter mixing cycles. Later developments in rotors followed the discovery that rotors operating at even speed, properly oriented to each other, produced better compound uniformity and quality. Many designs are currently available. Users must be careful in their choice of rotor design to assure their selection will perform over the entire range of the compounds they wish to mix as well as those they may wish to mix in the future. Rotor technology has progressed to the degree that ideal designs can be developed for special mixing applications. However, the most suitable rotor design for general rubber mixing is one that permits optimum versatility.

The Intermix rotors, unlike the Banbury's tangential rotors, are interlocking. As stated earlier, interlocking rotor mixers have gained their greatest popularity for mixing rubber compounds for technical rubber goods. Unlike the tangential rotor mixer, the interlocking design has a lower fill factor, but is noted for mixing compounds at lower temperatures. It is claimed the interlocking principal mixes compounds similar to the action of a two-roll mill as the difference in diameters from the nog to body act as a friction ratio. As with the tangential rotor mixer, the latest rotor designs have improved both cooling as well as the capability for larger batch sizes. Proper testing is imperative when selecting a mixer rotor design to assure it will fill all of the user's requirements.

Discharge Door – The discharge door is opened and closed by a hydraulically activated mechanical latch mechanism, in a somewhat clamshell fashion. At the conclusion of the mixing cycle, the signal for the door to open can be activated manually or automatically by a signal based on time, temperature, or integrated power. Once the door is opened, the time it remains opened can be adjusted to allow the batch to be completely discharged from the mixing chamber. The latest drop door design is drilled to optimize cooling, similar to the sides of the mixer. Two thermocouples are installed in the door-top of the Banbury mixer, which measure compound temperatures during the mixing cycle. For Intermeshing machinery the thermocouple is typically in the rotor end plate located between the two rotors or they can be located in the door top similar to the Banbury style mixer.

*Driving Mechanism* – Typically a gear reduction unit with an electric motor drives the internal batch mixer. Gearing and motors are selected to meet the power requirements of the mixer size and product mix requirements. Originally mixers were supplied with single speed or two-speed drive systems. The preference today is for variable speed systems that can provide greater versatility in mixer utilization. Variable speed is available with DC or variable frequency AC motors. Motors for internal batch mixers must be procured with sufficient over load capacity to sustain the power peaks that usually occur at the start of each mixing cycle. Overload requirements are usually in the range of 150-200%. Recently hydraulic drives started being used to drive the mixer rotors. They eliminate the requirement of a gear reduction unit. The Hydraulic motors can be directly connected to the rotors. A power supply unit supplying pressurized hydraulic oil to drive the hydraulic motor is required, and needs to be located in close proximity to the mixer.

## **The Mixing Process**

Following the selection of the proper mixing machine for the application, optimum utilization becomes the next major requirement. As in any mixing process, whether it be food or chemicals, the proper tools and combination of materials are important. With the internal batch mixer, the following principals must be addressed:

- Batch Size
- Ram Pressure
- Rotor Speed
- Machine Temperature Control
- Mixing Procedures (order of addition, number of additions, number of ram raises or ram cleaning events)
- · Means of Cycle Control

Batch Size – For an internal batch mixer with tangential rotors the batch weight is nominally calculated at a 75% fill factor. This translates to filling the mixing chamber to 75% of the net chamber volume so that some free volume remains

in the mixing chamber for the compound to move around. For example an 80 liter mixer would utilize approximately 60 liters for optimum mixing. Besides the fill factor, compound specific gravity is required to calculate the optimum batch size. The formula for batch size is as follows:

Compound Specific Gravity x Fill Factor x Mixer Net Chamber Volume

Both compound density and mixer net chamber volume are known values; however the fill factor will be a variable. Fill factor relates to compound viscosity. A soft, high oil-extended rubber compound of very low Mooney viscosity may mix very well at a fill factor of 80-85%, whereas a high-viscosity compound may require a fill factor as low as 65-70% to insure good quality. An improper batch weight will prevent the rotors from accomplishing their task of dispersing and blending compound ingredients. In the case of the interlocking rotor type mixer, fill factors are somewhat lower, in the order of 60-65%, and the same formula for batch size may still be applied. In either case, batch size is critical. There must be sufficient space within the mixing chamber for the rubber compound to move and take full advantage of the dispersive and distributive capabilities of the rotor design.

Ram Pressure – Ram pressure is the force on the bottom of the ram forcing the ingredients to be mixed into the mixing chamber, or holding it in the mixing chamber while mixing is occurring. Pressure is applied to the ram by a ram rod that is connected to either a pneumatic or hydraulic cylinder(s). Most batch mixers in the past were outfitted with a simple system having a regulator for control of the air supplied to the pneumatic cylinder. Experimentation has proven that regulated pressure can be more beneficial to the mixing process. If a particular compound being mixed is very soft, excessive ram pressure can restrict flow within the mixing chamber. Mixers can now be provided with pressure regulation that permits pressure changes during a mixing cycle by orders from a PLC. High pressure may be more useful at the initiation of a mixing cycle to rapidly force rubber into the mixing chamber followed by pressure reduction during oil injection or as the compound viscosity softens later in the cycle. Ram movement is an important indicator of good mixing. It indicates aggressive mixing within the mixing chamber as well as the correct batch size. Awareness of ram position is equally important. The modern RPI in combination with ram pressure control can be major contributors to identifying proper batch size and an optimum mixing process.

*Mixing procedures* – Even with all of the proper tools and best ingredients poor quality can result when compound ingredients are mixed in the wrong sequence. In most cases the classic order of addition is to charge the polymer, followed by the filler and some minor dry ingredients, with the oils or plasticizers later. If the correct order of addition is not established, mixing cycles may be extended, and poor quality will result. In some cases pre-mastication of the polymer may be necessary, to render it more receptive to the fillers. When a compound contains more than a single polymer it is good practice to blend the polymers prior to the addition of fillers. If the formula is based upon a blend of a low and a high

viscosity polymer, adding the rubber and fillers at the same time may result in a non-uniform concentration of the filler into the rubber. The fillers may be ingested rapidly by the softer polymer, resulting in a poor quality mix and unacceptable physical properties of the product. Developing an ideal mixing sequence is as important as selecting the correct ingredients for the compound. Meltables such as antioxidants and waxes added at the wrong times can interfere with good dispersion of hard particle fillers. There are certain rules in mixing, but most of the techniques are developed from the rubber chemist's experience with each compound. A major deviation from the classic order of mixing is the "upsidedown" mix procedure. With this mixing procedure all of the ingredients are charged into the mixer followed by the polymer. This technique is popular with highly filled EPDM compounds.

*Rotor Speed* – When the Banbury Mixer was introduced, rotor speeds were available in only single or dual speeds. Speed was initially controlled with single or two speed gear reducers, followed by two speed motors at a later time. The gear reducer was set to provide a gear ratio of approximately 1.125:1.00, similar to the traditional ratio set on two-roll rubber mixing mills at the time. Typically, tire rubber compounds were mixed in two or more cycles, using the higher speed for rubber mastication or the non-productive pass, followed by the lower speed for the final or productive pass containing the curing system. With the advent of variable speed D.C. motors variable speed rotor mixers became popular. This added versatility, permitted mixing at faster rotor speeds, making rapid temperature rise and shorter cycles possible. Further, the lower speed spermitted more delicate mixing of temperature sensitive compounds and longer cycles when special compounds were mixed. The variable speed benefit was most useful to mechanical rubber goods manufacturers who were faced with a wide variety of elastomers and chemicals which required unique mixing cycles.

Presently, by using automatically controlled variable speed, the internal batch mixer may be programmed to reach target temperatures and sustain those temperatures for a period of time, to perform some reaction or desired effect by increasing or decreasing rotor speed. Later developments by the Farrel Corporation on the study of rotor speeds, established the concept of Synchronous Rotor Technology. This technology established the benefits of operating the tangential mixer rotors at even speed (1:1 ratio), when synchronized in a fixed relationship to each other, resulting in improved uniformity in the rubber compound, as well as increased productivity. These improvements resulted in optimizing material flow within the mixing chamber.

Synchronous Rotor Technology influenced new rotor designs, the first of which was the ST[®] rotor followed by the NST[®] rotor. This advancement in rotor design through improved cooling passages and changes in rotor helix angles, achieved new dimensions in mixing technology. Many designs of rotors exist in the market today, so caution must be used in selecting a rotor design to be certain the design will be versatile enough to handle the entire range of compounds they must mix.

*Mixer Temperature Control* – The early designs of internal batch mixers were inadequately cooled compared to today's standards. As described earlier in the sections on mixer design, cooling passages in the mixing chamber and rotors permit more precise control of machine temperatures. Where the earlier designs required very cold water to control mixing temperatures, current designs perform best with tempered water. It is common knowledge that different materials will adhere or release from warm or cold surfaces. Using this understanding, one should temper a mixer such that drag will occur on the walls of the mixing chamber while freedom of movement can be achieved on the rotors. In this manner shear is optimized between the rotor tips and the mixing chamber surfaces, while the rotors can move compound around freely to achieve uniformity and good materials distribution. For example a compound of SBR rubber would mix best at an approximate chamber temperature of 60°C, whereas a compound based upon natural rubber would mix better at a machine temperature of about 45°C.

The application of a temperature control system results in reduced power consumption, shorter mixing cycles, and improved quality. A properly designed temperature system should consist of three zones: controlling the mixer chamber, rotors, and mixer drop door. The drop door is controlled to assist in release of the batch at discharge. The systems generally use ambient water for cooling, but has provisions for heating the water by the introduction of steam through heat exchangers. If steam is not available, heat can be achieved using electrical heaters. A closed-loop temperature control system provides regulation of the water temperature, and also assures achieving the proper turbulent flow through the cooling channels. Mixer cooling temperature control can yield some of the greatest benefits, but is perhaps the most disregarded element in the process of mixing.

The understanding of machine designs is important to users in order to fully utilize their potential. Mixing machines are very durable and last for many years if properly maintained. It is not cost effective to replace machines each time a new innovation is introduced. It is possible in many cases to adapt many of the new concepts to existing units. The applications of machines do not change and the rules of good mixing procedures still prevail. The genius of the rubber chemist is critical in his selection of raw materials and adjustments of his compounds to provide good quality compounds with the machines available to him. Machines for mixing rubber compounds must be in harmony with good mixing procedures.

#### The Rubber Extruder

Extruders used in the rubber industry have several applications. They may be used as batch handling devices under internal batch mixers in place of two-roll mills, as devices to produce specific preform shapes for subsequent fabrication, and to extrude final parts that simply require vulcanization.

Batch Handling (Dump) Extruders – Extruders in this category are designed to handle batches as they are discharged from an internal batch mixer. They are characterized by having low compression ratio screws and relatively short L/D

ratios to minimize increases in temperature as the rubber passes through them. The largest size extruders fall in this category, having been designed to handle batches in a range from 150 to 1200 pounds. These units are simple pumps that can deliver batches from the mixer in mixing cycles as short as 1.0 minute. Batch handling extruders have very large hoppers to accommodate the relatively large pieces of rubber product as they fall from the mixer. To facilitate feed efficiency the hoppers are usually outfitted with hydraulic or pneumatic pushers to assist in driving the irregular pieces into the screw. Extruders in this category receive their nomenclature from the types of extruder heads used. Figure 6 is a photo of a batch handling (dump) extruder, with a pelletizing head.



Figure 6: Single Screw Dump Extruder with Pusher and Pelletizing Head

Rubber Pelletizer – This extruder design is outfitted with a die plate having multiple holes. A rotary cutter equipped with several knife blades is installed to cut the rubber as it passes through the die plate into pellets. An anti-tack solution is directed over the knife blades to facilitate cutting and to coat the pellets to prevent them from sticking together. The pellets then pass over a de-watering screen to a dryer. After being dried and cooled the pellets are pneumatically conveyed to large holding hoppers where they may be blended or automatically conveyed to a mixer for their next operation, which is normally a final mix. Pelletizing lends itself mainly to the production of master batches in a tire factory. Major benefits are the ability to blend batches and to automatically feed mixers for subsequent passes. Pelletizing has been used on a limited scale in the production of cable insulation grade rubber compounds. In these instances much smaller pellets are produced to facilitate feeding crosshead wire coating extruders.

Pork Chop Extruder – This extruder design has a fixed bar or knife at the head end of the extruder. As rubber is delivered from the screw, the knife delivers "pie" or "pork chop" shaped pieces to a conveyor. The conveyor delivers the pieces to a two-roll mill, which forms a sheet that can be delivered to the festoon cooling system. With this type of design, head pressure is minimal and rubber discharge temperature exhibits little or no increase over mixer discharge temperature.

Roller Die/Roller Head - This design consists of a two-roll calender adapted to a spreader die at the head end of the extruder. As with a dump extruder below an internal batch mixer, this device will produce a continuous sheet that is directed through an anti-tack bath into a festoon cooler. Machines of this design have been popular in the shoe industry for preforming sheets of rubber prior to molding. In this application the roller die is fed from a rubber warm-up mill or may be fed directly from a batch or continuous mixer. The rolls at the head end of the extruder are drilled or bored for cooling, and the spreader die is designed to maintain minimal backpressure in order to deliver the rubber sheet with little temperature increase. The original design of this type of extruder located the two rolls in a separate stand which could be moved from the head end of the extruder during compound changes or for cleaning. A later design had the rolls attached to the head end of the extruder, which saved space and permitted more rapid opening when necessary. One problem with extruders used as batch handling units is the occasional poor feed characteristic. This is minimized to some extent with single or dual rubber pushers. These units, installed in the extruder hopper to assist feeding, can be somewhat high in maintenance requirements and in some instances ineffective regarding optimizing extruder efficiency.

*Twin-Screw Sheeter* – The twin-screw sheeter is the latest design for handling rubber batches from an internal mixer. This design follows the concept of the roller die by producing a sheet form for further processing. It differs however, in containing two counter rotating, intermeshing screws. The efficiency that it exhibits in ingesting the rubber batch eliminates the need for pushers. In combination with its head design and cooling efficiency, little or no temperature increase is exhibited in the rubber batch as it passes through the extruder. This design, as shown in Figure 7, has become the favorite device for handling rubber batches from internal batch mixers in the tire industry.



Figure 7: Twin Screw Sheeter

Pin Barrel Extruders - This unique extruder design, as shown in Figure 8, is used for both extruded profiles and as a warm-up pre-feeder for rubber calenders. Prior to the development of this type of extruder, profile extruders were classified as hot-feed devices, requiring pre-masticated stock, supplied in strip form from a mill. The pin barrel extruder accepts cold rubber in strip or sheet form, warms and masticates the rubber, and delivers the desired shape below the crosslinking temperature of the compound being processed. The design of the pin barrel extruder consists of a barrel with pins inserted in strategic locations. The screw flights are interrupted with slots so as not to interfere with the pins as the screw rotates. The hopper is outfitted with a roller feed device to draw the rubber strip or sheet into the screw without any manual assistance. It is possible to group as many as four of these extruders together, delivering several rubber compounds through a common die. The extruders in this type of arrangement may be of different sizes. This approach is popular in the tire industry where certain preforms may consist of two or three different rubber compounds. Many hot feed extruders still exist in the rubber industry however, providing a variety of shapes required for technical rubber goods.



Figure 8: Pin Barrel Extruder

# The Rubber Calender

The purpose of the calender designed for rubber is to produce a sheet. This may be the rough sheet form as produced by a roller head die sheeter under a batch mixer, or the precise gauge sheet form used for roofing material. Calenders are designed in many configurations, from simple two-roll units to as many as four and five roll configurations (Figure 9 contains schematics of various calender configurations, while Figure 10 shows a 4 roll "Z" calender). The rolls are always provided with the provision to control roll surface temperature. Since rubber will usually follow the faster roll and often the warmer roll, variable friction is used to track the rubber to the desired direction. Fabric and metal substrates can be combined with rubber to form a composite sheet from a calender. A popular calender configuration used for this purpose is designated an inverted "L" calender. With this configuration, rubber can be fed to the top two rolls, forming a sheet of the required thickness, which then passes through the center roll where the substrate may be introduced. The bottom roll can be used to apply pressure and achieve the final required thickness. If the construction requires a substrate to be embedded between two layers of rubber, rubber may then be introduced through the lower two rolls, thereby applying rubber to the lower surface of the substrate simultaneously as rubber is being applied to the upper surface.



Figure 9: Various Calender Configurations

Setting up a complete calender line can be a very complex arrangement. First a method to provide continuous, pre-masticated rubber to feed the calender must be addressed. The calender size and roll configuration must be selected to provide the required width and thickness of the sheet. Rolls must be configured to permit application of a substrate if required. Roll speeds must be adjustable to lead the rubber in the desired direction. Several designs must be considered for controlling uniformity of sheet thickness, such as roll bending and cross axis adjustments. When the sheet finally leaves the calender, special tension and roll forming mechanisms are necessary to maintain quality of the calendered sheet. With the most sophisticated systems, Beta gauges are used to control and maintain sheet thickness. These gauges are synchronized with calender adjustments to achieve this control automatically.

The selection of materials, machinery and processing techniques are equally

important in producing quality end products. It may not be possible to have the latest machinery innovations in one's facility. Compound formula adjustments and processing techniques can often be modified to achieve the best results with the equipment available. Most important however in the quest for optimum results is strict adherence to those methods that have been established to yield the best quality.



Figure 10: Four Roll "Z" Calender

# VULCANIZATION

# **Stock Preparation**

Rubber stocks ready for assembly for vulcanization may be in a number of forms such as calendered strips or sheets, plied up slabs, extruded tubes and other cross-sections, or partially combined with fabrics that were previously frictioned or skimmed. Tires, tubes, hose, belts, footwear, rolls and many other articles are built to proximate finished forms before vulcanization. The various stocks that are combined to form such articles must be dimensionally stable, free from bloom and partitioning agents, and possess the required building tack; all of which depend upon proper compounding and processing.

The building tack in EPDM, NBR and SBR, and some heavily loaded rubber compounds can be improved to some extent by the use of pine tar, rosin esters and various coal tar or petroleum derivatives. The use of cements or solvents is necessary in some cases to prevent ply separation or splice failure during cure.

# **Curing Methods**

Natural and synthetic rubber articles usually require the application of heat to convert them to their finished form. This operation is broadly described as

vulcanization or curing and may be done by a number of methods, depending on the compounds in process, the size, shape and overall structure of the finished article.

# Press Curing

Press Curing includes the molding of articles by compression, transfer, or injection methods (which are covered in greater detail in the MOLDED GOODS chapter of this Handbook). Blocked-in articles, as well as unblocked slabs, which are cured directly between press-platens, also come under this classification. The heat source is usually saturated steam, heat transfer fluid, or electrically heated molds and/or platens. Microwave energy is also used as a means of continuous curing or for pre-heating slabs and blanks to reduce the press cure time.

Compounds for press curing must be designed to flow properly without scorching before the desired shape is reached, and to cure rapidly in order to minimize the cure cycle. They must be easily removable from the molds after curing, and exhibit suitable surfaces in the finished form.

The stock's flow characteristics depend on the plasticity of the uncured compound, as well as selection of the proper acceleration system to permit complete filling of the cavity before the cure begins.

Some of the typical problems encountered during molding are:

*Porosity* – Failure to obtain a dense finished product may be caused by undercuring or by insufficient external pressure during the initial stages of cure. The thickest part in the cross-section of a molded article is the place to look for porosity, and the curing cycle must be adjusted accordingly. Undercuring can usually be corrected by use of a more suitable acceleration system, or by increasing the cure time. Sudden development of porosity in stocks that have been running trouble free may be caused by moisture in the fillers or improper dispersion of the cure system or accelerators in the compound. Improper mold design or the use of insufficient or improperly shaped stock to fill the mold cavity can also contribute to porosity.

*Trapped Air* – This common problem in some press cured articles may be due to improper mold design, the use of too soft a compound, or unsuitable stock blanks for molding. For compression molding the uncured stock should be shaped as near as possible to the form of the finished article before being placed in the mold, and the press and/or mold should be "bumped" (applying full hydraulic ram pressure and relieving it quickly after the press closes, then reapplying pressure). Injection or transfer molding operations minimize defects of this type.

Removal from Mold – All molded articles should be easily removable from the mold after curing. The combination of the proper compound, mold design, and efficient mold lubrication will usually result in efficient part removal. The spray from a cold water bottle can be helpful where the hot, freshly cured part must be

stretched upon removal. Low-sulfur or sulfur-donor compounds of the general purpose polymers usually have the necessary mechanical strength at elevated temperatures to permit removal without tearing. When tearing occurs the addition of a processing aid or plasticizer such as VANFRE® AP-2 or VANPLAST® R to the stock may be a suitable corrective measure.

# Flat Belting Curing Methods

*Slab Cures* - in articles of this type, the press platens and side strips control the dimensions of the finished article. The platens should be maintained in good mechanical condition, and low spots should be shimmed or padded to assure freedom from porosity and blisters in the finished article.

Both flat-transmission and conveyor belts are built to their approximate finished shapes before curing. The belt fabrics were dried and stretched before frictioning and skim-coating, and an additional stretch is applied to each section in the press prior to and during curing. Residual moisture in the fabric is permitted to escape by venting the end sections before the press is closed, and it is usually considered good practice to bump the press before the cure begins. Relatively flat rate of cure compounds are required in press-platen cured belting, since overlapping sections receive a double cure as each section progresses through the press. Obviously this isn't true of the Rotocured belting covered in the continuous curing section below.

Curing slabs for soling, tile, or matting also present problems of blistering and porosity. Stocks for these press cured applications must possess suitable flow characteristics, and they must be properly accelerated to permit "cycling" in multi-stage presses without developing porosity as the pressure is released and reapplied during cure.

Slabs for such articles as soling, tile and mechanical packings are built to their approximate finished thickness into sheets or strips on a calender or a sheeting mill, and preform blanks are usually die-cut from these sheets and strips.

*Continuous Curing* - continuously cured flat-belting is normally vulcanized on a Rotocure[®], as depicted in Figure 11.



Figure 11: Schematic of Rotocuring of Flat Belting

Rotocured flat-belting is typically built from single or multi-plies of dried, stretched, frictioned and skimmed fabric basically assembled like slab-cured belting, but without a molded edge. Additional stretch is continuously applied by a belt-stretching machine between the uncured belt playoff and the Rotocure.

Rotocured flat-belting can be produced in widths over 72 inches with a normally unfinished edge. The lack of preformed edges allows venting of residual fabric moisture and the press's curing action reduces the tendency for trapped surface air, eliminating the need for bumping.

Rotocured products, which can include sheet goods and matting, are usually not made to a finished width, but are processed thru a slitter after exiting the curing section, producing rolls of various widths.

## **Open Steam Curing**

Open steam curing is used in the production of hose, wire and cable, and other extruded articles such as tubing or channel stripping. With this method, the article may be in direct contact with the steam, wrapped with fabric tape, encased in an extruded covering of lead, or supported by soapstone in a shielded pan. Equipment may consist of a standard steam autoclave, preferably with a heated jacket to cut down condensation, and a closed chamber in which the articles are placed and steam is introduced.



Figure 12: Open Steam Vulcanizer Photo courtesy of WSF Industries, Buffalo, NY

In operating a closed-chamber steam vulcanizer, the curing cycle consists of a rise to a predetermined pressure, a holding period at the required curing pressure, and a blowdown to atmospheric pressure. Too slow a rise of pressure or fluctuations as curing conditions are reached may cause porosity. With soft stocks the blowdown must also be carefully controlled.

Another method of open steam curing is used for the production of insulated wire and cable. This method, known as the CV (continuous vulcanization) process utilizes jacketed tubes which may be 60 meters (200 feet) in length and operate under internal steam pressure upward of 1.4 MPa (200 psi) as compared to the 200-550 kPa (30-80 psi) range of the conventional steam vulcanizer. In the CV process, extruded wire or cable covering goes directly from a tuber into steam at curing pressure and, with the latest design of equipment, passes through a water or condensation seal prior to emerging from the tube at atmospheric pressure.

# **Dry Heating Curing**

Articles such as rubber coated fabrics and rubber footwear may be cured in heated dry air. Coated fabrics are generally festooned in heaters and cured at atmospheric pressure, although by the use of BUTYL EIGHT[®] acceleration, curing in a roll as it comes from the calender can be accomplished at room or slightly elevated temperatures. Rubber footwear heaters are generally operated at 200 kPa (30 psi) air pressure, and ammonia gas is sometimes used to produce a glossy surface on the finished article.



Figure 13: Schematic Interior of Festoon Heater

# **Continuous Curing of Extrusions**

The continuous curing of extrusions as the rubber exits the extruder has grown considerably over the last decade. In addition to minimizing handling and labor costs, very fast line speeds can be obtained. These factors provide economical extruded articles when product can be run for long periods without changing compounds or profiles (dies).

The method of heating the profile after extrusion varies, but all methods (except the CV process discussed above) are pressureless. The rapid curing of rubber at atmospheric pressure puts some unique constraints on compounding. The particular curing method employed may put additional requirements on compound development. The selection of polymer, fillers, oils, cure system, antidegradants and the use of specialized additives or extruders all must be carefully considered.

*Porosity* can easily occur in atmospheric cures, as only the viscosity of the compound resists sponging. Porosity can be due to trapped air, moisture from compounding ingredients or volatile oils. Trapped air and some moisture is commonly removed with a vented (vacuum) extruder. In addition, it is considered good compounding practice to add 5-10 phr calcium oxide as desiccant. The desiccant is generally dispersed in oil and wrapped in polybags to prevent premature reaction with humid air. Hydrous fillers are usually avoided; calcined clay is the preferred mineral filler. Higher viscosity, less volatile paraffinic oils or

sometimes waxes are used to soften compounds.

Deformation or Collapse of the extrudate during cure is another potential problem. Polymers with high hot green strength are desirable. An EPDM example would be Vistalon[™] 6505. Also, non-thermoplastic softeners such as vulcanized vegetable oils can be helpful.

*Reversion* can occur due to curing temperatures in excess of 200°C (400°F). Residence times are short, generally 1-2 minutes, requiring very fast cure systems. The cure system must also be adjusted to the speed at which heat will be added by the particular curing method employed.

#### **Extrusion Curing Methods**

Conventional Hot Air can be used to provide the heat for vulcanization. This method gives a clean, attractive surface and has a wide processing latitude to easily make a variety of shapes. The negative aspects are the poor heat transfer of air and the possibility of oxidation during cure. Shearing head extruders are a relatively recent development. They heat the compound to vulcanization temperature before it exits the die, thus overcoming some of the problems with poor heat transfer of air.

*Fluidized Beds* improve heat transfer over air alone. High velocity air is pumped upward in the curing trough to fluidize small glass beads (Ballotini). Beads adhering to the profile are normally removed by spray or brushes as the extrusion exits the fluidized bed. However, complex profiles can make complete removal difficult.

Liquid Cure Medium (LCM) uses a eutectic mixture of salts to heat the extrudate. The molten salt bath usually has a metal conveyor to keep the rubber compound submersed. This method has good heat transfer to the rubber. However, cleaning salt off the profile can be difficult, and satisfactory disposal of dilute salt rinse is becoming increasingly difficult. The method is advantageous for low compression set articles using peroxides. Sulfur can be used as a coagent to minimize surface tack. Also, deformation problems versus other atmospheric methods are usually minimized.

*Microwave with Hot Air Soak* is another current method that is particularly effective for thick section profiles. It also retains the clean extrudate surface of the straight hot air method, but with significantly faster heating. Nevertheless, microwave methods put additional constraints on compounding.

In a microwave field, heating occurs simultaneously throughout the rubber. Polar rubbers such as Neoprene and NBR will usually heat very rapidly in the microwave unit. Hydrocarbon rubbers heat much slower unless they contain 20-40 percent volume of carbon black. Larger particle size blacks such as SRF and N990 can be used in the 30-40% range; HAF and FEF types are limited to 20-30%. Localized hot spots can develop if the black loading is too high or if dispersion is poor. High zinc oxide levels, to 20 phr, can also improve microwave heating.



Figure 14: Flow Diagram for Rubber Goods Manufacture



Figure 14: Flow Diagram for Rubber Goods Manufacture (continued)

Operation and Equipment	Object	Problems Involved
Breakdown Banbury Mixer Open-roll mills	To reduce nerve and viscosity.	Cost (equipment, time, power) temperature control.
Masterbatching Banbury Mixer Open-roll mills	To add pigments and curatives.	Dispersion.
Batch Mixing Banbury Mixer Open-roll mills	To obtain a homogeneous mixture of ingredients.	General efficiency, good dispersion, scorching.
Straining Extruder with screens	To remove undispersed material.	Screen life, plugging.
<i>Cooling</i> Air, Sprays, Dip tanks	To minimize scorching hazard and eliminate tacky surfaces.	Efficiency of method or equipment.
Storage Racks, bins or silos	To have stock available for scheduling and use.	Scorch.
Warm-up Mills	To add cure and prepare for operations and use.	Scorch.
<i>Mill-slabbing</i> Mill with rotary Knife-blades	To provide banks for molding or strips for feeding extruders.	Mechanical handling and scorch.
Sheeting, Frictioning & Skim Coating Calender Open-roll mills	To apply stock to fabrics or provide unsupported sheet.	Scorch, blistering, roughness tack, bloom.
Extruding Tread extruders Conventional extruders Crosshead extruders	To obtain desired cross-sections, to coat wire or cable, and cover hose carcasses.	Extrusion rate, scorch, dimensional stability.
Building Specialized equipment depending on product	To assemble "green" articles: tires, belts, boots, etc.	Tack, bloom, gauge- control accuracy.

# Table 1: Processing Operations and Problems

		Problems
Operation and Equipment	Object	Involved
Conventional Curing Presses and molds	To obtain desired size	Mold lubrications,
	and shape during cure.	flow and satisfactory knitting, uniformity of cure.
Steam tubes, Autoclaves	To cure by direct contact or in lead, talc, or other supporting devices.	Steam pressure and quality, blistering, sagging, shape change before or during cure.
Pressurized Vulcanizers		
Vulcanizers pressurized	To obtain attractive	Blistering, porosity,
Hot water tanks	To control exotherm in	appearance of surface.
	hard rubber, and for soft roll stocks.	Blistering, porosity, sagging.
Atmospheric Curing		
Festooning heaters	To cure coated fabrics.	Adhesion to fabrics and uniformity of cure.
Continuous Cures	To cure extrusions.	Porosity, deformation and reversion.

 Table 1: Processing Operations and Problems (continued)



# CHAPTER 6 Rubber Product Applications

#### PNEUMATIC TIRE COMPOUNDING

#### by David Benko, Paul Sandstrom & Marty Cohen

The Goodyear Tire & Rubber Company Akron, OH

The pneumatic tire is an advanced composite and a flexible pressure container providing load-carrying capability, cushioning, and road handling abilities. The tire is fitted to a wheel which absorbs and controls the forces between the axle and the road. Steering response and braking torgue are transmitted through the tire. The tire's unique construction and damping characteristics define its response¹. Understanding how the tire mechanically transmits its response between the vehicle and the road is an essential step in tire development². By looking at individual tire components with reference to the physics of tire operation the material characteristics needed in each component can be defined. The stress, tire component strain and cyclic loading can be related to material viscoelastic properties. Laboratory dynamic tests can be used to measure viscoelastic properties, and to some extent to predict performance characteristics. The tire is a complex system of interacting components, each with specific properties designed for maximum effectiveness. The performance of a tire depends on the properties of the components, their interaction, and the service conditions of the tire².

#### **Tire Components**

A tire is a composite of several rubber components, each of which serves a specific and unique function. These components are designed, compounded and fabricated to meet the mobility requirements of a vehicle, which include load-carrying capability, control of the vehicle, handling, ride, traction, durability, etc. Tire components are made from materials such as natural rubber and/or synthetic rubbers³, chemicals which function as antidegradants, curatives, and processing aids⁴, reinforcing fillers such as carbon black and silica, and cords composed of textile, fiberglass, and steel wire (brass, bronze or zinc plated). These materials are selected for their mechanical and physical properties and for their interactions with other constituent materials, in order to provide a broad range of properties. Figures 1 and 2 illustrate the components of an example radial passenger tire and an example radial truck tire respectively.



Figure 1: Components of One Particular Radial Passenger Tire



# Figure 2: Cross-Section of One Typical Radial Medium Truck Tire

A tire can be divided into two major segments: (i) the tread area, which includes the tread compound and belts, and may include additional components such as base, cushion, wedges and overlay, and (ii) the casing, which includes the carcass plies, sidewall, bead, innerliner, apex, chafer, etc. A brief discussion of each tire component and its effect on tire performance follows:

*Apex* - The apex is formulated for good dynamic stiffness, flex fatigue, tear strength and adhesion, with regard to ride and handling.

Base - The base is formulated to have low hysteresis and good fatigue and tear resistance. Tire rolling resistance, ride and handling can be affected by the formulation of the base.

Bead Insulation - The bead usually consists of multiple strands of high tensile, bronze or zinc-plated steel, coated with rubber and formed into inextensible hoops to seal the tire against the rim, and to provide hoop tension to prevent air leakage. It acts as a load transfer mechanism between the tire and the rim.

*Belt Coat* - The belts are layers of angled rubber-coated cord, made of textile, fiberglass or brass-plated steel, which wrap circumferentially around the tire. The coat compound is normally formulated to provide good adhesion to the cord, stiffness, and tear and fatigue resistance.

*Chafer* - The chafer protects the plies from wearing and cutting against the rim, distributes the hoop stress of the bead and prevents moisture and dirt from penetrating into the tire.

*Innerliner* - The innerliner is formulated to provide good impermeability to air and moisture, and flex fatigue resistance.

*Ply Coat* - The ply is a composite of rubber-coated cords that serves as the reinforcing element of a tire carcass by locking the bead into the carcass. Plies contain inflation pressure along the cord direction, especially under load.

*Sidewall* - The sidewall compound is formulated for resistance to weathering, ozone, abrasion, tear, radial and circumferential cracking, and for good fatigue life.

*Tread* - The tread is designed and compounded for a balance of abrasion resistance, traction, low rolling resistance, and protection of the casing. It provides frictional contact for the transmission of driving, braking and cornering forces.

*Wedge* - The shoulder wedge is placed under the belt edge to reduce interply shear strain, and is formulated for high dynamic stiffness, resilience, good fatigue, adhesion and tear resistance.

The interactions of tire components with tire performance are given in Figure 3.

	<b>MAINTAIN SHAPE</b>	<b>RIM FITMENT</b>	<b>AIR RETENTION</b>	STRENGTH	TREADWEAR	TRACTION	FUEL EFFICIENCY	HANDLING	RIDE	HIGH SPEED	NOISE	INFORMATION	STYLING
INNERLINER			X				X						
PLY	X			X	X		X	X	X	X			
BEAD	X	X		X									
APEX					X		X	X	X	X			
CHAFER		X					X	X					
TOEGUARD			X										
SIDEWALL							Χ		X			X	X
BELT	X			X	X		X	X	X	X			
TREAD					Χ	X	X	Χ	X	X	X		
TREAD DESIGN					X	X	X	X	X	X	X		X

Figure 3: Tire Component / Performance Interactions

# Tire Materials

Tire materials may be classified into several major types:

- elastomer (rubber polymer)
- reinforcing filler
- oil
- rubber chemicals
- fabric reinforcement
- steel reinforcement

The matrix of the rubber compound is the elastomer. For most of the components of the tire, one or more of the "general purpose rubbers" (GPR) are used. The major GPRs are natural rubber (NR), synthetic polyisoprene (IR), polybutadiene (BR) and styrene-butadiene rubber (SBR). SBR may be prepared using either solution (S-SBR) or emulsion (E-SBR) polymerization processes. Some components such as innerliner and white sidewall may use other elastomers such as butyl rubber (IIR), halogenated butyl (bromobutyl or chlorobutyl) rubber (BIIR, CIIR) and ethylene-propylene diene modified rubber (EPDM).

The elastomer is given increased stiffness, tensile strength, and abrasion and tear resistance by addition of a reinforcing filler, typically carbon black and/or silica. Silica use, particularly in passenger tire treads, has increased significantly

for its ability to provide an improved balance of low rolling resistance with good wet traction.

Hydrocarbon oil is used in many tire compounds to aid incorporation of filler and enhance processability. Oils low in polycyclic aromatic (PCA) hydrocarbon content are now predominantly used.

Numerous chemical additives comprise the general category of "rubber chemicals". These are used for vulcanization, stabilization and environmental protection, processing, enhanced cured stiffness, modifying viscoelastic properties and other specific purposes.

Fabric is used in the form of continuous reinforcing cords in the carcass plies of passenger and light truck tires. These may consist of polyester, nylon, rayon, aramid and other organic materials.

Steel is used in the wires which compose the bead and the belts, as well as the plies of medium truck tires. A specific type of brass-coated steel is used to maximize adhesion to the rubber compounds used to coat the wire in belts and plies.

The breakdown by weight of the materials by type averaged across a broad representation of tire constructions is shown in Figure 4.



Figure 4: Tire Composition by Material Type

#### Passenger Tires

Tire performance is a function of materials, tire tread design and construction. Some performance characteristics relate primarily to the tire tread area, such as rolling resistance, tread wear, and traction in wet, dry, snow, mud and ice conditions. These performance characteristics, although significantly affected by the belt construction area and tread design, can be significantly modified by the tread compound. It is known that polymer selection involves trade-offs in traction, wear and rolling resistance, properties which are affected by polymer glass transition temperature ( $T_g$ ). Data on the  $T_g$  of various elastomers are needed in order to formulate a proper compound.

When designing a passenger tread compound to meet specific performance criteria, the first decision should therefore be the choice of synthetic polymer or polymer blends. Polymer selection helps to provide the proper balance of wear, traction and rolling resistance⁵. Laboratory tests evaluating the polymer's dynamic response over a broad range of temperatures can be used to select the type of polymer system. Figure 5 depicts the viscoelastic response of an ideal tread compound optimized to give a favorable balance of wet traction and rolling resistance.



Figure 5: Viscoelastic Response for RR and Wet Traction

The next step is to select the loading and type of filler. The interaction of tread compound with tread design controls the tread stiffness range. The type of carbon black or silica strongly influences hysteresis: it is usually increased by the selection of very small particle size and high structure fillers, and reduced by lower filler loading. The intended service requirements also contribute to overall tire performance. Wear is generally optimized at an intermediate level of filler, dependent on the severity of wear, types of polymers used, and oil level. Wet traction is generally improved by high filler content, but snow traction is improved by low filler levels (or low compound stiffness). Tread compounding requires balancing competing and often conflicting performance attributes (Table 1).

	Desired Polymer			Desired Filler			
Property	Туре	MW	Tg	Туре	Loading		
Treadwear	BR	Hight	Low	Black	Intermediate		
Snow Traction	BR/NR	-	Low	Silica	Low		
Dry Traction	SBR	-	High	Black	High		
Wet Traction	SBR	-	High	Silica	High		
Rolling Resistance	S-SBR, NR	High	Low	Silica	Low		
Processability	E-SBR, IR	Low	-	Black	Low		

Table 1: Materials Influence on Tread Properties

The tire's crown area accounts for a larger portion of many performance properties. However, all the tire's components interact to define its total performance package.

## **Truck Tires**

Market requirements for long haul truck tires include: (i) retreadability, (ii) fuel economy, (iii) tread life, and (iv) ride, wet traction and handling.

The total life cycle of the tire is strongly affected by the performance of the casing. Compounding for plies, belts, apex and sidewall demands special attention to ensure that the rubber compounds and reinforcement can survive the strain cycles and service conditions encountered over 750,000 tire miles.

Fuel economy is important in truck tires because it is an important cost factor. A vehicle's aerodynamic drag can be the largest fuel cost factor. The tire's crown area usually contributes most to its fuel economy. Each tire position: steer, drive and trailer, contributes to a vehicle's fuel cost. The properties of the tread compound must balance fuel economy with other performance and service requirements.

# Compounding

Individual compounds are designed and formulated to meet the specific performance requirements of each tire component. This is primarily accomplished through the selection of elastomer type(s), fillers, chemicals for vulcanization, materials for processing and tire manufacturing, and the choice of additional materials for specific in-service performance needs. Table 2 summarizes the desirable properties of tire compounds. Table 3 lists laboratory tests used to evaluate the physical performance of tire compounds^{6, 7}. Table 4 is a summary of the general composition of representative individual tire compounds: elastomers, reinforcing fillers, the cure system and additional important ingredients.
	Tread	Sidewall	Wire Coat	Ply Coat	Innerliner
Maximum					
	Traction	Tear Resistance	Wire Adhesion	Cord Adhesion	Ply Adhesion
		Thermal Oxidative Stability			Thermal Oxidative Stability
		Cleanability			
Minimum					
	Rolling Resistance	Weather Cracking	Heat Buildup	Heat Buildup	Air and Water Permeability
	Wear	Flex Cracking			Flex Cracking
	Cut Growth	Heat Buildup			Heat Build up
	Groove Cracking	Curb Scuffing			

# Table 2: Desirable Properties of Tire Components

# Table 3: Representative Laboratory Tests for Tire Compounds^{6,7}

	ASTM Test	Component
D 412	Tension	Tread
D 413	Adhesion to Flexible Substrate	Ply Coat
D 429	Adhesion to Rigid Substrate	Wire Coat
D 430	Dynamic Fatigue	Sidewall, Wire Coat, Ply Coat, Innerliner
D 518	Surface Cracking	Sidewall
D 572	Deterioration by Heat and Oxygen	Sidewall
D 573	Deterioration in an Air Oven	Sidewall, Innerliner
D 623	Heat Generation and Flexing Fatigue in Compression	All
D 624	Tear Resistance	Tread
D 1054	Resilience by Rebound Pendulum	Tread, Wire Coat, Ply Coat
D 1149	Surface Ozone Cracking	Sidewall
D 1415	International Hardness	All
D 1434	Gas Permeability Coefficient	Innerliner
D 1630	Abrasion Resistance	Sidewall
D 1646	Viscosity and Vulcanization	All
D 2084	Oscillating Disk Cure Meter	All
D 2137	Brittleness Point of Flexible Polymers and Coated Fabric	Ply Coat, Innerliner
D 2138	Adhesion to Textile Cord	Ply Coat

	ASTM Test	Component
D2228	Abrasion Resistance	Tread
D 2229	Adhesion to Steel Cord	Wire Coat
D 2231	Forced Vibration	Tread, Wire Coat, Ply Coat
D 2240	Durometer Hardness	All
D 3395	Dynamic Ozone Cracking	Sidewall
D 3985	Oxygen Gas Transmission Rate	Innerliner
D 6601	Dynamic Properties using RPA 2000	All

### Table 3: Representative Laboratory Tests for Tire Compounds^{6,7} (continued)

#### Table 4: Representative Examples of Composition of Tire Compounds

Tread	Sidewall	Wire Coat	Ply Coat	Innerliner
Elastomers NR BR SBR	NR BR EPDM	NR IR	NR BR SBR	Halogenated IIR NR SBR
Reinforcing Fillers           Blacks:           N110         N550           N120         N660           N220           N234           N299		N330 N326	N660	N660
Non-blacks: Silica	Silica	Silica		Clay
<i>Cure System</i> Low/Normal Sulfur	Adapted to Polymer	High Sulfur	Normal Sulfur	Adapted to Polymer
Additional Ingredients Low PCA Oil	Antidegradants: VANWAX [®] H AGERITE [®] RESIN D [®] 6PPD Polystay [®] 100	Adhesion Promoters: Cobalt Salts	Resins: Hydrocarbon resins Hexamethylenetetram Hexamethoxymethyln Phenol-formaldehyde	nine nelamine resins

Tables 5 through 10 at the end of this chapter provide formulas and physical properties for representative examples of compounds for important tire components.

It is important to note that each compound has a specific recipe that relates to its expected tire application, i.e. tread, sidewall, innerliner, etc. However, in addition to the recipe, the compound's physical properties and final tire performance are very dependent upon the exact processing conditions. These include the mixing sequence (addition of the chemical ingredients), mixing time, mixing energy and stock temperature, and downstream processing methods such as remilling, calendering, and extruding. Finally, it is important to note that the examples provided here are representative, and that each recipe should be adjusted for specific processing constraints and performance requirements.

#### Interactions

Interactions between the individual compounds and components of the tire system occur during tire fabrication, curing, and service⁸. The first type of interaction is based on the migration of ingredients between tire components. This occurs, for example, whenever chemicals used as curatives (sulfur, accelerators, activators), processing aids (oils, peptizers, tackifiers) and antidegradants (antioxidants, antiozonants, waxes) differ in concentration in adjoining components. As a result of migration, the levels of curatives may be different from those specified in the original formulation. This could impact the state of cure in adjoining compounds, particularly at the interface. Migration of antidegradants from the sidewall compound into the carcass could occur but could also be offset by migration from the carcass into the sidewall.

The second type of interaction is based on differences in physical characteristics between components. For example, the hardest compositions are those of the bead area and the belts. In order to distribute stress the multi-component tire system may be designed to have compounds decrease stepwise in modulus according to their distance from the high modulus components.

## Curing

Both the cure rate and final cure state of a rubber compound are important. Accelerators are used to increase the rate of sulfur vulcanization of tire compounds and to improve their physical properties. The most important characteristics of accelerators are their effect on scorch time (period after addition before vulcanization begins), cure rate (period required for full vulcanization) and plateau times (period during which properties are constant). Scorch time is important because once vulcanization has begun, stocks cannot be readily processed. The rate of cure, or cure time, is important because the desired final state of cure must be achieved in the shortest time after cure has started.

The tire curing process involves applying specified temperatures and pressures over a period of time to effect simultaneous vulcanization of the various rubber compounds in the tire in order to form one composite. In conventional manufacturing processes this is accomplished in an automatic curing press which uses steam to maintain temperature in the shell around the metal mold. It also has an attached heat-resistant rubber bladder to supply internal heat and pressure. When the press is completely closed, the tread and sidewall components are forced into the mold pattern by pressure from the expandable bladder. Then vulcanization begins. Since each component of the tire undergoes a different rate of cure (time-temperature cycle) and can have very different proximities to the bladder and mold, it is important to produce the optimum state of cure (plateau) for each component during the tire curing cycle. This is accomplished by the selection and adjustment of the cure ingredients, namely sulfur, activators, accelerators, and retarders. The cured tire should

have the final form and physical properties, including final cure state, required for service.

### Performance in Service

The components of a tire composite have a targeted set of physical properties when removed from the mold and cooled to ambient temperature. Changes in compound physical properties can occur from (i) heat generated in the tire by energy loss in service, (ii) by friction due to braking, and (iii) any increased crosslinking caused by thermo- and mechano-chemical oxidation. These processes are retarded by the addition of antioxidants, for example secondary arylamines. Thermo-oxidation stability is also promoted by using low sulfur/high accelerator (semi-efficient) cure systems. Tire compounds, components and overall tire design are all developed to allow for proper tire performance throughout its intended service.

Weathering affects the outer surface of the tire, particularly the sidewalls. Thus, chemical antiozonants are added to the black sidewall compound at levels effective under both static and dynamic tire service conditions. The antiozonant is continually depleted from the sidewall surface by reaction with ozone, and by physical abrasion caused by curb scuffing and washing, and thus is continually replenished by fresh antiozonant which migrates from within the tire to the surface. All practical chemical antiozonants for rubber are staining materials, which cause sidewall discoloration after use, and prohibit their use in white or non-black sidewall components. Suitably blended petroleum waxes serve as effective protectants against ozone under static conditions, but must be used in conjunction with highly active chemical antiozonants for protection of the tire in dynamic service.

### Summary

The development of tire compounds requires a clear understanding of the service requirements. This knowledge must relate back to the components.

The selection of materials for the components are related to stress, strain and cyclic loading that the tire will experience in service. Experimental compounds can be tested and evaluated in the laboratory under simulated service conditions.

Knowledge of elastomer viscoelastic properties, filler reinforcement, and cure can simplify this process.

Ingredients	Carbon Black (phr)	Silica (phr)
Buna VSL 5025-2 HM, SBR		96.25
PLF 1723 SBR	110.00	
BUD 1207 BR	20.00	30.00
N299 Carbon Black	60.00	
Zeosil 1165MP Silica	5.00	70.00
Naphthenic Oil	7.75	5.00
VANWAX H	3.80	3.00
Santoflex 6PPD		1.00
AGERITE RESIN D		1.00
Polystay 100	1.15	
Stearic Acid	2.00	2.00
Zinc Oxide	1.75	3.50
Evonik Si 266		11.00
Sulfur	1.70	1.70
DURAX®	1.70	2.00
DPG	0.25	2.00
Total	215.10	228.45
Rheometer	160°C	150°C
M _H -M _L (dN•m)	11.5	18.1
ť 90 (min)	8.9	20.4
Original Physical Properties, Cured 1	4 min. @ 160°C	
300% Modulus, MPa	7.8	9.2
Tensile, MPa	14.8	16.2
Elongation, %	492	460
Rebound @ 22°C, %	42	32
Dynamic Mechanical Properties, ASTM	D 6601, RPAº, 10% strain a	amplitude, 1 Hz, @ 100°C
Storage Modulus, KPa	1098	1867
Tan Delta	0.107	0.117

# Table 5: Passenger Tire Tread Recipes

# Table 6: Truck Tire Tread Recipes

Ingredients	Natural Rubber (phr)	Synthetic Rubber (phr)
TSR 20 Natural Rubber	100.0	
PLF 1502 SBR		100.0
N299 Carbon Black	50.0	50.0
AGERITE RESIN D	2.0	2.0
Naphthenic Oil	5.0	5.0
Stearic Acid	1.0	2.0
Zinc Oxide	5.0	3.0
Sulfur	1.4	1.0
VANAX [®] NS	1.0	1.0
DPG		1.0
Total	165.4	165.0
Rheometer @ 150°C		
M _H -M _L (dN•m)	14.4	13.3
ť 90 (min.)	11.5	16.9

Original Physical Properties,		
Cure time @ 150°C	32 min.	36 min.
300% Modulus, MPa	14.0	11.3
Tensile, MPa	24.4	23.6
Elongation, %	469	512
Rebound @ 22°C, %	51	45
Dynamic Mechanical Properties, AS	TM D 6601, RPA ⁹ , 10% strain	amplitude, 1 Hz, 100°C
Storage Modulus, KPa	1330	1101
Tan Delta	0.116	0.162

# Table 6: Truck Tire Tread Recipes (continued)

	Black	White
Ingredients	(phr)	(phr)
TSR 20 Natural Rubber	40.0	
TSR L Natural Rubber		40.00
BUD 1207 BR	60.0	
Exxon [™] Chlorobutyl 1066		50.00
Royalene 505		10.00
N550 Carbon Black	50.0	
Naphthenic Oil	12.0	6.00
Titanox 1000 Titanium Dioxide		35.00
Nucap 100G Clay		65.00
Stearic Acid	1.0	1.00
AGERITE RESIN D	2.0	
Santoflex 6PPD	4.0	
Vistalon [™] 7000		1.00
VANWAX H	1.5	
SP-1068 Resin		2.00
Zinc Oxide	3.0	5.00
Sulfur	1.6	1.60
VANAX NS	0.4	1.60
DOTG		0.45
Total	175.5	218.65
Rheometer @ 150°C		
M _H -M⊢(dN•m)	8.3	24.8
ť 9 (min.)	19.6	18.5
Original Physical Properties		
Cure time @ 150°C	32 min.	25 min.
300% Modulus. MPa	5.0	4.5
Tensile. MPa	14.1	9.6
Elongation. %	632	659
Rebound @ 22°C, %	56	35
Dynamic Mechanical Properties, ASTM	1 D 6601, RPA ⁹ , 10% stra	in amplitude, 1 Hz, 100°C
Storage Modulus, KPa	800	701
Tan Delta	0.116	0.147

# Table 7: Tire Sidewall Recipes

Ingredients	Wire Coat (phr)	Fabric Ply (phr)
#2 RSS Natural Rubber	100.00	
SMR 20 Natural Rubber		80.0
PLF 1778 SBR		27.5
N326 Carbon Black	60.00	
N550 Carbon Black		50.0
Naphthenic oil	1.00	1.5
Zinc Oxide	8.00	3.0
Stearic Acid	2.00	1.0
SP-1068	1.00	1.0
Penacolite B-19-S	2.00	1.0
Cyrez CRA 100	2.80	1.8
Cobalt Naphthenate	3.00	
AGERITE RESIN D		1.0
Polystay 100	0.75	
	1.15	
		1.4
	0.20	
	 5.00	0.1
Cryslex H5	5.00	3.0
Total	186.90	172.3
Rheometer	155°C	150°C
M _H -M _⊢ (dN•m)	32.3	15.8
ť 90 (min.)	12.1	7.5
Original Physical Properties, Cured	35 min./155°C	23 min./170°C
100% Modulus, MPa	4.3	1.8
300% Modulus, MPa		11.5
Tensile, MPa	16.6	13.2
Elongation, %	306	353
Rebound @ 22°C, %	43	55
Dynamic Mechanical Properties, ASTM	D 6601, RPA ⁹ , 10% strai	n amplitude, 1 Hz, 100°C
Storage Modulus, KPa	3298	1234
Tan Delta	0.122	0.103

Table 8:	Tire	Body	Ply	Reci	pes
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Table 9:	Tire	Innerliner	Recipe
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Ingredients	phr
Bromobutyl 2222	100.00
N660 Carbon Black	60.00
SP-1068	1.00
Naphthenic Oil	6.00
Stearic Acid	0.50
Struktol 40 MS	10.00
Magnesium Oxide	0.15
Zinc Oxide	1.00
ALTAX®	1.70
METHYL TUADS®	0.17
Total	180.52

Rheometer @ 170°C	
M _H -M ₁ (dN•m)	2.3
ť 90 (min)	6.4
Original Physical Properties, Cured 23 min. @ 170 C	
300% Modulus, MPa	2.6
Tensile, MPa	7.1
Elongation, %	774
Hardness, Shore A	56
Dynamic Mechanical Properties, ASTM D 6601, RPA9, 10% strain	amplitude, 1 Hz, 100°C
Storage Modulus, KPa	428
Tan Delta	0.310

 Table 9: Tire Innerliner Recipe (continued)

Table 10:         Tire Apex and Bead Insulation Recipes	•
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Ingredients	Apex (phr)	Bead Insulation (phr)
TSR 20 Natural Rubber	60.00	
PLF 1502 SBR	40.00	100.00
N326 Carbon Black	80.00	125.00
Hi-Sil 342 LD		7.00
Naphthenic Oil	10.00	24.00
Struktol 40 MS		10.00
Stearic Acid	2.00	3.00
SP-1068	3.00	
HRJ-11995		2.50
Durez 31459	5.00	
Cyrez CRA 100		2.80
Hexamethylenetetramine	3.00	
Zinc Oxide	3.00	4.50
AGERITE RESIN D		2.00
DPG		0.25
Crystex HS	3.75	5.00
Sulfur	1.00	
Vulkacit DZ	2.70	
DURAX		1.65
Total	213.45	287.70
Rheometer	150°C	155°C
M _⊔ -M₁ (dN•m)	52.4	43.7
ť 90 (min.)	14.6	25.6
Original Physical Properties		
Cured	6 min. @ 170°C	30 min. @ 155°C
100% Modulus, MPa	8.6	8.3
Tensile, MPa	17.1	14.0
Elongation, %	189	200
Hardness, Shore A	88	92
Dynamic Mechanical Properties, ASTM I	D 6601, RPA ⁹ , 10% strai	in amplitude, 1 Hz, 100°C
Storage Modulus, KPa	4686	4488
Tan Delta	0.230	0.252

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#### TIRE RETREADING

#### by David L. Bender

Bridgestone Bandag, LLC Muscatine, IA

### Introduction

Commercial tire retreading provides an economical means of extending the utilization of worn tires. The worn tire, referred to as the casing, is a valuable resource that is often not utilized to the fullest potential. The retreaded tire can provide performance similar to that of the new tire at a fraction of the cost. The benefit to the environment is also becoming more of a reason to consider the retreading of tires.

Early retreaded tire products were primarily passenger tires with reliability, durability and wear performance issues. With the global radialization of truck tires, the truck industry began to shift towards retreading. The radial truck tire has a greatly increased casing life as compared to its bias casing predecessors. Eventually the focus of the tire retreading industry shifted to truck tire retreading. The majority of the tires retreaded today are for truck applications.

New technologies continue to be introduced into the truck tire industry to the point where the casing durability and reliability are high enough to allow quality truck tires to last several product lifetimes (complete wear out of the tread). Improvements in casing inspection and repair have enabled the reuse of damaged casings to provide a product capable of completing the next product life.

Debris along the highway from failed tires continues to be attributed mainly to the inferior durability of retread tire products. A recent study has shown that tire debris is produced equally by new and retreaded tires¹. A large percentage of the failures of tires can be related to under inflation, excessive heat or road hazards, but not to a deficiency in the tires themselves¹.

In 2008 the estimated number of medium truck tires retreaded in the US was 14.7 million². An additional 1 million tires including passenger, aircraft, large OTR, light truck, etc., were also estimated to have been manufactured in 2008³.

Recently the ecological aspects of retreading have become a major issue in the selection of tire products. Approximately 22 gallons of oil is required to produce a new truck tire, while remanufacturing a tire with a new tread requires only about 7 gallons of oil⁴. With the current focus on the prudent use of our natural resources there is increased interest by the end user in tire retreading.

Of obvious interest to the end user is the lower cost of the retreaded truck tire. The reuse of quality casings can result in a savings of over 50 percent, with typical savings of over \$270 per tire². If the purchase of a casing is required the savings is reduced to over \$200 of that of a new tire². The widespread use of retreaded truck tires by large fleet end users is testimony to the value and the reliability of the retreaded tire product.

### **Retreading Technologies**

There are two primary methods currently used to retread tires: *mold cure* and *precure* processes. The preparation of the casing is essentially the same in both cases.

In the mold cure process the tread rubber is applied in the uncured state to the tire casing and the product is cured in much the same manner as new tires. In the pre-cured technology, the tread is supplied to the retreading factory already cured, with the tread design already in place. The treads are supplied in rolls of various lengths typically 12 to 30 feet in length or as rings which can be stretched onto the casing. In precured retreading a bonding material, referred to as cushion or tie gum, is applied to the tread or casing prior to the application of the tread.

Approximately 90 percent of the medium and light truck retreaded tires produced in North America in 2007 were manufactured using the precured technology⁵. The remainder of this chapter will focus on this retreading method.

#### **The Precured Retread Process**

The major steps of the precured retreading process are:

- · Casing inspection
- Buffing
- Repair
- · Application of the cushion
- · Application of the tread
- Enveloping
- · Curing
- · Final inspection

Casing Procurement – Worn tires to be used for retreading may be obtained from a number of sources. In agreements with end users, retreading facilities will inspect and retread their tires (referred to as custom retreading). The end user may be an individual owner-operator or could be a fleet with several hundred trucks. In many instances the casings are obtained from casing brokers who accumulate casings of popular sizes and sell these to the retreading factories. The condition of the casings as well as the tire manufacturer, and in some cases the actual tire product (manufacturer, brand and series), may be specified by the tire retreader.

*Casing Inspection* – As shown in Figure 1, the initial inspection of the casing is done by visual and tactile means. This inspection examines the casing for injury and determines its viability for retreading.



Figure 1: Initial Inspection of the Tire Casing

The outside of the casing is examined to determine if there are broken radial cables and to detect damage due to impact, puncturing or cutting. The inside of the tire is inspected to determine the state of previous repairs and to detect excessive oxidation of the inner liner (occurring during running the tire in an under inflated condition). The bead is examined for cracking or tearing of the rubber covering the bead and damage to the bead bundle itself.

There are guidelines used to establish the ability of the casing to be retreaded. If the product is produced for a particular customer, there may be more stringent criteria for acceptability of the casing (number and types of injuries, casing age, etc.). After passing the initial inspection, the tire may also be inspected using a number of devices designed to detect specific injuries to the casing. These include ultrasonic, x-ray and shearographic casing inspection tools, as shown in Figures 2 and 3. If the casing is determined to be a viable candidate for retreading, the unwanted remaining tread is removed by buffing.



Figure 2: Inspection of the Casing for Nail Holes



Figure 3: Shearographic Inspection of the Casing

*Buffing* – The buffing process, as shown in Figure 4, provides a contaminant free surface of uniform texture for the application of the new tread. During the buffing process the casing is also brought to a uniform circumference with the correct toroidal radius and correct width for the proper tread size for the casing.



Figure 4: Buffing of the Casing

A modern buffing device (buffer) is much like a CNC machine. The device is computer controlled and consists primarily of a motor driven expandable hub and a motor driven high speed rasp mounted on an X-Y table. The rasp is comprised of a series of blades evenly spaced like a set of dado saw blades. The rasp is placed at a slight offset angle to the circumferential axis of the tire. The rasp is rotated at a high speed and has the ability to change the radius of attack to the tire. This is to allow removal of the proper amount of material above the belt package (some tires are "rounder" in the radial direction than others).

During the buffing process, the tire is mounted on an expandable hub which provides the proper orientation of the tire relative to the rasp. The hub is expanded with compressed air to the proper rim size to seal the tire at the bead. The tire is then inflated and the tire and rim assembly are rotated and brought into contact with the rotating rasp. Rubber is removed from the casing by the rasp with successive passes of the rasp across the face of the casing. The tire debris is removed by suction to a storage area. The buffing process is halted when the proper amount of rubber has been removed. Next, the rasp is positioned at the desired angle relative to the casing and rubber is removed from the edge of the casing. This process sizes the casing to the proper width for the application of the tread product.

*Repair* – It is at this point that the majority of the repair to the casing is usually performed. The main purpose of repairing the casing is to restore the ability of the casing to maintain air pressure and to return mechanical properties of the casing to a level high enough to endure at least the next use life. The types of repairs to the casing that are performed include those for protrusions through the casing (nail hole) and for damage to a larger portion of the casing or broken and damaged body cords (section repairs).

*Cementing* – After buffing the casing, a thin layer of contact adhesive is usually applied to the buffed portion of the casing. This material, normally referred to as cement, aids in the retread tire fabrication process by providing increased tack and adhesion between the casing and the cushion. The cementing of the casings is optional, but is widely used in retreading. Cements are rubber-based materials with solvent or water carriers.

*Tread Application* – After the repair of the casing is completed, the tread is applied. The application of the tread to the casing is referred to as building the retreaded tire. As the first step of the building processes, the casing is placed on a builder equipped with an expandable hub, like that on the buffer. The hub is expanded as in the buffing operation and the tire is inflated.

There are several methods of building retreaded tires with variations in the type of cushion and the use or exclusion of cement to the casing. The most widely used method is the extruder applied cushion building method, with no cement applied to the casing. With this building method the cushion is extruded onto either the casing or the tread. The majority of extruders in use today apply the cushion to the casing, as shown in Figure 5.



Figure 5: Cushion Application Using an Extruder

The tread is prepared by cutting the leading edge of the tread perpendicular to its length to provide a uniform uncontaminated surface for bonding. The tread is then applied to the casing and cut to the proper length to fit the casing, as shown in Figure 6.



Figure 6: Application of Precured Tire Tread

Cement is applied to the freshly cut ends of the tread and is allowed to dry. A layer of calendered cushion is typically applied to one of the ends of the tread. The ends are then joined at the surface of the casing and any air is removed between the components with manual pressure. Metal staples are applied across the ends of the tread (splice) to hold the ends of the tread together during curing. The tread is then stitched in place with a pressure roller (stitcher).

After stitching, an air exhausting device called a wick is applied to the tire. The wick may be made of a loosely woven cloth, felt, or a rubber sheet with groves molded in. The wick is usually positioned in the radial direction across the design of the tread and a portion of the sidewall to facilitate the flow of air under the envelope (see next section for the enveloping process). The wick is stapled in place to prevent movement during the enveloping process. The wick and the envelope allow maximum pressure to be applied to the tread to press it onto the casing during curing.

*Enveloping* – The next step in the process is the placing of the "built" tire in a rubber containment device called an envelope. The envelope is a rubber device that fits around a tire and is sealed at the beads of the tire on both sides. The tire is inserted by stretching one of the openings of the envelope to a circumference large enough to allow insertion of the tire, as shown in Figure 7.



Figure 7: Placing the Assembled Tire into a Curing Envelope

The tire is positioned so that the envelope exhaust valve is located over the wick to allow proper air flow from between the tire and the envelope. The opening is then relaxed and the envelope is sealed against the beads. The sealing is accomplished by a number of devices, primarily different for bias than for radial tires. In radial tires typically a rubber ring is inserted inside the envelope at the tire bead and expanded to press the envelope against the bead by the use of an expandable metal band.

*Curing* – As shown in Figure 8, the enveloped tires are then placed in a curing chamber (essentially a large autoclave), which is usually electrically heated.



Figure 8: Placing the Enveloped Tire into the Curing Chamber

The enveloped tires are then connected to air-exhaust lines inside the chamber via a valve in the envelope. The chamber is heated and pressurized. During the pressurization the air is allowed to evacuate from inside the envelope. The operating pressure of the chamber is typically at least 70 psi, with a curing temperature range of 100 to 141°C. The cure time of the tire is dependent on the thickness of the tread, the composition of the cushion and the curing temperature. After curing, the tire is removed from the chamber and the envelope is taken off the tire.

*Final Inspection* – The tire is visually inspected after cooling for proper adhesion of the tread and repairs. The tire is typically painted with a product to improve appearance and to improve protection from attack of oxygen and

ozone. The product is then provided with the appropriate labeling for safety and identification.

### **Truck Tread Compounds**

The previous sections of this chapter have dealt with the procedures used to prepare a retreaded tire using the appropriate materials. This section will deal with the preparation and composition of tire treads and cushion for precured truck tire retreading.

The number of tread compounds for tire retreading applications continues to grow by addressing the higher segmentation of the market for the increased end-user demands for improved tire performance. Because of the large number of truck-tread market segments a listing of examples of tread compounds for each segment would be beyond the scope of this chapter. Instead, general examples are provided to aid the tire technologist in the understanding of truck tread compounding.

There are a variety of compounding concepts that can be used to produce treads for truck tire retreading that have adequate performance. These may include those used for new truck tire products. As compared to passenger tire treads, truck tread compounds are usually lower in oil and carbon black levels. Retreaded truck tire treads can be based on synthetic or natural rubber.

With advances in computer aided experimentation, the selection of ingredient type and level can be made to maximize specific properties such as tread wear or fuel economy. This technique can also be used to minimize the effect of ingredient type on other key properties such as traction and resistance to cutting, tearing and chipping.

*Polymers* – Typical classes of compounds used in treads for retreading include, SBR, SBR/BR, NR, NR/BR or NR/SBR and NR/SBR/BR (triblend). Compounds based on these polymer systems can have good overall properties with particular optimized attributes. SBR treads tend to have good wear and good wet-traction, NR treads, low-rolling resistance. BR is added to tread compounds to improve wear and sometimes improve rolling resistance. Compounds based on triblends can provide a balance of properties by changing polymer ratios to optimize desired properties.

*Carbon Blacks* – The selection of carbon black for retread truck treads depends upon many things including the final properties desired and the cost of the compound. Typical carbon blacks used for truck treads are the 200 and 300 series blacks. The type and amount of carbon black used can have a significant effect on tread wear, rolling resistance and tear resistance.

Process Oils – Until recently, high aromatic process oils were used in most truck tread formulations. Impending European legislation does not allow the use of these oils in the products sold in the participating nations. A number of tire and retread manufacturers are reformulating all or a portion of their products to comply with this legislation. The replacement oils must comply with the

legislation by having reduced Poly Aromatic Hydrocarbon contents (PAH). The PAH components may be removed from oils, or oils with low enough PAH levels (like naphthenics) may be used.

*Curatives* – The curative packages used in treads vary according to the polymer types used and the desired final properties. The cure systems range from conventional to efficient. One primary consideration in the development of the cure package is the scorch safety of the compound. The processing steps after mixing may require much longer scorch safety than required in other applications.

Antidegradants – The antidegradants packages used in retread products are formulated for protection from ozone and oxygen under both static and dynamic conditions. The types of materials used are similar to those used in other applications. Staining antidegradants can be used as there are no color constraints on these products.

Other Additives – There are a number of materials added to tread formulations to impart specific properties to the products. These materials include silica, resins, fibers and process aids. These products impart properties such as improved tear, rolling resistance, lower viscosity and increased filler dispersion.

#### **Retread Tread Manufacture**

The methods and equipment used to manufacture the tread compounds are the same as those used to prepare new tire tread materials including Banbury mixers, batch handling equipment, mills and extruders.

For the mold-cured tread process the tread compounds are supplied to the retread factory as uncured as strip stock or die-sized extrusions. The viscosity of these compounds may be lower than those used for a new tire or precured tread. The lower viscosity aids the application of rubber to a prepared casing and flow of the material into the tire mold. The storage life of the rubber may be an issue since the rubber is in storage much longer than in a typical manufacturing process. This is sometimes addressed by modification of the cure package.

In the precured tread manufacturing process, the compounds are mixed according normal procedures. This stock is then used to prepare extrusions in the desired length and cross-sectional profile. The extrusions are fed into two-plate flat molds in multi-platen curing presses. The tread molds are typically 12 or 30 feet in length. The curing temperatures for the treads vary depending on the compound. After curing, the treads are removed from the press, cooled and finished. The finishing process involves trimming unwanted flash and buffing the non-design side of the tread to provide a contaminant free surface of uniform surface roughness. After buffing, a thin layer of cement is applied to the freshly buffed surface. For packaging, a poly film is applied to the cemented surface, and the treads are rolled and readied for shipment. Examples of truck tread formulations are provided in Table 1:

Ingredients (phr)	Natural Rubber	Synthetic Rubber
First Pass: Natural Rubber SBR 1502	80.0	- 75.0
High- <i>Cis</i> Butadiene Rubber N299 Carbon Black	20.0 45.0	25.0 55.0
High Aromatic Process Oil 6-PPD	5.0 2.0	10.0 2.0
AGERITE® RESIN D® Stearic Acid Zinc Oxide	2.0 2.0 5.0	2.0 2.0 4.0
Totals	161.0	175.0
Second Pass: Masterbatch Sulfur DURAX®	161.0 1.4 1.8	175.0 2.0 1.0
Totals	164.2	178.0
Mooney Viscosity, ML 1+4, 100°C	62	70
Mooney Scorch @ 138°C, Minutes	11.7	17.5
Original Physical Properties Hardness, Shore A 300% Modulus, MPa Tensile, MPa Elongation, % Tear, Die C, MPa	65 11.79 27.80 567 2.82	70 11.53 21.16 494 1.83
Goodrich Heat Build-Up (°C)	12.2	40
Goodrich Flex Set, % MDR t' 90 @ 149°C (min) MDR t' 90 @ 182°C (min) MDR M _H	3.8 9.2 - 16.1	11.9 - 3.4 15.0
DIN Abrasion (mg loss)	48	43

**Table 1: Precured Truck Tread Formulations** 

### **Cushion Gum Manufacture**

The manufacture of cushion gum involves the same equipment as tread manufacture with the possible use of a calender instead of an extruder. As the cushion can be supplied in a number of forms, the form dictates the equipment used in its manufacture. The calendered stock can be produced on a standard three-roll calender. In the case of cushion supplied as strip stock for use with an extruder, the material is typically produced by cutting milled sheet stock.

## **Cushion Gum Formulation**

The basic formulation of the cushion gum materials has changed little in the last 20 years. The primary attributes necessary for a cushion gum formulation are:

- Good adhesion to cured rubber stocks casing to cushion to tread.
- Tack necessary to hold the components in place until and during curing. This may also require good aged tack.
- Physical properties this depends on the application (mining to light truck).
- Weathering resistance the cushion may be exposed to the environment, particularly in the sidewall area.
- Uncured aging the material may be stored for several months prior to use.

As previously stated, the cushion is an adhesive layer used to hold the tread in contact with the casing. These compounds are usually low in viscosity, allowing the flow of the material into the interstices of the tread and casing. This flow maximizes the contact area for enhancing chemical adhesion with some improvement of mechanical adhesion.

The polymer portion of typical cushion compounds is primarily NR, with some BR or SBR normally present. The carbon blacks tend to be lower in surface area, closer to carcass-black types. The oil loading in these compounds can vary greatly.

The curative package used is dependent on the cure temperature used in the particular retread process. The higher temperature cushions can use more conventional accelerators. The cure systems for the lower temperature cushions require accelerators having correspondingly lower activation temperatures to provide acceptable cure times. Typical cure temperatures range from 93 to 138°C.

Table 2 is an example of a cushion and repair gum formulation from a previous *The Vanderbilt Rubber Handbook* edition⁶.

Ingredients	phr
No.1 Smoked Sheet	80.00
SBR 1506	20.00
Reogen®	2.00
Zinc Oxide	5.00
Stearic Acid	3.00
AGERITE SUPERFLEX [®] SOLID G	1.00
N550 Carbon Black	50.00
Aromatic Oil	25.00
Pine Tar	3.00
AMAX®	1.35
UNADS®	0.15
Crystex Sulfur	2.00
Total	192.50
Density, gm/cm ³	1.11
Mooney Scorch @ 127°C	35
Minutes to 5 pt. rise	25
ODR @ 138°C	
ť 80 (min)	23
Original Physical Properties, Press Cured 30 min. @ 138°C	
Hardness, Shore A	60
300% Modulus, MPa	7.24
Tensile, MPa	23.44
Elongation, %	625

Table 2: Cushion and Repair Gum Compound

#### The Future of Retreading

In the trucking industry retreading is an integral part of a good tire management program. The use of retreading is expected to continue to grow, particularly globally, with the increase in radialization in commercial applications and improvement of transportation infrastructures. Fleet consolidation is expected to result in improvements in tire maintenance and tire management programs, and should increase the use of retreaded tires.

In addition, the improvements in the durability of casings, the use of smaller diameter rim sizes and the use of the super-single tires will provide additional opportunities for the retreading industry. There will also be continuing advantages found in retreading as environmental mandates make recycling more attractive or possibly mandatory.

Another area of opportunity in the retreading industry lies in the use of novel materials. Although not in widespread commercial use at this time, there continue to be reports of the use of unconventional materials in retreading.

There are some technologies that allow the manufacture and retreading of tires with urethane treads⁷. In the recent past the use of one- or two- part urethane adhesives have shown application as a precured tread-to-casing adhesive. An adhesive based on a commercially available off-the-road tire repair system was

successfully used to perform precured tire retreading⁸. The use of a one-part heat curable urethane adhesive was also used in this application⁹.

As improvements continue to be made in the areas of nontraditional retread materials the expectation is to see their eventual implementation in retread production.

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### EXTRUDED RUBBER PRODUCTS

### by Ralph A. Annicelli*

Uniroyal Chemical *Retired

### Introduction

Rubber is a common material used in virtually every industrial application. Although different rubber processing methods exist, extrusion remains a popular choice for many manufacturers. The production of extruded rubber products is one of the most economically important procedures in the rubber industry. Extrusion is the process of forcing a rubber mass through a die to form a long, continuous article of constant cross-sectional shape and size. The simplest example is a solid rod, which can be square or any other shape. Extruded articles are often called profiles or extrudates. They can have one or more continuous internal passages or hollow areas. The simplest of these is round tubing.

Extruded rubber profiles are used in a wide variety of industries, including aerospace, automotive, lighting, appliance, electronics, construction and medical industries. Many common articles which are seen every day are extruded. The seals on refrigerator and dishwasher doors are extruded. The insulation and jacket on ignition wires or cords on electrical tools are extruded. The seals around the hood, trunk and doors of your car are extruded.

#### EXTRUDERS

An extruder is basically a power driven screw contained in a cylinder, called the barrel. Rubber is fed in at one end and transferred through the barrel by the rotating screw. As the material enters the barrel, it is softened by heating and then pressurized through the rotation of the screw. The pressure pushes the rubber through the die, located at the discharge end of the extruder. The rubber then emerges from the extruder in a profile resembling the die shape. After being extruded, the material is vulcanized using various methods that include autoclave, salt bath, hot air, and microwave curing. At the end of the line a cutter or coiling does the final handling of the product. This is known as a continuous process.

Since the development of single screw extruders in the late 1800's these machines have become increasingly sophisticated. Much of this has been due to economic forces, which have motivated changes to improve efficiency and quality. To illustrate this, the following is a description of two general classes of extruders, curing systems, and finishing methods.

### **Hot-Feed Extruders**

Initially, extruders were fed with rubber that was pre-warmed and plasticized on two-roll mills. In this process, called hot-feed extrusion, the extruder merely conveyed and forced the rubber through the die. These extruders were short barreled and had provisions for water-cooling the screw, barrel, and sometimes part of the head. Provisions for heating the die plate were common as this improved the smoothness of the extrudate. As is implied, very little additional work or energy was put into the rubber in this type of extruder.

## **Cold-Feed Extruders**

In recent years major modifications in extruder and screw design have made it possible to feed room temperature rubber compound strips directly to the extruder without the pre-milling warm-up operation. Figure 1 shows a single screw cold-feed extruder prior to a microwave curing line.



Figure 1: Single Screw Cold-Feed Extruder

These machines have long barrels and screws. The screws are of more complex design, and the machines are equipped to provide cooling or heating. Cold-feed extruders are designed to incorporate the function of feeding, conveying, pressurizing, warming, plasticizing, and finally forming. All of these are necessary to obtain an extrudate with thermal and mechanical homogeneity. Cooling and heating controls are used to maintain uniform plasticity and flow through the head and die. Several substantial advantages of this type of extruder are: increased throughput, lower labor expense, improved materials scorch control, and potentially better process uniformity.

For general use, a standard rubber screw with a constant diameter root and a thread of decreasing pitch is preferred. With such a screw, pressure is gradually increased as the stock progresses through the extruder and as a result of the kneading action developed, entrapped air is reduced and a uniform extruded section is produced.

#### Advantages of Cold-Feed Extruders

- Labor cost savings (warm-up operation is eliminated)
- Improvement in gauge control and extrusion quality due to uniform stock temperature and viscosity
- · Cure rate can be increased with less sacrifice to scorch resistance

## METHODS OF VULCANIZATION

### Open Steam Cure

Following the extrusion process, there are various methods of conveying and curing the extrudate. Open steam (autoclave) curing has been the most common method utilized for extruded product vulcanization for many years. The extrudate may be in direct contact with the steam or the article may be wrapped with fabric tape, encased in an extruded cover or supported by soapstone in a shielded pan. Extruded shapes vulcanized in this manner are generally supported on formed trays to avoid deformation of the cross-section while being heated. This prevents the finished part from developing a permanent curvature. Product lengths are confined to the size of the trays and the length of the autoclave available. Autoclave curing produces a dense non-porous end product because the pressure resists the volatility of various components within the rubber compound. Steam curing continues to be economical and practical for many products and is used in the production of hose, wire and cable and other extruded articles such as tubing or channel stripping.

### **Continuous Vulcanization (CV) Process**

Batch autoclave vulcanization of extrudates is steadily giving way to various continuous vulcanization (CV) processes. While there are several methods of continuous vulcanization, they are alike in basic concept; that is to extrude the product directly through a curing medium. After extrusion the extrudate is continuously conveyed through several heat transfer media such as: *hot air, liquid curing media (salt batch), fluidized bed (Ballotini) or microwave.* Once cured, the extrudate can be cut or coiled and finished in continuous line operations. In addition to minimizing handling and labor cost, very fast line speeds can be obtained. These factors make for economical extruded articles when a particular item can be run for long periods without changing compounds or die profiles.

The method of heating the profile after extrusion varies, but all methods are at atmospheric pressure, except the autoclave CV process for wire and cable products and hose. The particular curing method employed may put additional requirements on compound development. The selection of polymer, filler, oil, cure system, antidegradants and the use of specialty additives or extruders all must be carefully considered.

Porosity is likely in atmospheric cures, as only the compound's viscosity offers resistance to sponging. Porosity can be due to trapped air, moisture from compound ingredients or volatile oils. Trapped air and some moisture are commonly removed with a vented vacuum extruder. In addition, it is usually good compounding practice to add 5-10 phr of calcium oxide as a desiccant.

Hydrous fillers are usually avoided; calcined clay is the preferred mineral filler. Higher viscosity, less volatile paraffinic oils or waxes are used to soften compounds. Deformation or collapse of the extrudate during cure is another potential problem. Polymers with high green strength are desirable. Reversion, the break down of polymer chains, can occur due to the high cure temperatures in excess of 200°C (400°F). Residence times are short, generally 1-2 minutes, requiring very fast cure systems. The cure system must also be adjusted to the speed at which heat will be added by the particular curing method employed.

## Liquid Cure Medium (LCM) Process

In the LCM process, the extrudate is processed through a hot liquid medium at 200 to 300°C after leaving the extruder. LCM uses a eutectic mixture of salts to heat the extrudate. The molten salt bath usually has a metal conveyor to keep the rubber compound submerged. To provide uniform cure the extrusion is either submerged in, or showered with molten salts, or nitrogen pressurized salt. This method provides good heat transfer to the rubber and is advantageous for low compression set articles using peroxide cures. However, there is appreciable loss of heat-transfer salts; the profile must be post-cleaned and the salt rinse disposed. These factors can have a major impact on operational cost.

## Fluidized Beds (Ballotini)

Fluidized beds improve heat transfer vs. hot air alone. High velocity hot air is pumped upward in the curing trough to fluidize small glass beads (Ballotini). Beads adhering to the profile are normally removed by spray or brushes upon exit from the fluid bed. However, complex profiles can make complete removal difficult.

## **Hot Air Vulcanization Lines**

The continuous hot air oven is the most common method used in the industry due to its early origin, simplicity, and versatility. Profile extrusion, both cellular and dense, or in combination, are most commonly vulcanized continuously under atmospheric pressure. The continuous oven is usually fabricated in sections and fitted with a full length conveyor belt to transport the product. Hot air methods are particularly attractive for sponge products, where high production speeds can readily be achieved. Many dense products are also being produced by the same method, particularly those of smaller cross-sectional area. The process is simple, and the product emerges with a clean surface. There have been a number of enhancements made available in hot air vulcanization to increase productivity and efficiency, such as the introduction of high velocity air propulsion, incorporation of direct infrared heating techniques, and the use of microwave energy. Finishing operations may include: cutting to specific length, butt splice vulcanizing to form gaskets, notching, marking and other varied operations. A disadvantage of hot air vulcanization lines is flat spotting and contact surface marking caused by the profile lying on the conveyor belt.

## Microwave Vulcanization

The methods of vulcanization covered above depend on heat transfer from an

external source. Microwave curing, however, is based on the rapid heating of a dielectric mass, in this case the rubber from within the mass. Microwave heating is one of the newest methods for continuous vulcanization. The microwave method is very effective in heating an extrudate quickly and uniformly, thus making this system very energy efficient. Quite often microwave units are combined with LCM or hot air units to make up a CV system. The microwave unit is used first to heat the extrudate rapidly to curing temperature. The material then passes through one of the other CV systems for completion of cure. Advantages are: faster curing of larger extrusions, improvements in process control, and product uniformity. Figure 2 shows a typical microwave curing line downstream from the extruding operation.



Figure 2: Typical Microwave Curing Line

A requirement for using this method of vulcanization is that the elastomer and/or the compound be receptive to microwave energy. The most receptive elastomers are those that are chemically polar, so that the molecule may oscillate at high frequencies in response to the fluctuating microwave field, resulting in rapid heat build-up within the compound. Polar elastomers such as Neoprene and nitrile rubber will usually heat very fast in the microwave unit. Non-polar elastomers can be utilized in microwave units by incorporating microwave receptive ingredients into the compounds of these elastomers. Generally compounds containing 20-40 percent volume carbon black are sufficiently responsive to microwave energy. Microwave vulcanization is one of the cleanest forms of continuous vulcanization, and as a result, is used to vulcanize many dense and sponge profiles utilized in the automotive industry, and also for tubing and sponge insulation. With the increased emphasis on improved physical properties, greater productivity, decreased scrap rates and the elimination of environmental related problems, microwave curing appears to be the most popular choice in the future for continuous curing of extruded rubber products.

## COMPOUNDING FOR EXTRUSION

Compounding for extruded rubber products involves the balancing of many factors. The end use is the dominant criteria in compound design. Other factors include raw material cost and availability, product specifications and ease of processing through manufacturing operations.

The rubber chemist must understand the product application and specification requirements for the design of the compound. With this awareness, properties can be optimized for the criteria discussed. Selecting the compounding ingredients best suited for specific service conditions is critical. The base polymer, type and amount of fillers, antidegradants, processing aids, and curatives must be practical, readily obtainable and of consistent quality.

## Common polymers used in rubber extrusion include:

- natural rubber (NR)
- styrene-butadiene rubber (SBR)
- ethylene-propylene terpolymer rubber (EPDM)
- polychloroprene (CR)
- chlorosulfonated polyethylene (CSM)
- acrylonitrile-butadiene rubber (NBR)
- silicone (MQ)
- fluoroelastomer (FKM)

Material costs must balance with the processing characteristics and end product properties of the compound. For example, high cost accelerators can be employed if cure times are significantly shortened. Likewise, expensive polymers can be justified if the product's service environment has temperature or chemical extremes. The rubber chemist must keep in mind that the formula must process with a minimum of problems through the various plant operations: mixing, extruding, curing and finishing.

# Factors Affecting Extrudate Quality

For optimum product quality, the compound and process must be tuned to produce a smooth, uniform extrudate. In this way, high quality extruded goods with close dimensional tolerances will be produced. Factors that affect extrudate uniformity are both material and machine related. Generally, raw materials that produce low swell of the extrudate as it leaves the die (die swell) improve extrusion uniformity. Adequate mixing of the compound is also essential for uniformity and quality. Barrel, screw, head and die temperatures must be stable, as must screw speed and take away conveyor conditions.

### **Extrusion Compounds Examples**

The following is a series of examples of extrusion compounds for a number of product applications. Six different polymer systems, in several durometer ranges, are represented.

ASTM D 2000	AA 515*	AA 725*
Ingredients	phr	phr
SMR-5	100.00	100.00
Stearic Acid	0.50	0.50
Zinc Oxide	5.00	5.00
AGERITE [®] STALITE [®] S Antioxidant	2.00	2.00
VANFRE® AP-2 Process Aid	2.00	2.00
VANPLAST [®] R Plasticizer	5.00	5.00
Circo Light Oil	8.00	_
Neophax A	30.00	15.00
N550 FEF Carbon Black	30.00	80.00
McNAMEE [®] CLAY Filler	40.00	_
Sulfur	2.75	2.75
AMAX [®] Accelerator	1.00	1.00
METHYL TUADS [®] Accelerator	0.20	0.20
Totals	226.45	213.45
Mooney Scorch @ 121°C		
Minimum Viscosity	15	28
Minutes to 5 pt. rise	10	9
Original Physicals, Press Cured 10 min. @ 153°C		
Hardness, Shore A	50	68
300% Modulus, MPa	5.4	16.6
Tensile, MPa	13.8	18.8
Elongation, %	570	370
Tear Die A, kN/m	21.1	28.2
Original Physicals, Press Cured 5 min. @ 160°C		
Hardness, Shore A	50	67
300% Modulus, MPa	5.4	16.1
Tensile Strength, MPa	14.5	18.7
Elongation, %	530	380
Tear Die A, kN/m	56.3	33.4
Compression Set, 22 hrs. @ 70°C		
% Set	38	22

## **Natural Rubber Extrusion Compounds**

* Data from R.T. Vanderbilt Company, Inc. Laboratories

SBR Extrusion	Compounds
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ASTM D 2000	AA 515*	AA 720*
Ingredients	phr	phr
SBR 1502	100.0	100.0
Stearic Acid	2.0	2.0
Zinc Oxide	5.0	5.0
AGERITE STALITE S Antioxidant	2.0	2.0
VANFRE AP-2 Process Aid	2.0	2.0
VANPLAST PL Plasticizer	5.0	5.0
Circo Light Oil	15.0	_
Neophax A	25.0	15.0
N990 Carbon Black	40.0	50.0
N550 Carbon Black	35.0	60.0
Sulfur	2.0	2.0
MORFAX [®] Accelerator	1.4	1.4
METHYL CUMATE® Accelerator	0.2	_
Totals	234.6	244.4
Mooney Scorch @ 121°C		
Plasticity, M	37	80
Minutes to 5 pt. rise	9	13
Original Physicals, Press Cured 10 min. @ 153°C		
Hardness, Shore A	52	71
300% Modulus, MPa	7.4	_
Tensile, MPa	11.3	17.1
Elongation, %	500	200
Tear Die A, kN/m	15.8	18.5
Original Physicals, Press Cured 5 min. @ 160°C		
Hardness, Shore A	50	70
300% Modulus, MPa	6.4	—
Tensile, MPa	10.5	17.3
Elongation, %	510	220
Tear Die A, kN/m	13.2	17.6
Compression Set, 22 hrs. @ 70°C		
% Set	31	16

* Data from R.T. Vanderbilt Company, Inc. Laboratories

ASTM D 2000	BC 515*	BC 720*
Ingredients	phr	phr
Neoprene TW	100.0	100.0
Stearic Acid	1.0	1.0
Maglite [®] D	4.0	4.0
VANFRE AP-2 Process Aid	2.0	2.0
VANPLAST R Plasticizer	5.0	5.0
AGERITE STALITE S Antioxidant	2.0	2.0
Neophax A	35.0	15.0
Sundex [®] 790	10.0	—
N550 Carbon Black	20.0	30.0
N990 Carbon Black	40.0	55.0
Zinc Oxide	5.0	5.0
THIATE [®] U Accelerator	1.5	1.5
Totals	225.5	220.5
Mooney Scorch @ 121°C		
Scorch, t5, minutes	9	6
Plasticity, ML	37	61
Original Physicals, Press Cured 30 min. @ 153°C		
Hardness, Shore A	51	68
200% Modulus, MPa	4.3	13.3
Tensile Strength, MPa	11.7	16.5
Elongation, &	400	250
Tear Die A, kN/m	10.6	13.2
Original Physicals, Press Cured 5 min. @ 171°C		
Hardness, Shore A	53	69
200% Modulus, MPa	5.4	13.8
Tensile Strength, MPa	13	16.5
Elongation, %	370	240
Tear Die A, kN/m	6.2	12.3
Compression Set, 22 hrs. @ 70°C		
% Set	34	16

# Neoprene Extrusion Compounds

* Data from R.T. Vanderbilt Company, Inc. Laboratories

Ingredients	Dense*	Sponge*
	pnr	pnr
Royalene® 547	100.0	100.0
N660 Carbon Black	90.0	90.0
N550 Carbon Black	20.0	20.0
N990 Carbon Black	60.0	60.0
Brown Factice	15.0	15.0
Zinc Oxide	5.0	5.0
Stearic Acid	1.0	1.0
TE-28, G-9 Process Aid	2.0	2.0
Sundex 2280 Paraffinic Oil	110.0	110.0
ALTAX [®] (MBTS) Accelerator	1.3	1.3
ETHYL TELLURAC [®] Accelerator	0.5	0.5
BUTYL ZIMATE [®] Accelerator	1.0	1.0
METHYL ZIMATE [®] Accelerator	0.5	0.5
SULFADS [®] Accelerator	1.2	1.2
Sulfur	1.8	1.8
Celogen [®] OT	_	2.0
Celogen 754 A	_	4.0
Totals	409.3	415.3
Mooney Viscosity $M_L$ 1 + 4 @ 100°C	40	40
Mooney Scorch @ 125°C		
Minutes to 3 pt. rise	2.7	2.7
Microwave/Hot Air Cured 3 min. @ 205°C		
Expanded Density g/cm ³ (lbs/ft ³ )	_	0.58
Original Devision Brass Curred 15 min @ 175%		0.00
Hardness Shore A	70	_
Tensile MPa	95	_
Elongation %	350	_
Tear Die C. kN/m	27.3	_
Compression Set 22 hrs. @ 70%		
% Set	17.1	_
Compression Set, 168 hrs. @ 80°C	44	_
Garvey Die Extrusion	very smooth	very smooth

## Dual Durometer EPDM Automotive Extrusion Compounds For Microwave/ Hot Air Curing

* Data Courtesy of Lion Copolymer LLC

Ingredients	phr
Royalene 694	175.0
N660 Carbon Black	65.0
N550 Carbon Black	25.0
Whiting	40.0
Mistron Vapor [®] Talc	30.0
Sundex 2280 Paraffinic Oil	80.0
Zinc Oxide	5.0
Stearic Acid	1.0
TE-28 Process Aid	15.0
Brown Factice	2.0
Celogen AZ-199	9.0
Celogen AZ-130	3.0
ALTAX (MBTS) Accelerator	1.5
SULFADS Accelerator	1.2
BUTYL ZIMATE Accelerator	1.0
ETHYL TELLURAC Accelerator	0.7
Sulfur	1.8
Total	456.2
Mooney Viscosity $M_L$ 1 + 4 @ 100°C	32
Mooney Scorch @ 125°C	
Minutes to 5 pt. rise	3.5
Microwave/Hot Air Cured 3 min. @ 205°C	
Expanded Density, g/cm ³	0.31

# Super-soft Closed Cell EPDM Extruded Sponge Compound for Microwave/Hot Air Curing*

* Data Courtesy of Lion Copolymer LLC

# **NBR Extrusion Compound***

Ingredients	phr
Paracril [®] BLT M80	100.0
N550 Carbon Black	60.0
Calcium Oxide Dispersion, 80%	8.0
Zinc Oxide	5.0
Stearic Acid	1.0
Paraplex G54	10.0
DOS	10.0
A-C [®] Polyethylene 617A	1.0
VANOX [®] CDPA Antioxidant	2.0
Spider Sulfur	1.0
ALIAX (MBIS) Accelerator	1.0
	1.0
METHYL ZIMATE Accelerator	1.5
Total	201.5
Mooney Viscosity $M_L$ 1 + 4 @ 100°C	56
Mooney Scorch @ 121°C	
Minutes to 3 pt. rise	4.0
Original Physicals	
Hardness, Shore A	61
Tensile, MPa	14.5
Elongation, %	370
Tear Die C, ppi	221
Physical Properties After Heat Aging in Air 70 hrs. @ 100°C	
Hardness, Pts Change	5
Tensile, % Change	-7
Elongation, % Change	-35
Compression Set, Method B, 70 hrs. @ 100°C	
% Set	24
Physical Properties After Aging in IRM 903 Oil, 70 hrs. @ 100°C	
Volume, % Change	12.1
Hardness, Pts. Change	-10
Brittle Point, °C	-36

* Data provided courtesy of Para Tec Elastomers LLC
| ASTM D 2000                                                                | HK 715 |
|----------------------------------------------------------------------------|--------|
| Ingredients                                                                | phr    |
| Viton [®] E-60 C                                                  | 100.0  |
| N990 Carbon Black                                                          | 25.0   |
| Carnauba Wax                                                               | 1.0    |
| Calcium Hydroxide                                                          | 6.0    |
| Maglite D                                                                  | 1.5    |
|                                                                            | 1.5    |
| Total                                                                      | 135.0  |
| Original Physicals, Press Cured 10 min. @ 177°C, Postcured 24 hrs. @ 200°C |        |
| Hardness, Shore A                                                          | 74     |
| Tensile, MPa                                                               | 10.4   |
| Elongation, %                                                              | 190    |
| Physical Properties After Heat Aging in Air, 70 hrs. @ 280°C               |        |
| Hardness, Pts. Change                                                      | 2      |
| Tensile, % Change                                                          | -20    |
| Elongation, % Change                                                       | -8     |
| Weight, % Loss                                                             | -2     |
| Compression Set, 22 hrs. @ 200°C                                           |        |
| % Set                                                                      | 12     |
| Physical Properties After Aging in Fuel B, 70 hrs. @ 23°C                  |        |
| Hardness, Pts. Change                                                      | 2      |
| Tensile, % Change                                                          | -16    |
| Elongation, % Change                                                       | -10    |
| Volume, % Change                                                           | 2      |

## Fluoroelastomer Extrusion Compound

#### MOLDED GOODS

#### by James F. Walder

Precix New Bedford, MA

"Molded goods" are an array of products where a mold is used to produce the required geometry. Among the parts produced by this technique are seals, diaphragms, weather strips, bushings, mountings, blades, and other similar parts. The mold is subjected to elevated temperature and pressure to promote the vulcanization reaction of the compound and produce the required dimensions.

#### Molds and Presses

The rubber mold, along with the molding compound, are the "heart and soul" of molded goods. Simply put, the mold provides the appropriate geometry for proper visual, dimensional, and functional characteristics.

The tooling for molded goods is usually made of steel for durability. It may be cut out of solid plates or inserted, the former being less expensive initially, but the latter having more flexibility.

The choice of steel ranges from free machining types to hardened varieties. Cost, durability, and part dimensions are factors to be considered, along with the type of material to be molded. Stainless steel or chrome plating may be necessary for corrosive materials or to control sticking.

The part to be molded strongly influences the mold design. Items such as dimensional control, air venting, demolding, finishing requirements, critical areas, and the inclusion of fabric or inserts all must be considered. These items will determine the size of the tool, the number of mold plates, and the intricacy of the mold cavity.

Shrinkage of the molded part is also factored into the mold design. This is influenced by the temperature differences between the stock and mold, the polymer content of the formula, and volatile compounding additives. Shrinkages will generally range from 1.5 to 4.0 percent.

A critical aspect of mold design is the registration, or alignment, of one plate to another. In its simplest form, dowels and bushings in each corner of the mold center the mold plates. However, a more foolproof approach is the self-registering cavity (Figures 1, 2). Each cavity finds its own center, with at least one insert (top or bottom) floating independently of the mold plates. This approach is more expensive and may not be needed for less critical parts.



Figure 2: Self Registering Cavity - Closed

The press for rubber molding must exert enough clamp pressure to maintain a closed tool during curing. Presses are usually hydraulic and operate from a self-contained or central hydraulic system. The central hydraulic system usually delivers fluid at 14 MPa (2000 psi) line pressure. Clamp forces of 45 to 550 Mg (50 to 600 tons) are normally encountered.

Heating is generally accomplished via platens. The platens, in contact with the mold surface, are heated by steam, electricity, or hot oil. Each method has its own benefits and costs. In practice, the higher the temperature, the faster the cure. Uniform heating across the platen is most important for part quality.

#### **Stock Preparation**

The rubber compound, after mixing, must be preformed into a convenient shape for the subsequent molding operation. This may be accomplished through a variety of techniques, including extrusion or calendering.

In the simplest procedure, the rubber is conveniently shaped by the takeoff equipment from the mixing operation. The strip feed required for injection molding can usually be done in this manner. Labor savings are also achieved through in-line extruders or calenders.

For compression molding, a variety of shapes or sizes may be required. Strips, pads, slugs, and cylinders are all employed. Careful consideration is given to the preform shape, because dimensions, stock flow and air venting all hinge on this decision. In most cases, the cutting accuracy, after shaping, is critical for weight control.

For transfer molding, the preform is less critical, with weight accuracy much more important than shape. Again, extruders or calenders are used.

Regardless of the equipment used, the "heat history" of the unvulcanized material must be kept to a minimum. Water or air cooling is used in extrusion or calendering. A "ram" extruder is preferred if heat history is a problem.

Great care must be taken in the preforming operation to minimize air entrapment, as air pockets may show up as defects in the molded part. The use of a vented extruder can minimize air in the preform.

The preformed materials may be stored in cloth liners, trays, books or large totes. If preforms come into contact with one another, an anti-stick coating must be employed.

The optimum time from preforming to curing must be determined. This time is usually as short as possible. Occasionally, extra time to increase viscosity is necessary to minimize air entrapment when molding.

#### Selection of Molding Process

The selection of the molding process must take into account a variety of factors. Among these are tolerance control, flash restrictions, part complexity, flow characteristics, productivity, and cost. No single process can optimally fit all parts. The most common molding techniques are compression, transfer, and injection.

Several "hybrid" processes have also been developed to combine the advantages of several molding techniques. Among these options are injection-compression and injection-transfer.

Table 1 summarizes the major advantages and disadvantages of compression, transfer, and injection molding.

Advantages	Disadvantages
Compression Usually the least expensive mold Minimal waste Short change times when artificial flash is used to remove parts Large cavity density possible	<ul> <li>Longest cure time</li> <li>Most finishing operations</li> <li>Least tolerance control</li> </ul>
Transfer Molding <ul> <li>Better tolerance control</li> <li>Mold closed before rubber is introduced</li> <li>Best for parts with inserts</li> <li>Shorter cure times</li> </ul>	<ul> <li>More waste</li> <li>Moderate finishing</li> <li>More expensive mold</li> </ul>
Injection Molding • Best tolerance control • Mold closed before rubber is introduced • High potential for full automation • Lowest rubber prepping cost • Shortest cure times	<ul> <li>Most expensive tool</li> <li>Most waste if cold runner system is not used</li> </ul>

 Table 1: Selection of Molding Process

#### **Compression Molding**

Compression molding is the simplest and most widely used molding method. As the name indicates, a piece of preformed material is placed directly in the mold cavity and compressed under hydraulic clamp pressure (Figures 3, 4). At the completion of the required cure cycle, the hydraulic clamp is released and the part is stripped from the mold.

Compression molding is usually done in hydraulically clamped presses acting through a ram. Presses are either slab-sided or have posts in each corner. Platens are attached to the top and bottom bolsters of the press and provide the vulcanization temperatures required. Occasionally, more than one mold may be run in a press and more than two platens may be required.

A mold of virtually any size is possible as long as adequate clamp pressure is provided. However, the mold should not greatly exceed the ram area in order to ensure dimensional control. Required pressures vary depending on geometry and compound flow. Cavity pressures on the stock of between 10 to 48 MPa (1450 to 7000 psi) have been measured.

As the mold cavities are open when the preform is introduced, compression molding usually possesses the least tolerance control and most flash. Good weight control is required at the preforming stage to minimize dimensional variation. Stock flow and air venting must also be carefully addressed in compression molding. Besides the preform shape, careful selection of the press closing rate and the bump cycle are required. The press bumping is a short pressure release after initial clamping to "burp" the mold.



Figure 3: Compression Mold - Open



Figure 4: Compression Mold - Closed

As little shear is evident in the compression process, temperatures are obtained only by platen contact with the mold. Occasionally, preheating of the rubber is used to speed the curing process.

Large tools with high cavity density, low mold cost and low waste frequently offset the higher finishing cost and longer cure times of this process. The dimensional requirements of the part most often determine whether or not to use compression methods.

#### **Transfer Molding**

Transfer molding is a precision molding technique. The preformed stock flows from a transfer pot, usually above the mold cavities, to the parts below through sprues (Figures 5, 6). The transfer ram and pot can either be part of the mold or the press.



Figure 5: Transfer Mold - Open



Figure 6: Transfer Mold - Closed

When incorporated in the press, the transfer hardware is usually referred to as a "bottomless pot".

During the curing cycle of a transfer mold, both the parts and the residual material left in the pot vulcanize. This transfer pad is usually considered to be waste and is discarded. In order to minimize waste, the transfer pot may be insulated. After curing is complete, the mold is removed from the press to strip the parts. The transfer pad may be removed as the first operation or the last. This can affect whether the parts remain on the top or bottom of the mold cavity for stripping.

Many of the design parameters governing compression molding also apply to transfer molding. However, two major differences must be considered. First, because the stock flows further in transfer molding, lower viscosity compounds and higher pressures are required. Second, the transfer pot must always be bigger than the projected area of the cavities below. If not, the mold clamp is exceeded by the hydraulic pressure of the unvulcanized rubber parts. The mold plates would then be forced open at the parting line.

Since all transfer molding is done with a closed cavity, less finishing is required. More precision is also obtained. However, transfer molding is a low shear process and little self-heating of the compound takes place. Cure times are therefore not much shorter than compression molding.

#### **Injection Molding**

Injection molding is a versatile and high precision process. It is often the least expensive method of production for large volume products. However, the press and molds are the most expensive of the three molding processes.

The injection process employs a closed mold, with the stock delivered under high shear from an injection barrel (Figures 7, 8). Several advantages result from this high shear. First, the rubber is at elevated temperature as it enters the cavity, allowing for short cure times. This is particularly advantageous for thick cross-section parts. Second, the viscosity of the rubber compound is lowered, allowing for considerable thermoplastic flow.

Injection presses can be vertical or horizontal. They can use either a ram or a screw to masticate the uncured compound and deliver it to the mold. The reciprocating screw masticates stock better and maintains even heat, but injection-shot sizes are limited. The ram can deliver large quantities of stock to the mold, frequently at the expense of uniform mastication and heat. Hybrid processes with a screw/ram combination are therefore used. The screw is used for stock mastication, while the ram is used for injection.

The uncured stock is delivered through an injection nozzle into a sprue bushing (Figures 7, 8). Rubber flows through the runner system into the parts via sprues. It is most important that the flow of stock and the heat history of the compound be as uniform as possible. Symmetrical or "balanced" runner systems are therefore employed.



Figure 7: Injection Mold - Before Shot



Figure 8: Injection Mold - Filled

As the mold is closed and the rubber heated during injection, tight tolerance control is achieved with minimal flash. If finishing is required, a bulk cryogenic tumbling technique is usually adequate.

Automation possibilities are numerous in injection molding. For example, a single injection system can be set up to "shoot" several molds, either by the nozzle traversing to different locations, or by molds rotating to a fixed injection nozzle. Two shuttling molds can also be used with one injection unit. In this case, one mold is stripped while the second mold is curing. Upon completion of the curing cycle, the empty mold then shuttles to the injection station while the filled mold is ready for the demolding operation.

Other likely areas to automate are part removal and sprue capture. Plates containing cavities may be rotated out of the press to be mechanically ejected. Automatic brushing of cavity-containing plates is also done. Sprue waste can be captured by rubber flow through special porous cloth. The rubber flow is not impeded, and the cloth material containing the sprues is automatically indexed and discarded.

The versatility of injection molding lends itself to composite and dual material parts. Mold plates or injection nozzles can be shuttled, allowing multi-component

moldings. These advanced techniques facilitate cost reduction and product throughput.

New materials have been developed that utilize the advantages of injection molding. Silicone rubber is available as a liquid (LSR), and can be molded by Liquid Injection Molding (LIM). Very fast cure times are achieved.

A disadvantage of injection molding is the large amount of waste material generated through the runner system. "Cold runner systems" have been designed to address this deficiency (Figure 9). With this approach, the runner system is insulated from the mold and does not cure; the amount of waste is limited to a small runner and sprue.



Figure 9: Cold Runner Schematic (injection)

On balance, injection molding has many advantages. However, tooling for this process is more expensive, as high precision, hardened tools are often required for the high volumes encountered.

### Finishing

Regardless of the molding process chosen, some excess rubber, or flash, must usually be removed from the part. With transfer or injection molding, the amount of flash is minimal because the cavity is closed before uncured stock is introduced. Compression molding presents the most flash to be removed. Occasionally, "artificial" flash is purposely designed into a compression tool to assist part removal.

The simplest method is to remove flash manually. "Tear trimming", usually done by the press operator, may be designed into the mold. In this case, a bead of rubber is located 0.25 to 0.75 mm (0.01 to 0.03 inch) from the cavity's edge, and is simply torn away. Other manual methods include scissor trimming, sanding and buffing.

Simple mechanical devices may also aid in the finishing of molded goods. Die or knife trims are frequently used. In other cases, parts are tumbled with a media of steel or plastic. The tumbling of parts is conducted in a cold environment, provided by liquid nitrogen or carbon dioxide. The thin flash is frozen and broken off by the media and/or the tumbling action.

In the final analysis, the application will dictate the degree of finishing required. For less critical parts, the "as molded" condition may be acceptable.

### Thermoplastics

This chapter on molded goods applies to the traditional thermosetting materials. However, thermoplastic elastomers have displaced thermosets in some traditional applications. This is especially true in lower temperature environments.

The molding techniques and processing of thermoplastics differ from the above discussion. Essentially, the materials flow with applied heat and shear, and "set" when cooled. Injection molding is used for molded goods based on thermoplastics.

### by George Burrowes

Veyance Technologies, Inc. Fairlawn, OH

Around 1500, Leonardo da Vinci is believed to have sketched the first "drive" to transmit power from one location to another. Leather flat belt drives evolved in England throughout the early 19th century but there were problems maintaining belt tensions, keeping the belts on badly aligned drives and the space requirements for the drives were excessive. The first use of multiple-spliced rope drives wedged in deep grooves was recorded in 1856 in Belfast, Northern Ireland. The next evolutionary step, in the 1890s, was the plying up and cutting of leather and fabric into "V" shaped belts to run in similarly shaped pulley grooves.

The embryonic automobile industry had been following the same trends as the industrial drives, with spliced leather flat belts being used on two-pulley fan drives to cool the engines. However, by 1916 there were engines of over 100 hp which required larger cooling fans. In addition, the new electric horns, lights and starters meant that a new accessory, the generator, had to be added to the fan belt. To meet these demands, the rubber industry developed a molded rubber V-belt with cotton cord fabric for strength and a cover of rubberized, woven cotton fabric. The rubberizing of the fabric (with natural rubber based materials) increased the coefficient of friction for improved power transmission. The V-shape provided the added advantage of increasing the forces against the sheaves because of the wedging action. In 1922 SAE adopted a recommended practice for fan belt systems that included V-belts; by 1937 flat belts had been dropped from this standard.

Power transmission belts are used today in a wide variety of automotive, industrial, agricultural and domestic applications when power needs to be transmitted from a driving pulley on the power source to one or more driven parts of the engine/equipment. These belts may be broadly classified into two types, either "Synchronous" for drives that require synchronization or timing (to be discussed later) or "Non-Synchronous" where there is no synchronization requirement for the drive.

## V-Belts

Examples:

- Fabric-covered and raw edge V-belts (Figures 1, 2). The inner surface or base of the V-belt is sometimes cogged (notched) to increase its flexibility around small pulleys and increase airflow for cooler operation.
- Variable speed belts used when precise continuous control of pulley speed ratios is required.
- Joined V-belts, in which belts are banded side by side in a single unit to prevent turnover and reduce vibration.

- Double-V (Hexagonal) back-to-back V-belts that can transfer power from either side.
- V-ribbed belts (Figures 3, 4, 5).

V-Belts are made up of several components (Figures 1, 2) as follows:

- 1. A rubber base material, usually containing short fibers (in certain belts, fabric plies are also built into the compression area/cushion).
- 2. A load carrying tensile member.
- Conventional fabric-covered belts are surrounded by a rubberized woven cotton/synthetic envelope, one or more plies, for protection against wear and environmental hazards and control of coefficient of friction.
- 4. Raw edge belts do not have an envelope, but include a rubberized cotton/ synthetic backing fabric.

The various belt components are discussed in more detail below.



Figure 1: Components of a Fabric Covered V-Belt



Figure 2: Components of a Raw Edge V-Belt

Though Natural Rubber was the early elastomer choice, due to shortages of this commodity during World War II V-belts from the mid-1940s onwards were being produced from materials based on synthetic rubber, mainly SBR. Today, general purpose elastomers like SBR and Polybutadiene are used in cost sensitive belt applications. Polychloroprene, mainly the sulfur modified grades, has also proved to be a good base elastomer for most V-belts because of its unique combination of properties: resistance to flex fatigue, wear and oil, its tear strength and adhesion capability to other belt components.

Short fibers are added as a compounding ingredient to the rubber under the belt cord layer in most V-belts. To be effective, the fibers need to be very evenly dispersed and highly oriented in the elastomer matrix to maximize their anisotropic reinforcement capability. This allows the development of a high modulus in the fiber orientation (belt lateral) direction, enabling the belt to resist compressive sidewall forces and ensuring that the cords remain in a horizontal plane with the load evenly distributed over all of them. A low modulus is also developed in the fiber perpendicular (belt circumferential) direction, enabling the belt to be flexible in that direction. Additionally, fibers will modify the frictional and noise behavior of raw edge belts. Commonly used fibers are cotton, polyester, aramid and unregenerated cellulose. Some fibers have a rubber adhesive treatment. Lengths are typically 1-10 mm; compound fiber loads may vary up to about 20% by weight. Fibrillated para-aramid fiber ("pulp"), which must be used in elastomer masterbatch form, finds application in belts requiring increased lateral stiffness for high load carrying capability.

During the 1940s, rayon, with its higher modulus and lower stretch, replaced cotton as the tensile cord of choice for V-belts. The introduction of polyester cord in the 1950s offered further improvement in reducing belt stretch. Today, polyester, offering the best price/strength ratio of all reinforcing materials, has become the dominant material for tension carrying cords used in V-belts. Aramid cords, because of their high dimensional stability, very high modulus and low growth are used in some heavy-duty belts, e.g., variable speed belts. Low modulus/high twist polyamide cords can impart some "elastic" character to belts, which is desirable in washing machine and dryer applications. Steel cords find only limited use, mainly in special V-belts for high temperature applications.

For high performance V-belts, the following properties are required of the polyester cord:

- · resistance to fatigue
- · adhesion to the rubber components
- high modulus
- minimized heat shrinkage and heat shrinkage forces
- sufficient tack for the build process.

Adhesion to the elastomer matrix is obtained by dipping the cord in a resorcinolformaldehyde latex (RFL) dip with vinylpyridine or an elastomer latex, usually polychloroprene. The resulting modulus, creep and heat shrinkage force, all depend on the tension applied to the cord during the heat treatment stage in the process, as well as the cure time and temperature used in the treating unit. For raw edge belts, it is additionally required that the cords be stiff to prevent the fraying of filaments during the belt cutting operation. This is achieved by including a predip, often based on a diisocyanate prepolymer in solvent, in the treating process. A rubber cement coating is sometimes applied over the RFL layer to improve cord tack and prevent dip deterioration during storage. Twist level influences the cord's fatigue resistance, modulus and elongation.

### V-ribbed Belts

V-ribbed belts, which are becoming increasingly important, have been the subject of intense research activity in recent years. Basically a flat belt, they have a series of longitudinal ribs on the driving face which mate with corresponding grooves in the pulley rim, (Figures 3, 4, 5). V-ribbed belts offer the power transmission capability of a V-belt together with the flexibility of a flat belt.

Though first patented in 1952, it was the use of a single V-ribbed belt to drive all the front-end accessories in the Ford Mustang V-8 engine of the late 1970s that established these "serpentine" drives in the automotive industry. V-ribbed belts, which are relatively thin, perform better than conventional V-belts on drives with small pulleys, high speeds, reverse bends and high pulley speed ratios. This is why virtually all automobiles produced today use a V-ribbed belt ("K" cross-section) on their accessory drive. The back of the belt usually drives either a reverse-bend idler or a loaded pulley. A typical automotive front-end accessory drive is shown below (Figure 3). Three cross-sections designated "J", "L" and "M" cover a broad range of industrial v-ribbed belt applications, while a smaller section, "H", is used for some miniature drives.



Figure 3: Automotive V-ribbed Belt Drive

The V-ribbed belt must be capable of transmitting the required torque to a required efficiency throughout its useful lifetime. Failure usually occurs as a result of radial cracks in the belt ribs, often leading to loss of part of the rib. During service, tacky wear debris sometimes collects at the bottom of the belt ribs - a phenomenon known as "pilling" - which can be controlled by careful formulation of the rib rubber compound. Slip between belt and pulley, as well as misalignment of the pulleys, can each result in noise generation. This can also be controlled by the rib rubber compound and the rib design.

In recent years, vehicle manufacturers in their efforts to reduce engine noise have exerted pressure on belt suppliers to eliminate the noise produced by the belt. A notable development in response to this has been to change the design of the V-ribbed belt to cogged instead of continuous ribs. Parallel grooves are molded across the longitudinal ribs at an angle other than perpendicular, so that transverse grooves in adjacent ribs are offset from each other. This design feature, as shown in Figure 4, has been found to significantly reduce belt operating noise.



Figure 4: V-ribbed Belt – Transverse Grooves

V-ribbed belts have the following components (see Figure 5):

- 1. A tension member generally made of polyester cord; glass, aramid and polyamide "stretch" cords are used in certain specialized applications.
- 2. A rubber compound to encapsulate and adhere to the cords.
- 3. A rib compound, which may be reinforced by short fibers oriented in the belt lateral direction. In certain constructions, the ribs are covered with a facing fabric.
- 4. A backing, either a rubber compound or a rubberized fabric.



Figure 5: Components of a V-ribbed Belt

Polychloroprene, particularly the sulfur modified grades, was originally the preferred elastomer of choice for V-ribbed belt materials. Today, it continues to

be used in this type of belt, especially in industrial applications. This is because polychloroprene offers, as discussed earlier, a unique blend of properties suitable for many belt applications.

However, in recent times the automotive sector's push towards improved fuel efficiency has led to hotter operating engines and more aerodynamic vehicle styling, which has in turn restricted the size of the engine compartment and decreased air circulation. All of this has resulted in significantly increased engine compartment temperatures, now often averaging 125 to 135°C, with peaks as high as 150°C. At the same time, vehicle manufacturers' warranty periods are being extended on all components, including the belts. This has meant that polychloroprene-based materials, which possess only moderate heat resistance, are no longer suitable for much of today's automotive V-ribbed belt service.

Chlorosulfonated Polyethylene (CSM) was proposed as a base elastomer for automotive V-ribbed belts because its saturated backbone would offer improved heat and ozone resistance over polychloroprene. However, CSM-based materials tend to have high hysteresis and limited low temperature capabilities. To address these concerns, the chlorine content of conventional CSM was reduced to improve low temperature properties and hysteresis. In addition, pendant alkyl groups were introduced onto the backbone to reduce crystallinity, thereby improving flex fatigue resistance. The result is a family of Alkylated Chlorosulfonated Polyethylene (ACSM) elastomers covering a range of chlorine and alkyl content, molecular weight and molecular weight distribution, while retaining the sulfonyl chloride cure site of CSM. ACSM-based rubber materials are considered suitable candidates for automotive V-ribbed belts.

Ethylene-alpha-olefin elastomers, most notably the terpolymer ethylenepropylene-diene monomer (EPDM), used alone or in blends with other elastomers, are also candidates for automotive V-ribbed belt materials. This type of elastomer is currently the subject of intense research and development activity in the belt industry. EPDM elastomers are more economical and offer a much wider operating temperature range than polychloroprene and other elastomers. The saturated backbone provides good heat and ozone resistance. Though inherently deficient in oil resistance, carefully formulated EPDM-based materials are considered suitable for high performance automotive V-ribbed belts.

#### Synchronous Belts

As mentioned earlier, synchronous or timing belts are used on drives, both industrial and automotive, which require synchronization or timing. This type of belt differs from those discussed above in having a toothed inner surface. The teeth mesh with corresponding axial pulley grooves to give non-slip engagement, resulting in a fixed rpm ratio between the driver and driven pulleys.

The first timing belt patent, issued in 1946, was for a belt which synchronized movement in a sewing machine. Further developments occurred in other industrial applications. In 1965 Pontiac introduced its new 6-cylinder overhead cam engine with a synchronous belt drive. This marked the beginning of the major

current application for timing belts, to drive the valve-train in synchronization with the auto engine crankshaft (Figure 6). This type of belt has grown in importance with the increasing use of small-sized overhead camshaft and diesel engines in passenger cars, particularly in Europe and Japan. Since belt failure can result in serious damage, the automobile manufacturers' goal is a maintenance-free belt which lasts for the entire life of the engine.



Figure 6: Automotive Synchronous Belt Drive

Materials selection and designs for synchronous belts have been the subject of intensive research and development effort in recent years. Modern drive systems based on belts are generally quieter, more efficient, lighter weight and lubrication-free as compared to the alternative metal chains or gears. A major development has centered around obtaining a significant reduction in belt tooth engagement noise and a major improvement in power capacity through the use of a helical offset tooth pattern. The result resembles a "herring bone" gear, which meshes with a corresponding pulley (Figure 7).



Figure 7: Low Noise, High Power Synchronous Belt

Synchronous belts have the following components, as shown in Figure 8:

- 1. A tension member having very low growth, high modulus and high dimensional stability; most often made of helically wound fiberglass cord, though in some instances aramid and steel cords are used.
- 2. A facing fabric, usually of polyamide, adhered to the surface of the teeth, to provide wear resistance and reinforce the teeth. The fabric is woven with crimped fibers for stretchability to permit tooth formation.
- 3. A rubber compound forming the belt teeth and backing; the requirements for this compound are discussed below.



Figure 8: Components of a Synchronous Belt

Synchronous belts usually fail because of tooth root cracking. This can cause the tooth to be completely sheared off, or if still attached it cannot support the load, so that the belt becomes unable to transmit power. To obtain maximum belt life, the rubber forming the teeth needs to have high rigidity in order to minimize tooth deflection under load. Dynamic deformation must be minimized to prevent 'time lag' between pulley and belt. In addition, the tooth rubber requires good resistance to flex fatigue cracking and the ability to adhere strongly to cord and fabric. In automotive applications, these properties must be maintained over the operating temperature and rpm range of the engine. The belt may also be exposed to hot engine oil in the form of mist or drops; the materials must resist oil swelling and tooth dynamic stiffness needs to be maintained.

The original synchronous belts were made from polychloroprene-based materials since this elastomer, as previously discussed, provides a useful balance of belt properties. Polychloroprene is still used in some synchronous belts.

However, as discussed above, recent changes in automotive design resulting in significantly increased engine compartment temperatures, along with the extension of belt warranty periods, have given rise to considerable research to improve the performance of synchronous belt materials in demanding automotive applications. Polychloroprene has largely been replaced in automotive belts by more heat resistant specialty elastomers. Along with the move to the high performance base elastomers, the positive attributes of polychloroprene (adhesion capability, high tear strength, resistance to oil, ozone and flex cracking) must all be maintained or exceeded by the new materials in order to meet belt performance targets. First introduced in the mid 1980s, the hydrogenated nitrile butadiene (HNBR) elastomer family has, despite relatively high cost, displaced polychloroprene as the elastomer of choice in many of today's automotive synchronous belts. Compared to polychloroprene, HNBR offers improvements in heat and oil resistance, dynamic properties and low temperature performance. In addition, HNBR-based materials are claimed to be capable of maintaining most physical and dynamic properties over a much broader temperature range than does polychloroprene.

HNBR Elastomers are made by catalytic hydrogenation of the carbon-carbon double bonds in acrylonitrile-butadiene (NBR). Resistance to heat and ozone increases with the degree of hydrogenation; partially unsaturated grades may be cured using sulfur-based systems, while those approaching full saturation require peroxides. The oil resistance of HNBR elastomers increases with the acrylonitrile content. Sulfur/thiuram-cured HNBR has become standard for most automotive synchronous belt tooth compounds.

A new generation of enhanced performance belt materials has been obtained by utilizing the greater heat resistance of the more saturated HNBR grades in conjunction with boosting the reinforcement (load carrying capability). The preferred means of increasing HNBR elastomer reinforcement is by the use of resin coagents, e.g., functionalized acrylate systems, selected because of their proven reinforcing capability in other elastomers. One approach to obtaining this reinforcement has been the addition of preformed acrylate salts of zinc to the peroxide-cured HNBR compound. An alternative approach is to use HBR elastomers made by the *in situ* reaction of methacrylic acid with zinc oxide and prepared by a proprietary process. This class of elastomers must be cured using peroxide systems.

In the 1980s, Chlorosulfonated Polyethylene (CSM) elastomers were evaluated for synchronous belts because of their better heat resistance compared to polychloroprene and their cost effectiveness compared to HNBR. This direction was not widely adopted because of CSM's limitations as described earlier. The Alkylated Chlorosulfonated Polyethylene (ACSM) family of elastomers was developed to address the shortcomings of CSM. ACSM has been proposed as a more cost effective elastomer candidate than HNBR for synchronous belt materials to give improved belt life over polychloroprene. ACSM has a completely saturated backbone which gives the required heat and ozone resistance. Control of the elastomer's chlorine content, the amount and type of pendant alkyl groups and the molecular architecture is claimed to result in the necessary mechanical and dynamic performance for high performance synchronous belts.

#### Formulations

Following the Bibliography section is a series of typical transmission belting formulations for the various transmission belt designs.

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## Polychloroprene V-Ribbed Belt Formulations

(Courtesy of DuPont Performance Elastomers L.L.C.)

Ingredients	Rib (phr)	Backing (phr)	Adhesion (phr)
Neoprene GRT M2	90.00	95.0	100.0
N650 Carbon Black	30.00		35.0
N762 Carbon Black		50.0	
Hi-Sil [®] 233			15.0
Budene®		5.0	
Kevlar [®] Engineered Elastomer 1F735	13.00		
Sundex [®] 790		15.0	
SRF-1501 Resin			2.0
Cyrez [®] 963			6.0
AGERITE® STALITE®	2.00	2.0	2.0
VANOX® ZMTI	1.00		
Wingstay [®] 100AZ	1.00		
Maglite [®] D	4.00	4.0	4.0
ALIAX [®]	0.75	0.5	0.5
Stearic Acid	1.00	0.5	1.0
Zinc Oxide	5.00	5.0	5.0
Ethylene Thiourea (75% dispersion in EPDM)		0.3	170 5
Iotais	147.75	1/7.3	170.5
Mooney Viscosity, M _L 1+4 @ 100°C	67	39	80
Mooney Scorch @ 125°C			~~~~
Minimum Viscosity	23.7	15.4	36.8
Minutes to 5 pt. rise	17.8	11.2	17.8
MDR @ 160°C, 30 min. chart			
M₋ (dN•m)	2.0	1.3	3.0
M _H (dN•m)	27.0	19.3	38.7
t _s 2 (min)	2.2	2.5	1.8
ť 90 (min)	12.8	9.1	20.8
Original Physicals			
Hardness, Shore A	71	58	79
25% Modulus, MPa	4.1	0.9	2.0
50% Modulus, MPa	7.3	1.4	2.9
Tensile, MPa	18.3	17.3	20.5
Elongation, %	425	505	380
Physical Properties After Heat Aging in Air, 168 hrs.	@ 125°C	:	
Hardness, Pts. Change	13	24	14
Tensile, % Change	-13	-22	-35
Elongation, % Change	-75	-67	-90
Physical Properties After Heat Aging in Air 168 hrs.	@ 100°C		
Hardness Pts Change	1	12	8
Tensile % Change	-9	-7	-3
Flongation % Change	-19	-28	-42
Toor $Dia C \oslash Boom Tomporature (kN/m)$	62.2	40.0	56.0
Tear, Die C @ Коотт Temperature (кту/т)	03.Z	49.0	0.00
70 hrs @ 100°C %	74	63	67
24 hrs. @ -10°C, %	56	34	85

## Polychloroprene V-Ribbed Belt Formulations (continued)

DeMattia Flex (x1000) Nicked	189	225	45
MTS Dynamic Tester - 5% Deflection ± 2-1/2 % Cycle			
10 Hz (Room Temperature)			
K*, N/mm	364	201	651
Tan Delta	0.107	0.119	0.181
80 Hz (Room Temperature)			
K*, N/mm	412	230	748
Tan Delta	0.173	0.189	0.221
DSC Glass Transition Temperature $(T_g)$ °C	-37	-38	-38

## EPDM V-Ribbed Belt Formulation

(Courtesy of Lion Copolymer, LLC)

Ingredients	phr	
Royalene [®] 580-HT	100.0	
N650 Carbon Black	50.0	
Sunpar 2280	15.0	
Zinc Oxide	5.0	
VANOX CDPA	1.0	
VANOX ZMTI	1.5	
Chopped Fiber	15.0	
VANAX [®] MBM	1.0	
VAROX® DCP-40KE	8.0	
Total	196.5	
Mooney Viscosity, M⊥ (1+4) @ 100°C	85	
MDR @ 170°C		
M₋ (dN•m)	8.5	
M _H (dN•m)	56.6	
ts2 (min)	0.9	
ť 90 (min)	7.8	
Original Physicals, Pressed Cured 15 min. @ 170 C		
Hardness, Shore A	74	
100% Modulus, MPa	4.6	
Tensile, MPa	10.7	
Elongation, %	265	
Uncured Green Strength		
25% Modulus, MPa	0.9	
50% Modulus, MPa	1.2	
Tensile, MPa	1.5	
Elongation, %	107	
Temperature Retraction, °C		
TR-10	-48	
TR-30	-38	
TR-50	-30	
TR–70	-20	

## ACSM V-Ribbed Belt - Rib Formulation

Ingredients	phr	phr
Acsium [®] HPR-6367	75.0	75.0
Hypalon [®] 6525	25.0	25.0
N762 Carbon Black	40.0	40.0
Polyester Flock	6.0	6.0
Kevlar Pulp	4.0	4.0
A-C [®] 617A Polyethylene	3.0	3.0
Paraffin Wax	2.0	2.0
TOTM (Trioctyl Trimellitate)	4.0	4.0
Sundex 790	4.0	4.0
Maglite D	4.0	4.0
PE-200 (Pentaerythritol)	3.0	3.0
ALTAX	1.0	0.5
VANAX MBM	1.0	
Sulfur	0.5	
METHYL TUADS®	1.0	
SULFADS®		2.0
Totals	173.5	172.5
Mooney Viscosity, M _L 1+4 @ 100°C	55	55
Original Physicals, Pressed Cured 25 min. @ 1	60°C	
Hardness, Shore A	78	78
100% Modulus, MPa	6.2	6.2
Tensile, MPa	17.2	17.2
Elongation, %	275	275

#### (Courtesy of Dupont Performance Elastomers L.L.C.)

## **ACSM V-Ribbed Belt - Cushion Gum Formulation**

(Courtesy of DuPont Performance Elastomers L.L.C.)

Ingredients	phr
Acsium HPR-6367*	100.0
N762 Carbon Black	40.0
DOS	8.0
VANOX NBC	2.5
Maglite D	4.0
Calcium Oxide	5.0
PER-200	3.0
Sulfur	0.5
VANAX MBM	1.0
ALTAX	1.0
Maleated Polybutadiene	10.0
Total	175.0
* If higher modulus for reduced cord per out is needed	replace part or all of the

¹ If higher modulus for reduced cord pop-out is needed, replace part or all of the Acsium 6367 with higher Mooney Hypalon 6525.

## Polychloroprene Synchronous Belt Formulation

(Courtesy of Dupont Performance Elastomers L.L.C.)

Ingredients	phr
Neoprene GRT	100.0
Stearic Acid	1.0
Maglite D	4.0
N762 Carbon Black	50.0
A-C 617A Polyethylene	3.0
AGERITE STALITE S	3.0
Wingstay 100	1.0
Sundex 790	3.0
VANAX 552	0.7
Zinc Oxide	5.0
Total	170.7
(Mixed in OOC Banbury, upside down, discharged at 99°C, acc	elerated on cold mill)
Mooney Viscosity, ML 1+4 @ 100°C	26
Mooney Viscosity, ML 1+4 @ 121°C	20
Mooney Scorch @ 121°C	
Minimum Viscosity	10
Minutes to 8 pt. rise	20
ODR @ 160°C. 3° Arc. Microdie	
$M_{\rm H}$ (dN•m)	91.1
t _s 2 (min)	2.7
ť 90 (min)	15
Original Physicals, Press Cured 20 min. @ 160°C	
Hardness, Shore A	73
100% Modulus, MPa	4.3
300% Modulus, MPa	18.5
Tensile, MPa	20.4
Elongation, %	340

## HNBR Synchronous Belt Formulation - Sulfur Cure

(Courtesy of Zeon Chemicals L.P.)

Ingredients	phr
Zetpol [®] 2020	100.0
N774 Carbon Black	55.0
Ether/Ester Plasticizer	5.0
Zinc Oxide	5.0
Stearic Acid	0.5
AGERITE RESIN D®	1.0
CAPTAX®	1.0
METHYL TUADS	1.0
Spider Sulfur	0.5

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HNBR Synchronous Belt Formulation - Sulfur Cure (continued)		
Mooney Viscosity, ML 1+4 @ 100°C	86.2	
Mooney Scorch, 1+30 @ 125°C		
Minimum Viscosity	55.6	
Minutes to 5 pt. rise	4.3	
Minutes to 35 pt. rise	6.3	
MDR @ 160°C, 0.5° arc		
M _L (dN•m)	1.4	
M⊣ (dN•m)	16.0	
t _s 2 (min)	0.9	
ť 90 (min)	6.5	
Original Physicals, Press Cured 10 min. @ 160°C		
50% Modulus, MPa	1.9	
100% Modulus, MPa	3.0	
200% Modulus, MPa	7.2	
300% Modulus, MPa	12.1	
Tensile, MPa	24.4	
Elongation, %	548	

## HNBR Synchronous Belt Formulation - Preformed Acrylate Zinc Salt

(Courtesy of Lanxess Corporation)

Ingredients	phr	
Therban [®] C 3446	75.0	
Therban VP KA 8796 (Therban C 3467 + Zinc Diacrylate Monomers)	50.0	
VANOX CDPA	1.1	
VANOX ZMTI	0.4	
Maglite D Bar	2.0	
Zinkoxyd aktiv™	2.0	
N330 Carbon Black	30.0	
VAROX 802-40KE	7.0	
Total	167.5	
Sp. Gravity	1.145	
Mooney Viscosity, M _L 1+4 @ 100°C	71	
Mooney Scorch, @ 135°C		
Minutes to 5 pt. rise	13	
MDR @ 170°C, 1° arc		
M _L (dN•m)	1.52	
M _H (dN•m)	71	
t _s 1 (min)	0.53	
ť 50 (min)	2.34	
ť 90 (min)	9.72	
Original Physicals, Press Cured 15 min. @ 170°C		
Hardness, Shore A	76	
50% Modulus, MPa	4.6	
100% Modulus, MPa	11.2	
Tensile, MPa	31	
Elongation, %	236	

HNBR Synchronous Be	et Formulation - HINBR Reacted with Zi
	(Courtesy of Zeon Chemicals L.P.)
Ingredients	
Zetpol 2020	
Zeoforte [®] ZSC 2295	
N774 Carbon Black	
ТОТМ	
AGERITE STALITE S	
Zinc Oxide	

## HNBR Synchronous Belt Formulation - HNBR Reacted with ZnO & Methacrylic Acid

**phr** 60.00 40.00 15.00

#### 5.00 1.50 10.00 1.50 VANOX ZMTI VAROX 802-40KE 7.00 Total 140.00 Mooney Viscosity, M_L (1+4) @ 100°C 59.9 Mooney Scorch, 1+30 @ 125°C Minimum Viscosity 35.8 Minutes to 5 pt. rise 14 1 Minutes to 35 pt. rise >30 MDR @ 170°C. 0.5° arc M_L (dN•m) 0.7 M_H (dN•m) 21.4 t_s2 (min) 0.8 ť 90 min 11.2 Original Physicals, Press Cured 18 min. @ 170°C 50% Modulus, MPa 2.5 100% Modulus, MPa 5.4 200% Modulus, MPa 15.6 300% Modulus, MPa 34.5 Elongation, % 370

#### ACSM Synchronous Belt Formulation

(Courtesy of DuPont Performance Elastomers L.L.C.)

Ingredients	phr	Range
Acsium HPR-6367	100	100
N762 Carbon Black	35	35-45
DOS	0	0-5
Paraffin Wax	2	0-3
A-C Poly 617A Polyethylene	3	0-3
MgO	4	4-10
CaOH		5-8
Kevlar Pulp	0	0-5
PE-200	3	
Sulfur	1	Alternate
METHYL TUADS	1	Cure*
ALTAX	1	
VANAX MBM	1	2-3
Antox AT	0	2-3
Total	151	

* Use 5 parts CaOH in place of MgO with VANAX MBM/Antox AT

## ACSM Synchronous Belt Formulation (continued)

Mooney Viscosity, M _L 1+4 @ 100°C	60	40-60	
Mooney Scorch @ 121°C			
Minutes to 5 pt. rise	29.6	N/A	
Original Physicals, Press Cured 30 min. @ 161°C			
Hardness, Shore A	72	70 ± 5	
100% Modulus, MPa	4.0	2.8-5.5	
Tensile, MPa	20.9	12.4-20.7	
Elongation, %	584	300-600	
Physical Properties After Heat Aging in Air 70 hrs. @ 150°C			
Tensile, % Change	-20	-20 to +20	
Elongation, % Change	-50	-20 to -50	
Tear, Die C (kN/m)	38.5	26.3-40.0	
MTS Dynamic Tester, 5% Deflection ± 2-1/2 % Stroke, 20 Hz @ Room Temperature, 12M Cycles			
Tan Delta	0.117	0.1100-0.1900	

## ACSM Synchronous Belt - Adhesion Compound

(Courtesy of DuPont Performance Elastomers L.L.C.)

Ingredients	phr
Acsium HPR-6367	100.0
N762 Carbon Black	40.0
Calcium Carbonate	20.0
Aromatic Oil	20.0
DOS	10.0
Coumarone Indene Resin	10.0
Maglite D	4.0
PE-200	3.0
A-C 617A Polyethylene	2.0
Polyethylene glycol	2.0
SULFADS	2.0
VANAX MBM	1.0
Total	214.0
Mooney Viscosity, ML 1+4 @ 100°C	22.5
Mooney Scorch, @ 121°C	
Minimum Viscosity	3.5
Minutes to 5 pt. rise	12.5
Minutes to 10 pt. rise	23.0
ODR @ 160°C, 30 min. Chart	
M _L (dN•m)	3.7
M _H (dN•m)	65.6
t _s 2 (min)	2.1
ť 90 (min)	9.7
Original Physicals, Press Cured 20 min. @ 160°C	
Hardness, Shore A	65
50% Modulus, MPa	1.3
100% Modulus, MPa	2.4
Tensile, MPa	18.0
Elongation, %	430

## by Geoff Normanton

Fenner Dunlop Americas Scottsdale, GA

Heavy duty Conveyor Belts are utilized for the transportation of materials over very large distances in a number of industries including Aggregates, Cement, Timber and Coal, and also below ground in many mining applications. Light duty belting is commonly found in the packaging, airport baggage handling and food industries. These belts typically have a much lower overall gauge than their heavy duty counterparts, and utilize a variety of polymer types including conventional rubber polymers, Urethanes and PVC. Elevator belts are used in special applications were materials are moved vertically in buckets fastened to the belt by mechanical means. Flat transmission belting is not as common in today's industry but a number of applications remain important to some industries particularly in agriculture for driving hay baling machines etc.

#### **Belt Reinforcement**

Conveyor, elevator and flat-transmission belt reinforcements are made up of either textile yarn or steel cords. The yarns are typically Polyester or Polyamide fibers in general purpose applications, although Glass and Aramid fibers are used in special applications. The fibers are woven or interlaced, and the cords are laid, into *planar* structures called "plies." Although single ply carcasses are available in both textile and steel cord constructions, today's typical belting carcass consists of several individually woven textile plies "laminated" together with rubber compounds. A top and bottom cover layer of rubber is applied to provide the wear and carrying surface, and provide a means of transferring power from the conveyor drive system. Figure 1 depicts all of the belt's components.



Figure 1: Multi-ply Conveyor Belt Construction

## Belt Carcass Design

Reinforcing carcass components fulfill several basic functions within the manufactured belting product:

- · Imparts load carrying capacity
- Determines the durability & strength characteristics
- Provides dimensional characteristic, acting to disperse stress, and abuse
- Dictates the elongation and primary splicing attributes

The more prevalent carcass ply designs currently utilized in conveyor belting carcasses are characterized in the following paragraphs.

**Flat-duck** weave – the Flat-duck weave, as shown in Figure 2, is the most common, and least complicated, of the textile weave options. It is a weave having only one longitudinal/warp plane and only one transverse/weft plane. The most basic of the flat-duck weaves is the "Plain" weave. This particular fabric design is characterized by each warp yarn alternating over-and-under each successive weft yarn.



Figure 2: Flat-duck Plain Weave

**Broken Twill** or "crow's foot" weaves are designed to achieve enhanced physical properties beyond that which the traditional plain weave offers. As depicted in Figure 3, this more complex flat-duck weave version features warp yarns intersecting the weft yarns at every second or third weft position in a regular pattern, but without each warp yarn running together. As such, this particular weave design results in increased fastener holding and tear strength in the final carcass product.



Figure 3: Broken Twill Weave

**Straight-Warp** weave – this weave features parallel planes of straight-laid transverse/weft yarns, placed above and below straight-laid longitudinal/warp yarns, all locked together by a unique binder/warp yarn system. This design combines the benefits of using the desirable features of both high-modulus polyester yarns (straight-laid warps), and high-strength nylon yarns (transverse wefts, and the longitudinal binder warps). The result is a uniquely engineered weave, with inherent physical abuse resistant features.



Figure 4: Straight-laid Warp Weave

**Steel Cord** conveyor belt carcasses use individual steel cords made from high strength, carbon steel filament wires. Before final twisting (closing) into cords, these filament wires are galvanized or brass plated, primarily for corrosion resistance. This plating is also formulated for optimal rubber adhesion.

Offered only as a single-ply design, as shown in Figure 5, these steel cords can form carcasses of various tension relationships when they are subsequently sized and spaced adjacent to one another. For well over five decades, such steel cord carcasses have been used in belting applications that require high tensions and/or low stretch, levels of which typically exceed the practical limits of textile belting carcasses.



Figure 5: Steel Cord Belt

### **Conveyor Rubber Components**

Adhesion of Reinforcing Layers – is a key part of the conveyor belting manufacturing process for ensuring the steel and textile reinforcements are capable of being bonded to the rubber compounds used in the skim and cover layers. For steel this is achieved primarily through galvanization or brass plating. In textile reinforcements the fabrics are normally treated with resorcinol-formaldehyde latex (RFL) for adhesion promotion in a process that also heat sets the fabric for further processing.

*Belt Covers* – are typically identified by "RMA Grades" as a reference to "General Purpose" compounds. The RMA's <u>Flat Belt Technical Committee</u> provides a grade specification for end-users entitled "Conveyor Belt Cover Characteristics and Classifications." The properties, test values, and minimum requirements included serve as a guideline for acceptable performance for these basic of all field applications.

- RMA Grade 1:
  - Was the RMA's 1st rubber grade classification.
  - Referenced as "Cut/Gouge Resistant" rubber, with good abrasion resistance.
  - Qualified by a minimum tensile of 2500 psi, and a minimum elongation at break of 400 %.
  - The RMA guidelines suggest that the cover will consist of Natural or Synthetic rubber, or blends thereof, suitable for applications involving sharp and abrasive materials or severe loading conditions.
- RMA Grade 2:
  - Was the RMA's 2nd rubber grade classification.
  - Primarily referenced as a "Wear Resistant" rubber.
  - Qualified by minimum tensile strength of 2000 psi, and a minimum elongation at break of 400 %.
  - The RMA guidelines suggest an elastomeric composition similar to Grade I, "providing excellent service with abrasive materials", with somewhat less cut/gouge resistance than Grade I.

General purpose belt cover polymer selections include Natural, SBR and Polybutadiene rubbers. In addition to general purpose belt cover applications there are a number of industrial end-use belting applications which require specialized cover formulations to withstand exposure to heat, oil or chemicals, or are required to be fire retardant and static dissipating for operating in coal and other underground mining applications. For these applications the use of EPDM (EPM), NBR and Neoprene polymers are utilized.

## **Belt Vulcanization**

Vulcanization of the conveyor, elevator and flat-transmission belt composite products are typically done in sections of up to 20 meters in hydraulic presses, as shown in Figure 6, with one or more openings. Utilizing pressure of up to 700 psi on belting in widths up to 3.2 meters is now common within the industry.



Figure 6: Flat Belt Curing Press



Figure 7: Coiling Flat Press Vulcanized Belting

These types of belting can also be cured continuously in a rotary vulcanization machine called a Rotocure (see Figure 8). An endless steel band, wrapped around a set of heated steel drums, provides the curing pressure, and the heated drums provide the temperature for vulcanization. These machines run at much lower pressures but are useful for light weight (thinner cross-sectional) belting. The "Double Band" Rotocure has been developed to improve curing efficiency of this continuous curing process by increasing the time the belt is in contact with the pressure band.



Figure 8: Single Band Rotocure

High incline applications generally require the conveyor belt surface to be manufactured with a textured finish or molded surface impression. Special curing plates or fabric blankets are used as the molding surface for the belt top cover to provide the desired pattern for specific applications. Figure 9 shows a



molded cleated surface conveyor belt.

Figure 9: Cleated-Surface Conveyor Belt

## **Belt Formulations**

Starting-point belt formulations are provided in Table 1, 2 and 3.

Ingredients (phr)	Grade 1	Grade 2
Natural Rubber, Grade 20	80.0	
Polybutadiene Rubber		20.0
SBR 1500	20.0	80.0
Stearic Acid	1.0	1.0
Zinc Oxide	5.0	5.0
VANPLAST [®] R Process Aid	2.0	2.0
Aromatic Oil	10.0	10.0
AGERITE [®] RESIN D [®] Antioxidant	1.0	1.0
VANOX [®] 6PPD Antioznant	2.0	2.0
VANWAX [®] H Antiozonant	2.5	2.5
N220 Carbon Black	50.0	
N330 Carbon Black		50.0
METHYL TUADS [®] Accelerator	0.4	0.4
DURAX [®] (CBS) Accelerator	1.2	1.2
VANOX DPG Accelerator	0.2	0.2
Sulfur	1.5	1.5
Totals	176.8	176.8
Density, Mg/m ³	1.11	1.11
Mooney Scorch, ML @ 121°C		
Minimum Viscosity	60	60
t _s 5 (min)	18	18
Original Physical Properties, Press Cured 20 min. @ 150°C		
Hardness, Shore A	60	60
Tensile Strength, MPa	24	18
Elongation, %	500	500

Table 1: RMA Grade 1 and 2 Conveyor Belt Cover Formulations

Ingredients (phr)	Grade 1
SBR 1500	80.0
Natural Rubber	20.0
Stearic Acid	1.0
Zinc Oxide	4.0
VANPLAST R Process Aid	2.0
VANFRE® M Process Aid	7.0
Aromatic Oil	10.0
AGERITE RESIN D Antioxidant	1.5
N550 Carbon Black	20.0
N770 Carbon Black	30.0
METHYL TUADS Accelerator	0.5
DURAX (CBS) Accelerator	1.2
Sulfur	2.0
Total	179.2
Density, Mg/m ³	1.11
Mooney Scorch, ML @ 121°C	
Minimum Viscosity	35
t _s 5 (min)	2
Original Physical Properties, Press Cured 20 min. @ 150°C	
Hardness, Shore A	55
Tensile Strength, MPa	14.5
Elongation, %	600

Table 2: RMA Grade 1 Friction and Skim Formulation

## Table 3: High Temperature Resistant Flat-Transmission Belt Formulations

	Cover	Friction &
Ingredients (phr)		Skim
Vistalon [™] 2504	80.0	
Hypalon [®] 40	20.0	
Natural Rubber, Grade 5		100.0
Stearic Acid		1.0
Zinc Oxide	2.0	5.0
VANPLAST R Process Aid		2.0
Paraffinic Oil	7.0	
AGERITE RESIN D Antioxidant	1.0	1.5
Pine Tar		5.0
AGERITE HP-S Antioxidant		0.5
Ground Calcium Carbonate		15.0
N330 Carbon Black	55.0	
Sartomer SR-350 Coagent	1.5	
VAROX [®] DCP-40C Peroxide	7.0	
AMAX [®] Accelerator		1.0
Sulfur		3.0
Totals	173.5	134.0

# Table 3: High Temperature Resistant Flat-Transmission Belt Formulations (continued)

$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Density, Mg/m ³	1.11	1.05
Minimum Viscosity6330 $t_s 5$ (min)2038Original Physical Properties, Press Cured 20 min. @ 157°C40Hardness, Shore A6040300% Modulus, MPa6.91.4Tensile Strength, MPa13.815.2	Mooney Scorch, ML @ 121°C		
t _s 5 (min)         20         38           Original Physical Properties, Press Cured 20 min. @ 157°C         60         40           Hardness, Shore A         60         40           300% Modulus, MPa         6.9         1.4           Tensile Strength, MPa         13.8         15.2	Minimum Viscosity	63	30
Original Physical Properties, Press Cured 20 min. @ 157°CHardness, Shore A60300% Modulus, MPa6.91.4Tensile Strength, MPa13.8	t _s 5 (min)	20	38
Hardness, Shore A         60         40           300% Modulus, MPa         6.9         1.4           Tensile Strength, MPa         13.8         15.2	Original Physical Properties, Press Cured 20 min. @ 157°C	;	
300% Modulus, MPa         6.9         1.4           Tensile Strength, MPa         13.8         15.2	Hardness, Shore A	60	40
Tensile Strength, MPa 13.8 15.2	300% Modulus, MPa	6.9	1.4
	Tensile Strength, MPa	13.8	15.2
Elongation, % 550 750	Elongation, %	550	750
## by Kent Little

Written While Employed by Mark IV Industrial Presently Employed at Carlisle Power Transmission Springfield, MO

Hose is described in the RMA Hose Handbook as "a reinforced, flexible conduit used to move materials from one point to another or to transmit energy". Hoses are used in automotive, industrial, and consumer applications to convey a variety of substances under varied pressures and environments. Their use and construction is governed by several agencies, including UL (Underwriters Laboratories), RMA (Rubber Manufacturers Association), SAE (Society of Automotive Engineers), and various OEM's (Ford, General Motors, Caterpillar, etc.), and many others.

Hose can be categorized according to operating or working pressure in service, and/or by the nature of the substance conveyed. In considering the overall offering of hose products, a breakdown into major categories might be as follows:

## **High-Pressure Hose**

High-pressure hoses are used at working pressures of 2 to 20 MPa (several hundred to several thousand psi). They are relatively rigid and inflexible, and are often reinforced with steel wire and/or very high tensile textiles. Three common types of high-pressure hoses are steam hose, mining hose, and hoses which are a component of hydraulic systems. These hoses may share many design features due to their high-pressure ratings, including the type of reinforcement materials and methods of manufacture. Contrasts between these hoses are mainly found in the materials making up the inner (tube) and outer (cover) components, which must be formulated to be compatible with the fluid in use and resistant to harmful environmental exposure. For example, steam hose requires components which have superior heat resistance. Mining hose needs cover resistance to abrasive and harsh environments. Hydraulic hose tube materials must be resistant to attack and degradation by hydraulic fluids, and be able to withstand continuous impulsing.

## Low-Pressure, Small ID Hose

Low-pressure, small, less than 2.5 cm (1 inch) ID hose makes up the bulk of the hose market. This is a very broad category, which can be broken down into several subcategories.

*Fuel Dispensing Hose* – This category includes filling station pump hose, as well as hoses that dispense fuel for aircraft, marine, and farm applications.

*Chemical / Hydrocarbon* – This category comprises hoses used for chemical and hydrocarbon transfer, including hose for welding applications, anhydrous ammonia fertilization, hot tar and crude oil transfer, liquid propane gas (LPG) delivery, and others.

*Air / Water Hose* – This class of hoses includes garden and agricultural hoses, hoses used on home appliances (washing machines and dishwashers), and spray / washdown hoses. Low-pressure hose can be made using a variety of methods and techniques. As with high-pressure hoses, tube, reinforcement, and cover materials vary, depending upon the application of the hose.

#### Material-Handling Hose

Material-handling hoses usually have a large inside diameter (ID), and are used to convey materials in bulk by either gravity or suction. Many of the materials carried by these hoses are abrasive in nature. Examples are concrete, cement, sand and other building materials. Material-handling hoses can also convey chemicals, water, oils and fuels. While the operating pressures of these hoses are usually relatively low, an important concern is that they not collapse when negative pressure (suction) is applied. To prevent this, large hoses usually contain a helical wire or some other rigid component to maintain the shape of the hose. Special attention must be paid to the materials and compounding of tube and cover formulations in material-handling hose, in order to guard against degradation due to wear and abrasion, and to ensure compatibility with the substances conveyed.

## **Automotive Hose**

Hoses are integral to the operation of an automobile. A variety of fuels, lubricants, and cooling media are either circulated or transported under the hood, enabling the engine to operate. Hoses that can be found in virtually every automobile include radiator hose, air conditioning (Freon®) hose, heater hose, oil cooler hose, hydraulic brake hose and power steering hose. In addition to being compatible with the fluid being transported, automotive hoses must be able to withstand the scorching environment of high under-the-hood temperatures. As a result, many high temperature and specialty polymers are used in automotive hoses.

#### The Manufacture of Hose Components

The manufacture of hose involves several production steps because the finished hose product is a composite of multiple parts and components, which are usually produced in distinct processes and stages. Tube, layer, and cover components begin as compounds mixed from purchased raw materials in ratios according to a specific formula. Hose manufacturers typically use separate, off-line departments or areas where weigh-up, internal mixing, and batch-off of rubber compounds occurs. After compounds are mixed, they must be further processed into a useable form for subsequent production equipment, usually through extrusion, calendering, or molding processes. The thermoset or thermoplastic tube component serves as the starting point for the hose construction, and its properties must be compatible with the substance conveyed through the hose.

Other components must also be pre-processed before being incorporated into hose. Yarn, steel wire, fabric, or other types of reinforcement are prepared and packaged to fit equipment and manufacturing techniques. If a wrapped fabric or hand-built technique is used, reinforcement materials are calendered or frictioned with adhesive compounds in an off-line process. These components are then brought to wrapping equipment in the proper form (most often, rolls) to be applied to the hose in the production process.

### **Beginning Stages of Hose Production**

Hoses are built from the inside out. As a first step, the tube layer of the hose is either extruded through a die or applied as a ribbon, which is created as the result of a calendering process. In this stage of manufacture, the hose tube may be extruded or wrapped over a rigid mandrel (similar to a pipe) in order to maintain concentricity and a tight ID tolerance during the buildup of subsequent reinforcement and outside cover layers. After the hose is vulcanized (or cured), it is blown off or mechanically extracted from the mandrel. In contrast to using a rigid base, a flexible polymeric mandrel may serve as the foundation for hose manufacture, onto which layers of tube, reinforcement, and cover are extruded or applied. The flexible mandrel allows for production of longer lengths of product, since it can be coiled and flexed in the production processes. As a final option, the hose basis may be nothing more than the pressurized hose tube, to which other layers are added as the carcass moves through the manufacturing process.

Hose manufactured using a rigid or flexible mandrel base, although more costly and limited in available lengths, offers distinct advantages over the non-mandrel types. Advantages include tighter control of inside diameter and more consistent and controlled hydrostatic characteristics (length change, growth in diameter under pressure). Mandrel methods also provide the ability to manufacture hose containing thin walled tube components with resultant light weight and high flexibility. Mandrel produced hose is required for stringent service such as hydraulic, steam, and high-pressure transfer of liquids and gases.

Non-mandrel hose is usually used in air, water, garden, spray, welding, and low pressure liquid or gas transfer applications.

### **Hose Reinforcement**

The purpose of hose reinforcement is to provide strength to prevent burst or rupture during use. The hose design must provide for the maximum rated working pressure of the hose, as well as an appropriate safety factor. Safety factors vary greatly depending on the pressure in use and the relative danger of the substance being conveyed. Safety factors for low pressure, low risk discharge hoses can be as low as 2.5:1, and as high as 10:1 for steam hose. (A safety factor of 4:1 means that the point of hose rupture needs to be at least four times the rated maximum working pressure of the hose in service. The reinforcement component of the hose provides this resistance to rupture.)

The hose designer or engineer must be able to accurately calculate and predict hose burst pressure. This is accomplished through the use of geometry, mathematics, and vector analysis. Theoretical hose burst calculations are generated using reinforcement characteristics, such as ultimate tensile and elongation, applied to mathematical equations which take other details into account, such as hose dimensions and reinforcement geometry. These equations, which are provided for each of the various reinforcement techniques described in this article, have their origins in the application of thin-walled cylinder mechanics to reinforced hose.

Theoretically, the hose encounters forces both longitudinally and circumferentially, as would a thin-walled cylinder. Using thin-walled cylinder mechanics, the equations that define these forces are as follows:

$$F_1 = \text{longitudinal force} = (P \times D^2 \times \Pi) / 4$$

 $F_{\mu}$  = circumferential or "Hoop" force = (P x D x L) / 2

Where:

 $F_L$  = Longitudinal Force  $F_H$  = Circumferential Force P = Internal Pressure L = Mean Pitch Length D = Mean diameter of braid



Using vector mathematics, it can be determined that, under pressure, a resultant force will occur at a specified angle (called the neutral angle) from the hose axis. The tangent of this angle is the Hoop force, F_H, divided by the longitudinal force, F₁. Algebraic treatment of this equation leads to the determination of the angle of the resultant force to be 54.74 degrees from the hose axis. This angle, called the neutral angle, defines the orientation that the reinforcement elements of the hose prefer under pressure, relative to the hose axis. This is valuable information to the hose designer, for it means that at a braid or reinforcement angle of 54.74 degrees, the hose will approach ultimate rupture without any longitudinal or circumferential changes. If, however, the angle of reinforcement is less than the neutral angle, the hose will reduce in length and increase in diameter under pressure as orientation of reinforcement seeks to accommodate a neutral angle. The opposite phenomena occur when braid angles exceed the neutral angle. In the discussions that follow, burst formulas derived from hoop and longitudinal force equations are given for each of the different reinforcement techniques. In actual design practice, these equations are often "adjusted" with efficiency factors to obtain results consistent with observed hose burst results.

## Spiral and Braided Hose

Most hoses produced today contain spiral or braided reinforcement plies. The braiding technique is a process that helically spirals interwoven textile yarns or steel over the hose tube. The most common braid pattern is a two plaits over, two plaits under geometry, a "plait" being a wire or textile reinforcement package. Half the reinforcement is applied in the right-hand direction and the other half in the left-hand direction.

Spiral reinforced hose is very similar to braided hose, except that the righthanded and left-handed plies are laid over the hose tube separately, and there is no interweaving of the reinforcement yarns or wires. Since the spiraled layers are free of any contortion or bending (because of the lack of weave), the spiral reinforcement technique makes better use of the full strength of the reinforcement than does braiding. This results in a number of advantages for spiral hose over braided products. One is the ability of the engineer to design a more efficient hose due to better use of reinforcement properties. This promotes cost-effective use of an expensive hose component. A second is that spiraled hose is less likely to deteriorate as a result of reinforcement strand abrading or sawing on adjacent strands during flex, which increases longevity. Economically, today's spiral machines are faster than most braiders, making the process more cost-effective. Two possible disadvantages of spiral reinforced hose are that layers of reinforcement are more likely to be distorted from their placement during manufacture, and that spiraled hoses may not have coupling pull-off characteristics which are as high as those of their braided counterparts.

The formula used to determine the burst pressure for braided and spiral hose is as follows:

$$P = \frac{2 \times N \times R \times Sin\theta}{D \times L}$$

Where:	P=Burst Pressure	N=Total Number of Cords
	R=Break Strength of Cord	D= Ply Diameter
	L=Lead (Pitch)	θ=Braid Angle

When multiple braid or spiral layers are included in the hose construction, a rubber adhesion or insulation ply is inserted between the layers. The ply material is usually specially compounded to promote adhesion to adjacent layers, and flow into voids that may be present between reinforcing elements. The adhesion layer may be applied by wrapping the hose carcass with a specific width of calendered compound, by wiping on a layer of rubber cement or dough, or by extruding the layer with a crosshead extruder.

*Equipment* - Braiding machines are available in two orientations. The vertical braided process is employed for reasons of convenience and economy. In this method, the tube is extruded in very long lengths and placed on large trays or drums. From these trays, the hose carcass passes through the braider in a vertical direction. After braiding, the reinforced hose carcass is put on reels, or more trays, and taken to a cross head extruder where the cover is applied.

In the horizontal braiding process, the tube is usually extruded onto a rigid or semi-rigid steel or polymeric support mandrel. The braider is positioned so that the tubed hose carcass passes through the braider in a horizontal plane. After braiding, the cover is applied, either by cross head extrusion or by wrapping a specified width and thickness of calendered compound around the reinforced hose carcass.

Spiral machines, on the other hand, are horizontal in nature and, because of their faster speed, are often placed in-line with other manufacturing equipment. In the case of a well-designed spiral hose line, the hose will be in constant movement from tubing, through one or more layers of spiraled reinforcement, to cover application or extrusion, and even through the final vulcanization (curing) step. The opportunity for manufacturers to realize this improvement in efficiency and subsequent lower manufacturing costs has led to widespread replacement of braided hose with spiral products.

## Knit Hose

Another common way to reinforce hose is to apply a knit yarn pattern around the hose tube. In this process the yarn, cord, or wire are applied by special machines which produce a continuous cylindrical reinforcement of interlocking loops. The knit type of reinforcement is much less efficient than spiral or braids techniques, and is used only in low pressure applications. One advantage of knitting is that processing speeds are fast and hose can be made economically. Another useful aspect of knitted hose is that uncured reinforced hose can be bent and distorted to unnatural shapes, and then vulcanized without visual distortion of the knit pattern through the cover of the hose. This is particularly useful in making preformed hose products, such as radiator hose, Common products that employ the use of knitting techniques include garden hose, automotive heater and radiator hose, and other low-pressure hose products. The burst formula for knitted hose is as follows:

$$P = (2 \times V) / (D \times L)$$

#### $P = (2 \times R \times C \times Sin \theta \times e) / D$

Where:V = Hoop Force = R x C x Sin  $\theta$ R = Cord StrengthP = Burst PressureD = Ply DiameterC = Courses (per inch)L = Length of Fabric Unit (1")e = Efficiency Factor $\theta$  = Angle ofCircumferential Reinforcement

## Wrapped Hose

Wrapping is another common method of reinforcement. As the name implies, hose components, including reinforcement layers, are wrapped around the tube or hose carcass. The wrapped hose technique is especially useful in producing large hose constructions. Available sizes can range from 10 to over 60 cm (3/8 to over 24 inches). One disadvantage of wrapped hose is its weight and bulkiness as compared to a braided hose of comparable pressure rating. Wrapped hoses can be very heavy and limited in available lengths.

Wrapped hose employs the use of a rigid mandrel base. Tube compound is either extruded or wrapped around the mandrel, which can be as long as 125 m (400 ft). After the tubing process, a reinforcement layer consisting of a fabric

composite is wrapped around the hose carcass. To balance strength properties, fabric plies are usually wrapped around the hose in multiples of two, with each ply being wrapped in the opposite direction from the other.

The fabric composite that makes up the reinforcement member is produced off-line. The base fabric may consist of a square woven construction with load-bearing elements in both warp and fill directions, or it may possess a unidirectional strength member (e.g., tire cord). This base fabric is impregnated with rubber by a calendering process in order to promote adhesion to adjacent layers of the hose. Treatment with solvent rubber cement or chemicals can also serve to impregnate the base fabric. Finally, the fabric composite is bias cut at an approximate 45 degree angle and an appropriate width. It is then ready to be placed in a wrapping machine or hand-operated jig and applied to the hose.

Wrapped hose constructions may require multiple reinforcement layers. Besides fabric reinforcement, other components such as helical wires or textiles are often spiraled around the hose. The wrapping of cover materials around the carcass completes the building of the uncured hose. Finally, a shrinkable fabric is wrapped around the hose to promote inward pressure and molding of hose components during vulcanization. After cure the crosswrap is removed, the mandrel is extracted, and the hose is ready for shipment.

Wrapped hose can be further classified according to whether the carcass is built up by machine, or the components are applied by hand.

*Machine-wrapped* hose is generally available in sizes 5 mm through 75 mm (3/16" through 3") ID. Because of its bulk and stiffness (and thus its resistance to collapse), machine-wrapped hose finds many uses where suction or vacuum are involved, and where braided hose might be unsuitable. Another advantage that stiffness brings is suitability for handling abrasive materials. Machine-wrapped hose is commonly found in low-pressure steam, sandblasting, abrasive and corrosive liquid handling, and in heavy duty air and water services.

Hand-built hose, as the name implies, is produced by plying up various components of the hose by hand. This can occur because the base mandrel onto which hose is built is positioned into a chuck and turned at slow rpm by machine. Components are applied to the hose from a fixture on a cart that travels up and down the length of the mandrel at a set speed while the mandrel is turning. In this way, components can be applied at consistent wrap angles along the entire length of the hose. Large hoists are employed to move the long and heavy mandrels and hose carcasses from one area to another.

One advantage of the hand-building technique is that an almost unlimited number of sizes and constructions are possible. Strength, crush, collapse and hydrostatic characteristics of the hose can be customized by the addition of spirally wound cord, wire, or plastic monofilament, or by the use of different types of fabric in the same hose. Also, special end conditions and/or couplings can be built into the hose to provide for unique or unusual service conditions or materials which might be encountered. A common element of hand-built hose is the inclusion of a helix of heavy flat metal strip placed on the inside of the hose to prevent collapse. As a slightly different variation, a heavy round wire or flat strip (metal or plastic) helix can be built into the carcass of the hose to provide greater strength, and better resistance to collapse or kinking. Finally, hose may have a flat strip or half round wire placed in or over the outer surface to armor the hose against crushing, gouging or snagging.

Material-handling hoses are usually produced by the hand-building technique, as are large suction and discharge hoses. These hoses convey a variety of liquid materials including water, chemicals, and petroleum products.

The burst formula for wrapped hose is:

 $V = 2 \times S \times Sin 45 \times N$   $P = (2 \times V) / (D \times L)$   $P = (2.83 \times S \times N \times F) / D$   $When F = 0.80, P = (2.26 \times S \times N) / D$  Where: D = Mean Ply Diameter P = Burst Pressure S = Minimum Fabric Strength L = Length of Fabric Unit (1") N = Number of Plies F = Efficiency Factor V = Hoop Force

### Woven Carcass or Loom Hose

Woven or loom hose demonstrates yet another reinforcement technique. This process is characterized by weaving the reinforcement on a loom as the hose carcass travels through the equipment. The reinforcement layer is a seamless, tubular textile jacket around the hose, which provides crush resistance. As a subsequent process, woven reinforcement can be impregnated with rubber, or wrapped with a protective rubber cover which molds into the weave during cure. The woven reinforcement may also act as the cover. Fire hose is commonly manufactured by this process.

A specific type of loom, the Chernack loom, provides the flexibility to use multiple types of textiles or wires. Using this type of loom, alternate circular members may be wire or plastic monofilament instead of textile yarn or cord. A unique characteristic of woven hose is its resistance to collapse under vacuum or kinking. The woven hose method also provides the ability to manufacture relatively light weight hose. Hose of this type is usually found in suction or low-pressure services such as tank car delivery, water suction / discharge, and fire hose. Most woven hose is available in sizes under 10 cm (4 ") I.D.

The burst formula for woven hose is:

	P = H / (D ² x .7854) (By	y End Force)	
	$P = (2V) / (D \times L) (By Hoop Force)$		
Where:	$N_h$ = Total No. of Warp Ends $R_h$ = Strength of Wrap Cords $H = N_h x R_h$ P = Burst Pressure D = Diameter of Ply	$N_v =$ Total No. of Fill Cords V = Hoop Force $R_v =$ Strength of Fill Cord L = Unit Length V = N_v x R_v	

### **Additional Components**

After the reinforcement layer has been applied to the hose carcass, additional processing steps are taken to add other needed components. In a very simple construction, the hose may consist of only a tube and a reinforcement layer. The reinforcement layer serves as both strength member and cover. Other hoses consist of a tube, single reinforcement layer, and cover. Many highpressure hoses contain multiple reinforcement layers followed by a cover. Additionally, specialized hose constructions may contain other layers to lend unique properties. Some hoses may contain resin or thermoplastic layers, which serve as permeation barriers for the prevention of fuel or chemical release to the environment. Material handling hoses often contain helically wound steel or thermoplastic wire, which prevents hose collapse during suction or use in harsh environments. When further components are required, application usually involves movement of the hose carcass through an extruder or wrapping machine. If an extruder is used, the rubber or thermoplastic material is forced either onto the carcass at the desired thickness or to the desired outside diameter (OD) in a semi-molten state. If wrapping is used, the wrap added, whether calendered rubber compound, calendered fabric, or steel wire, is helically wound around the hose carcass. In this way, as many components and layers as are needed can be added to the hose carcass.

## Vulcanization

After all required layers of the hose carcass have been added, the "green" or uncured hose is ready to be vulcanized. When heated, the unvulcanized (uncured) rubber will first undergo a softening stage, which allows for flow and molding of the hose components, then a stage of rapid chemical crosslinking and property development, followed by a leveling off of properties and characteristics. The goal of the rubber formulator is to achieve an optimal degree of cure in a reasonable time that will deliver target hose properties. These properties are then expected to remain as constant as possible throughout the life of the hose.

There are many different ways in which to achieve vulcanization. Probably the most common vulcanization process involves the use of steam. Steam vulcanization is accomplished when uncured hose coils, reels, or straight / formed lengths are placed in vessels, which are then pressurized with steam. The pressurized steam provides the heat to initiate vulcanization and the force to compress the various components of the hose into a composite that behaves as a single entity. Usually temperatures of 150 to 175°C (302 to 347°F) are reached for periods of from 20 to 60 minutes, in order for the hose to be fully cured. In addition to the use of steam, forming pressure can be introduced from other sources, including "charging" the tube with air or water, or wrapping the cover of the hose with a woven fabric which shrinks and compresses the hose components together when they are heated. In the past, molten lead was commonly extruded as a sheath over the hose to promote cover smoothness and dimensional consistency during steam vulcanization. This practice has, for the most part, been discontinued due to safety considerations. However, the concept of sheathing hose prior to steam vulcanization is still practiced. Instead of lead, some manufacturers use thermoplastic materials to encapsulate the hose. After vulcanization, the sheath material is removed from the finished hose and recycled for subsequent use.

Vulcanization, like many of the processes used to make hose, is usually performed as an off-line batch process. The process involves the movement of specified lengths or volumes of hose from the building area to a cure vessel, where the hose is cured by exposure to pressurized steam for an appropriate time. After an initial length of hose is cured, the process is repeated using another length (or "batch") of hose. Batch and off-line processes involve the non-value added activity of moving product from one area to another (and often back again), which adds cost and labor to the product.

Continuous steam tube vulcanization is a more efficient technique that uses steam to cure hose while it moves through the production process. This eliminates the need to cut the product to fit the curing vessel's length or volume restrictions. In continuous steam tube vulcanization, hose built on a flexible mandrel is passed through a long, small diameter tube into which high-pressure steam is introduced. The hose is cured as it passes through the tube.

Another technique for continuous vulcanization has been termed the fluid bed continuous vulcanization system (FBCV). In this process, hose is passed through a long narrow bed of ballotini, or small glass spheres, that are transformed into a pseudoliquid by the passage of hot air or steam upward through the bed. In passing through the heated fluidized bed, the hose receives the necessary heat energy for vulcanization to take place.

Other methods of curing hose are used besides those discussed above. Among them are stimulation of the uncured product with microwaves, high velocity heated air, circulating heated fluids, or combinations of the above. These vulcanization techniques can be "mixed and matched" to be compatible with upstream manufacturing schemes. Any technique can be used, but the chemical makeup of the rubber components in the hose must be compatible and fully curable with the chosen vulcanization method, otherwise there might not be sufficient adhesion between layers to hold the hose components together during use. There are many variations of hose curing techniques. The best technique is one that produces the desired end product in an efficient, costeffective manner.

#### Coupling and Assembly

Bulk lengths of hose are of little use to the customer. Applications require specific lengths and the inclusion of compatible end fittings before the hose can be placed in service. The manufacture of assemblies (hose of specified lengths with end attachments) completes the usefulness of the hose to the customer.

*Clamps* – Clamps represent the simplest of devices used for hose attachment. Their effect is to apply external pressure to the hose cover, and thereby compress the hose against an insert that is attached to a port. Clamps may be comprised of a ring of spring steel that is flexed and then allowed to relax around the hose, or a strip of metal tightened around the hose by a screw and worm gear mechanism. Other types of clamping methods include the tightening of steel bands through the use of a banding machine, and the tightening with bolts of two clamping halves. Clamps are easily attached with hand tools and are used in low-pressure applications.

*Couplings* – "Couplings" is a very general term, which can be applied to a number of different designs and mechanisms. Usually, couplings are comprised of two parts, an insert and a ferrule. To assemble the hose, the insert is placed into the inner tube of the hose. Barbs machined on the outside of the insert "grip" and hold the coupling in place. The barbs also act as a barrier against leakage. The other component of the coupling, the ferrule, shrouds the cover of the hose. The inside of the ferrule may have machined serrations to "grip" the outside of the hose cover and hold it in place during use. Insert and ferrule are connected to an attachment having pipe threads or another means of attachment to the relevant connection.

Permanent Couplings – The act of creating a permanent coupling requires a deformation of the ferrule (by crimping) and/or insert (by internal expansion). Crimping is accomplished when the ferrule is mechanically pressed or squeezed to a smaller OD so that the hose wall is compressed between the insert and ferrule. Internal expansion occurs when the ID of the insert is mechanically made larger. This pushes the barbs that are on the outside of the insert into the hose tube. Both of these techniques result in the hose wall being compressed and held firmly in place between the insert and ferrule. In practice, crimping, expanding, or both procedures may be used. Permanent couplings ensure that hose attachments are secure, safe, and leakproof. Hose assemblies with permanent couplings are supplied for a variety of applications, including the garden, welding, and curb pump markets.

Reusable Couplings – Reusable couplings also involve two components, an insert and a ferrule (socket). The attachment of the insert and ferrule to the hose is achieved by screwing the components onto the hose. The ferrule is initially screwed onto the OD of the hose. The insert is then screwed into the ferrule. The opposite thread design between insert and ferrule "pulls" the insert into the hose to complete the assembly, compressing the hose wall. This accomplishes the same purpose as clamping or crimping. As the name implies, these couplings can be removed and reused. However, the end of the hose involved needs to be

cut off before an effective recoupling can take place.

## **Future Considerations for Hose Manufacturing**

Despite its varied and technically engineered uses, the making of hose remains for the most part a batch (one step at a time) process. The mixing of chemicals into the rubber formulation is an off-line task. Often, there are waiting periods after the hose carcass is extruded, after the reinforced is applied, after the cover is extruded, and so forth, before the final building up of layers is complete. If hose components are of a thermoset nature (requiring cure), the vulcanization process is yet another batch process required to complete the hose. These many separate steps can result in adding excessive time and cost to the final product.

As a result, most manufacturing improvements aim at making hose in a more cost effective way. Usually this involves arrangement of the hose building process and curing methods in a way that allows hose manufacture to flow from beginning to end in a continuous manner. As new methods of equipment control become available, this goal becomes more attainable. The use of computers to coordinate production equipment and operations is key to cost efficiency and consistent quality in hose production. Implementation of these techniques will lead to more consistent and economical production of hose.

## **Design Considerations**

In the simplest sense, the hose designer or engineer needs only to make a few decisions. Most often, the customer has already dictated the size of the hose (in terms of ID and OD). The method of manufacture is also often implied by the size of the hose, the type of hose, or the methods that are available. What remains for the engineer to determine are the components in terms of tube material, reinforcement, and outer cover, which will enable the product to deliver the appropriate fluid or media at the desired pressures.

*Choice of Reinforcements* – Several types of natural and synthetic fibers are used for reinforcement in hose construction. The most common are cotton, rayon, glass fiber, nylon, steel wire, polyester, para or meta aramid, and polyvinyl alcohol (PVA). Each of these materials possesses unique physical properties which allow the designer to tailor the hose to match end product requirements. The following graph (Figure 1) depicts differences in reinforcement materials. Note that some materials, such as para aramid, glass fiber, and steel wire have a mostly linear relationship between tensile and elongation. If the main design goal is to withstand high pressure, these reinforcement materials should be the first choice. There are, however, disadvantages to using these low elongation reinforcement materials. Hose flexibility is limited, as is the ability of the hose to absorb and dissipate energy caused by pressure spikes or impulses. Additionally, fatigue failure could be a problem due to reinforcement degradation in dynamic use. In spite of these limitations, para aramid, glass fiber, and steel wire are commonly used as reinforcement for hoses in a variety of applications.



Figure 1: Stress-Strain Behavior of Hose Reinforcement

In contrast to the more rigid reinforcement materials, polyester, rayon, nylon, and meta aramid have adequate elongation properties to allow for greater flexibility and dynamic or pulsing behavior in service. They also tend to be less expensive and easier to process on conventional manufacturing equipment. One disadvantage of these materials is that they provide less burst strength relative to the materials previously discussed. The final decision of which reinforcing materials to use depends highly upon the characteristics desired in the final hose product and the predicted dynamics of the hose in service.

Calculating theoretical burst characteristics is an important step to conduct before choosing a reinforcement. These calculations will make use of specific reinforcement properties, such as tensile and elongation, to predict burst pressure, percent reinforcement coverage, pitch and diameter at burst, and other properties. The equations given in the discussion of reinforcement application techniques are for this purpose. Through proper choice of reinforcement type and construction, the hose designer can lay the groundwork for manufacturing a valuable hose product.

#### Tube, Cover, and Layer Components

Equally important to reinforcement type is the chemical composition of the various rubber or thermoplastic layers which will make up the hose. Each of the different hose layers has specific functions that require unique properties.

Understanding the chemicals with which components are in contact, the operating conditions under which the hose is used, and the general functions of each part of the hose is critical to effective design.

While this article addresses the development and use of thermoset (rubber) components for hose, it should be mentioned that the use of thermoplastic materials for hose is becoming increasingly popular. These materials come preformulated from the supplier and ready to use in extrusion equipment. Most are also recyclable. Thermoplastic materials are used much like thermosets (rubber), but they do not require vulcanization. The use of thermoplastic materials is attractive to the hose producer who lacks formulating expertise or the massive and expensive mixing equipment needed for thermoset production and vulcanization.

*Tube* – The tube portion of the hose is in direct contact with the fluid or substance being conveyed. As such, compatibility with the conveyed chemical(s) is of paramount importance. A compatibility problem with the hose tube can result in excess swelling and subsequent restriction of the hose channel. Additionally, a fluid being conveyed may have a tendency to extract important chemicals or plasticizers from the tube compound, leaving the tube cracked or stiff. Permeation of chemicals through the tube of the hose may also be an issue, so that attention must be paid to the optimization of filler loadings or the choice of polymer. The balancing of tube properties to these and other requirements is a very typical agenda for the hose engineer or rubber chemist.

Adhesion Layer – An extra layer may be necessary to provide adhesion between two reinforcement components or two dissimilar hose compounds. Rubber compounds specifically designed for this purpose must be in intimate contact with their adjacent components so that adhesion can be obtained. Sometimes this requires high flow characteristics in order to fill voids between reinforcement elements. This "wetting" characteristic also influences the ability of the layer compound to insulate reinforcing members from one another so as to prevent their self-destruction in service during flexing or pulsating.

Specialized ingredients are often used in layer or adhesion compounds to enhance flow during vulcanization and to facilitate the high levels of chemical adhesion that are needed. These ingredients are often resins or other bonding chemicals. A unique cure system may be used which prolongs the onset of vulcanization, and thereby increases flow. The compounding of the insulating layer also requires the use of polymers which are compatible with those used in adjacent layers.

*Cover* - The primary function of the cover is to resist deterioration by the environmental conditions encountered during hose storage and use. Environmental conditions include outside or sunlight exposure, abrasion and splashing with oils, fuels or other chemicals or burning. Some polymers are inherently better suited to these situations than others. When the choice of polymer alone is not sufficient, the engineer or chemist must add additional chemicals to the rubber formulations to achieve desired properties. In most cases, a combination of environmental conditions requires several types of antidegradant additives. Since the cover is usually the only portion of the hose seen by the user, cover compounds are often brightly colored for sales appeal or as an indication of their expected application.

## **Rubber Compounding**

The various rubber layers used in hoses are actually defined as recipes or formulations. Each formulation consists of a listing of specific materials and chemicals mixed together in exact ratios. The science underlying the development of these formulations is a unique discipline, which is often performed by staff chemists and technical experts from chemical suppliers. The possible combinations and relative amounts of chemicals that could make up a recipe are unlimited. Although this field sometimes earns a mystical or magical reputation, the formulation of compounds can be understood if components of the formulation are broken down into functional areas.

*Polymers* - The primary building block of rubber formulations is the polymer. It forms the base into which all other chemical components are dispersed. Polymer options are many. Each polymer has its distinct strengths and weaknesses. Some polymers are distinctly suited to one specific part of the hose, but not another. Polymer properties encompass not only chemical compatibility with potential fluids and chemicals, but also environmental considerations such as exposure to sunlight, cold flex, color stability, abrasion resistance, etc. In order to provide a basic classification scheme for polymers, the American Society for Testing and Materials (ASTM) has developed a system that categorizes polymers on the basis of swell resistance to oil exposure and resistance to property changes at elevated temperatures. The chart below depicts how common polymers are rated for heat and oil resistance. For more information, please reference the ASTM D 2000 standard.



Figure 2: ASTM D 2000 Classification for Polymers

Generally speaking, the price of a polymer increases as more heat and/or solvent resistance are required.

Other Chemicals - Once an acceptable base polymer for the formulation is chosen, other materials and chemicals must be added to achieve the desired compound characteristics and properties. Among these chemical classifications are fillers, plasticizers, antidegradants, process aids and curatives. Fillers are materials such as carbon blacks, silicas or clays, which are used in relatively high amounts to give the compound structure and "body". Plasticizers are the liquid hydrocarbons or lubricants that determine softness (in the uncured stage) and flexibility after cure. Antidegradants prevent attack and breakage of chemical crosslinks by oxygen, ozone or heat while the hose is in use. Process aids are a very broad category of chemicals that include waxes, tackifiers, homogenizers and other materials. The final class of chemicals, curatives, either contains or facilitates the forming of chemical crosslinks within the polymer matrix. Curatives are used in very small amounts, but are crucial in building physical properties during vulcanization or cure.

The art of putting all these materials together in the correct ratios and amounts can be very complex and time-consuming. In the appendix are a number of formulations that have been successfully mixed and tested, and are recommended by major polymer and chemical suppliers to the rubber industry. The R.T. Vanderbilt Company, Inc. plays a leading role in providing the rubber industry with chemicals for all areas of rubber compounding. Many Vanderbilt materials find wide use in hose compounding, and assist the engineer or chemist in accomplishing specific goals. R.T. Vanderbilt Company also supplies expert technical service to assist the hose designer in obtaining an optimum balance of properties for incorporation into hose products.

#### Acknowledgments

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# **Power Steering Hose***

Ingredients	phr
Hypalon [®] 4085	100.0
Magnesium Oxide	20.0
A-C [®] 617A Polyethylene	3.0
Carbowax [®] 4000	3.0
N762 Carbon Black	60.0
N990 Carbon Black	25.0
Trioctyl Trimellitate	10.0
Kenflex® A1	5.0
VAROX [®] 802-40KE	5.0
Triallyl Cyanurate	3.0
Total	234.0
Density, Mg/m ³	1.42
Mooney Scorch @ 132°C	
Minimum Viscosity	69
Minutes to 5 pt. rise	15
Rheometer at 160°C (320°F)	
M _L (dN∙m)	8
M _H (dN∙m)	58
t _s 2 (min)	3
ť90 (min)	23
Original Physical Properties, Press Cured 30 min. @ 160°C	
Hardness, Shore A	83
100% Modulus, MPa	8.5
Tensile, MPa	16.1
Elongation %	230
Physical Properties After Heat Aging in Air, 70 hrs. @ 150°C	
Hardness, Pts. Change	+6
Tensile, % Change	-7
Elongation, % Change	-32

*Courtesy of DuPont Performance Elastomers

Air	Con	ditio	ning	Hose*
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Ingredients	phr
EXXON [™] Chlorobutyl 1066	100.0
N774 Carbon Black	70.0
Stearic Acid	1.0
Zinc Oxide	5.0
VANAX® 189	3.6
Total	179.6
Density, Mg/m ³	1.19
Rheometer at 160°C (320°F)	
M _L (dN•m)	2.5
M _H (dN∙m)	20.7
t _s 2 (min)	1.4
ť90 (min)	3.5
Original Physical Properties, Press Cured 10 min. @ 160°C	
Hardness, Shore A	72
100% Modulus, MPa	6.0
Tensile, MPa	13.2
Elongation %	205
Physical Properties After Heat Aging in Air, 70 hrs. @ 140°C	
Hardness, Pts. Change	+3
Tensile, % Change	+10
Elongation % Change	-3
Compression Set, 70 hrs. @ 140°C	
%	35

*Courtesy of ExxonMobil Chemical Company

Ingredients	phr	phr	
Vistalon [™] 7500 EPDM	100.0	100.0	
N650 Carbon Black	95.0	90.0	
VANTALC [®] 6H	75.0		
Paraffinic Oil, Type ASTM 104B	70.0	50.0	
Zinc Oxide	5.0	10.0	
Stearic Acid	1.0		
VANWAX [®] H Special		5.0	
AGERITE [®] MA Antioxidant		1.0	
VANOX [®] MTI Synergistic Antioxidant		2.0	
VAROX 802-40KE Peroxide		8.0	
SR-206, Ethylene Glycol Dimethacrylate		1.0	
Sulfur	0.3		
METHYL TUADS [®] Accelerator	0.6		
UNADS [®] Accelerator	0.6		
ETHYL TUADS [®] Accelerator	0.6		
BUTYL ZIMATE [®] Accelerator	1.5		
VANAX A	2.0		
Totals	351.6	267.0	
Density, Mg/m ³	1.26	1.12	
Mooney Scorch @ 132°C			
Minutes to 5 pt. rise	14	24	
Original Physical Properties, Press Cure	d 20 min. @	2 170°C	GM 6278 Spec.
Hardness, Shore A	68	65	60 to 75
200% Modulus, MPa	5.6	6.3	3.0 to 4.5
Tensile, MPa	13.4	14.9	7.6 min.
Elongation, %	530	410	300 min.
Physical Properties After Heat Aging in A	Air, 168 hrs.	@ 150°C	
Hardness, Pts. Change	+9	+7	+15 max.
Tensile, % Change	-3	0	-35 max.
Elongation, % Change	-48	-1	-65 max.
Coolant Immersion Aged 1000 hrs.			
Hardness, Pts. Change	-3		-10 to +10
Tensile, % Change	-3		-20 max.
Elongation, % Change	-13		-25 max.
Compression Set. 70 hrs. @ 125°C			
%	56	23	

Radiator Hose, Electrochemically Resistant, SAE J20D3*

*Courtesy of ExxonMobil Chemical Company

# Automotive Fuel Hose*

Ingredients	phr
Chemigum N685 NBR	100.00
N660 Carbon Black	70.00
McNAMEE [®] Clay	65.00
VANTALC 6H	20.00
Polyethylene Glycol	1.00
Zinc Oxide	5.00
Magnesium Oxide	4.00
Wingstay [®] 100	2.00
Stearic Acid	0.50
Dibutyl Phthalate	3.00
Dioctyl Phthalate	7.50
TP-95, Di(butoxy-ethoxy-ethyl) Adipate	7.50
Spider Sulfur	0.62
UNADS Accelerator	1.40
ETHYL TUADS Accelerator	0.10
Total	287.62
Density, Mg/m ³	1.46
Mooney Scorch @ 121°C	
Minimum Viscosity	29
Minutes to 5 pt. rise	18
Rheometer @ t 160°C	
M₁ (dN•m)	10.4
M _H (dN•m)	59.2
$t_s$ 1 (min)	4.4
ť 90 (min)	8.7
Original Physical Properties, Press Cured 9 min. @ 160°C	
Hardness, Shore A	79
100% Modulus, MPa	5.0
Tensile, MPa	11.1
Elongation, %	360
Physical Properties after Heat Aging in Air, 70 hrs. @ 125°C	
Hardness, Pts. Change	+13
Tensile, % Change	+7
Elongation, % Change	-49
Compression Set, 70 hrs. @ 125°C	
%	39.5

*Courtesy of Goodyear Tire and Rubber, now Eliokem

Ingredients (phr)	Black	Non-Black
Nipol [®] N917 NBR	100.00	
Oxy 200 PVC Resin	47.00	
Hypalon APG-6525		100.0
Cis-4 Polybutadiene		3.0
N762 Carbon Black	40.00	
Ultrasil 880 Precipitated Silica	40.00	
McNAMEE Clay	40.00	
Santicizer 261	20.00	
Paraplex G-63 Plasticizer	5.00	
Whiting		150.0
DIXIE CLAY®		50.0
Titanium Dioxide		20.0
Paraffinic Oil		40.0
Wingstay 100	2.00	
AGERITE CELTROL	1.00	
VANSTAY [®] 5956	1.00	
Zinc Oxide	4.00	
Stearic Acid	0.50	
MORFAX®	1.50	
Santogard PVI	0.20	
METHYL TUADS	2.00	2.0
Spider Sulfur	0.65	1.0
Carbowax 3350		3.0
A-C 617A Polyethylene		3.0
Magnesium Oxide		5.0
VANWAX H Special		3.0
Ultramarine Blue		0.1
Totals	304.85	380.1
Density, Mg/m ³	1.38	1.63
Mooney Scorch @ 121°C		
Minimum Viscosity	25	29
Minutes to 5 pt. rise	20+	26.5
Rheometer at 160°C		
M, (dN•m)	12.8	14.6
M _u (dN•m)	73.2	75.4
ť 90 (min)	10.0	14.4
Original Physical Properties,		
Press Cured @ 160°C	10 min.	30 min.
Hardness, Shore A	80	75
Tensile Strength, MPa	12.9	11.1
Elongation, %	370	485

# Curb Pump Hose Cover*

*Courtesy of Goodyear, now Zeon Chemicals & DuPont Performance Elastomers

Ingredients	phr
Hydrin [®] C2000LL	100.0
N762 Carbon Black	90.0
Plasthall P670	8.0
VANOX MTI	0.5
VANOX CDPA	1.0
Stearic Acid	1.0
Calcium Oxide	5.0
Magnesium Oxide	1.0
Calcium Carbonate	5.0
Zisnet F-PT	0.6
VANAX DPG	0.5
Santogard® PVI	0.7
Total	213.3
Density, Mg/m ³	1.50
Mooney Scorch @ 125°C	
Minimum Viscosity	81
Minutes to 5 pt. rise	4.8
Rheometer at 160°C	
M₁ (dN•m)	22.4
M _H (dN•m)	99.2
t _s 2 (min)	1.6
ť90 (min)	40.6
Original Physical Properties, Press Cured 60 min. @ 160°C	
Hardness. Shore A	74
100% Modulus, MPa	4.6
Tensile Strength. MPa	10.0
Elongation, %	240
Physical Properties after Heat Aging in Air, 70 hrs. @ 150°C	
Hardness, Pts. Change	+6
Tensile, % Change	-26
Elongation, % Change	-25
Notes: This formulation should be run on a very clean, hot mill to avoid sti This formulation is designed for a continuous cure process, and mo	cking. eets GM 6148.

Arctic Fuel Hose*

*Courtesy of Zeon Chemicals L.P.

# Mining Hose Cover*

Ingredients	phr
Masterbatch:	
Nipol X775 Carboxylated NBR	100.0
Oxy 200 PVC Resin	45.0
AGERITE GELTROL	1.0
Tributyl Tin Mercaptide	1.5
Wingstay L	1.5
Diamyl Hydroquinone	1.0
Dioctyl Phthalate	10.0
N650 Carbon Black	48.0
Wingtack [®] 95 Resin	4.0
Dibutyi Phthalate	5.0
Stearic Acid	2.0
Total 1 st pass	219.0
Cure Addition (in 2 nd pass):	
Kadox 911C Zinc Oxide	6.0
Spider Sulfur	1.6
UNADS Accelerator	0.1
AMAX Accelerator	1.5
Total	228.2
Density, Mg/m ³	1.21
Mooney Scorch @ 121°C	
Minimum Viscosity	22
Minutes to 5 pt. rise	12.7
Rheometer at 160°C	
M⊢ (dN•m)	7.5
M _H (dN•m)	39.0
$t_s 1$ (min)	3.7
ť90 (min)	34.2
Original Physical Properties, Press Cured 35 min. @ 160°C	
Hardness, Shore A	87
100% Modulus, MPa	10.0
Tensile Strength, MPa	23.3
Elongation, %	390
Physical Properties after Heat Aging in Air, 70 hrs. @ 125°C	
Hardness, Pts. Change	+4
Tensile, % Change	+7
Elongation, % Change	-21
Notes: The 1st pass of the mix must get above the flux point of the PVC, so	o dump @ 165-170°C.
Avoid zinc stearate in the slab dip because it causes scorch.	

*Courtesy of Goodyear Tire & Rubber, now Zeon Chemicals L.P.

Ingredients	phr
Nipol 1052 NBR	100.0
N774 Carbon Black	75.0
N550 Carbon Black	10.0
Ultrasil VN-3 Silica	5.0
Dioctyl Phthalate	10.0
Cumar P-25	3.0
Stearic Acid	1.0
	5.0
AGERITE RESIN D [®]	2.0
Spider Sultur	0.5
METHYLTUADS	2.0
Total	213.5
Density, Mg/m ³	1.20
Mooney Scorch @ 125°C	
Minimum Viscosity	47
Minutes to 5 pt. rise	14
Rheometer at 170°C	
M _L (dN•m)	6.2
M _H (dN•m)	44.5
t _s 1 (min)	1.4
ť'90 (min)	2.7
Original Physical Properties, Press Cured 10 min. @ 170°C	
Hardness, Shore A	70
100% Modulus, MPa	5.1
Tensile Strength, MPa	15.3
Elongation, %	370
Physical Properties after Heat Aging in Air, 70 hrs. @ 125°C	
Hardness, Pts. Change	+2
Tensile, % Change	+10
Elongation, % Change	-49
Compression Set, After 70 hrs. @ 125°C	
%	22
Notes: 2 phr AMAX and 1 phr ETHYL TUADS can be subsistuted for 2 ph better scorch safety and similar properties.	r METHYL TUADS for

# Hydraulic Hose*

*Courtesy of Zeon Chemicals L.P.

# **Oilfield High Temperature Hose***

Ingredients	phr	phr	phr
Nipol DN1205 NBR	108.00	54.00	
Zetpol [®] 2020 HNBR		50.00	100.00
N990 Carbon Black	15.00	15.00	15.00
Ultrasil 150	55.00	55.00	55.00
Silane A-174 DLC	1.00	1.00	1.00
Hercoflex [®] 600 Polyester Plasticizer	5.00	5.00	5.00
Magnesium Oxide	12.00	12.00	12.00
A-C 617A Polyethylene	2.00	2.00	2.00
VANOX MTI	2.00	2.00	2.00
AGERITE MA	2.00	2.00	2.00
Wingstay SN-1		4.00	8.00
VAROX 8002-40KE	3.75	3.75	3.75
VANAX MBM	0.50	0.50	0.50
Totals	206.25	206.25	206.25
Density, Mg/m ³	1.26	1.24	1.23
Mooney Scorch @ 121°C			
Minimum Viscosity	20	31	44
Minutes to 5 pt. rise	20+	20+	20+
Rheometer @ 182°C			
M _L (dN·m)	7.1	10.7	13.7
M _H (dN⋅m)	105.0	78.1	70.7
t _s 2 (min)	1.1	1.0	1.3
t'90 (min)	6.8	8.2	9.2
Original Physical Properties, Press Cured 20 min. @ 182°C			
Hardness, Shore A	73	77	74
100% Modulus, MPa	4.2	4.6	3.2
Tensile Strength, MPa	14.6	15.1	17.1
Elongation, %	315	325	550
Physical Properties After Heat Aging in Air, 70 hrs. @ 150°C			
Hardness, Pts. Change	+11	+8	+4
Tensile, % Change	-11	-2	+4
Elongation, % Change	-49	-36	-30
Physical Properties After Aging in IRM 903 Oil, 70 hrs. @ 150°C			
Hardness, Pts. Change	-5	-7	-8
Tensile, % Change	-12	-15	-1
Elongation, % Change	-31	-27	-10
Volume, % Change	+8	+10	+112
Compression Set, 70 hrs. @ 150°C			
%	40	43	51

*Courtesy of Goodyear Tire & Rubber, now Zeon Chemicals L.P.

## **Chlorobutyl Steam Hose***

Ingredients (phr)	Tube	Cover
EXXON Chlorobutyl 1066	100.0	100.0
N550 Carbon Black	20.0	30.0
Ultrasil 150 Precipitated Silica	60.0	
N330 Carbon Black		30.0
Paraffinic Oil	10.0	5.0
Stearic Acid	1.0	1.0
Paricin 1	4.0	
VANOX MBPC	1.0	1.0
Phenol-formaldehyde Resin	3.0	3.0
Diethylene Glycol	2.0	
Magnesium Oxide	2.0	2.0
Zinc Oxide	3.0	3.0
METHYL TUADS	2.0	1.0
ALTAX	1.0	2.0
Totals	209.0	178.0
Density, Mg/m ³	1.19	1.15
Mooney Scorch @ 132°C		
Minutes to 3 pt. rise	23	14
Original Physical Properties, Press Cured @ 153°C	60 min.	40 min.
Hardness, Shore A		68
300% Modulus, MPa	8.0	9.3
Tensile Strength, MPa	11.2	13.2
Elongation, %	430	500
Physical Properties after Heat Aging in Air, 168	hrs. @ 149°C	
Hardness, Pts. Change		+12
Tensile, % Change	-71	-48
Elongation, % Change	-79	-76
Compression Set, 2 hrs. @ 70°C		
%	18	

Note: Steam hose formulas based on EPDM and EXXPRO[™] can be found in the chapters discussing the respective polymers.

*Courtesy of ExxonMobil Chemical

## by Larry K. Adkins

Johnson Brothers Rubber Co. West Salem, OH

Sponge rubber is essentially an elastomeric material that has been manufactured in such a way as to incorporate a high degree of porosity. This manufacturing method produces a material that is soft and highly compressible, much like naturally occurring sponges. The term "elastomeric" encompasses many highly elastic materials that are polymer-based; however, sponge rubbers are typically differentiated from urethane, latex, thermoplastic, and RIM foams in that they are generally produced by simultaneously cross-linking and chemically blowing compounded dry (non-latex) polymer(s).

Sponge rubbers are further categorized based on the nature of their pores (or "cells"). Open-cell sponge has cells that are predominantly open (interconnected) to their neighboring cells. This creates a three-dimensional "tunnel" network that allows gases and fluids to flow freely through the cells. Closed-cell sponge, however, as its name suggests, predominately has cells that are entirely encapsulated within the rubber matrix and therefore strongly resist the flow of gases and fluids. A key test specification for closed-cell rubber is the amount of water absorbed while the sample is suspended under water within a vacuum atmosphere. Closed cells are generally much finer (smaller) than open cells, and in some cases can be barely visible to the naked eye. Open-cell sponge cells can range from 0.5 mm (very fine) or smaller, to 5 mm (very coarse) or greater.

Although open-cell rubber has an interconnected network of cells, its ability to seal "low pressure systems" can often rival closed-cell rubber, depending on the degree of compression applied to the sponge material, the firmness of the sponge material, and the pressure of the sealed system. Open-cell sponge is typically much more resistant to compression set under high temperature conditions than closed-cell sponge. The poor performance of closed-cell sponge is mainly due to the cellular gas permeating out of the sponge under heat and pressure. Once the compression and heat are removed, gases cannot return to the cells very quickly. Compression set tests for closed-cell rubber typically requires a 24 hour recovery before final measurement, while open-cell rubber usually requires 30 to 45 minutes.

Open-cell sponge has many properties that make it an ideal material for varied applications. It is low cost, low weight, soft, and highly compressible. It provides cushioning and absorption, and under compression, it provides sealing. Applications include cleaning sponges, air/gas systems sealing, plumbing sealing, structural sealing, toys, medical devices, cushions, padding, structural filler, vibration isolation and sound insulation.

Materials that compete with open-cell sponge include foams and, in some instances, closed-cell sponge. As the technology of thermoplastics, RIM

thermosets and castable urethane foams continues to evolve, the matching of material properties will become less of an issue. These materials are more expensive from the standpoint of raw material cost, but they lend themselves to highly automated processes and generally lower density, which can make them cost-competitive.

Sponge rubber is often technically specified. Various industry and corporate standards provide methodologies for specifying key properties such as cell structure, compression-deflection (firmness/hardness), heat aging resistance, oil/ fuel swell resistance, low temperature resistance, weathering and compression set. Commonly used standards include ASTM D 1056, SAE J18 and MIL-R-6130 (defunct but still specified in many instances).

Open-cell sponge rubber can be formulated from many different polymers; among the more familiar are SBR, NBR, NR, IR, EPDM and CR. The chemical and temperature resistance which the polymer imparts to the final compound is directionally similar to that of "dense" rubber.

Cells are produced in the rubber matrix by including one or more gas generating chemicals in the formulation. These chemicals, known as "blowing agents", produce gases when heated during the curing stage of production. The gases can be a by-product of the chemical reaction of two components or the decomposition of a single chemical. Sodium bicarbonate is the most commonly used blowing agent for making open-cell sponge rubber. It is rather inexpensive, safe, and generally produces large cells. Nitrogen-type blowing agents (e.g. dinitrosopentamethylenetetramine, DNPT) are sometimes used in combination with bicarbonate to create a finer cell structure and to give an extra "push" in blowing power. Fatty acids are added to help liberate carbon dioxide from sodium bicarbonate. The decomposition of sodium bicarbonate and its reaction with fatty acid are shown below.

Decomposition of Sodium Bicarbonate: 2 NaHCO₃  $\triangleq$  Na₂CO₃ + H₂O + CO₂

Fatty Acid/Bicarbonate Reaction: RCOOH + NaHCO₃  $\xrightarrow{\Delta}$  RCOONa + H₂O + CO₂

In order to obtain "open" cells during the curing process, the compound must have a very low viscosity and the blow must occur before too much cross-linking takes place. A sponge formulation usually begins with a low viscosity polymer, low reinforcing fillers such as whiting, clay, talc, or thermal black, and plenty of plasticizing oil. The oils must be highly compatible to accommodate the high dosage. Natural rubber has to be highly peptized to be effective in an open-cell formula. Because of the high loading and low viscosity of the mix, obtaining chemical dispersion is sometimes difficult, and chemical pre-dispersions (especially for blowing agents) are often used as an aid in obtaining uniform cell structure and higher chemical efficiency in the cure and blow reactions. The low viscosity and green strength also dictate that formulas not have too much tack and be processed at lower temperatures.

The generous use of clays and whitings in sponge formulations means that the manufacture of colored sponge is usually easy and inexpensive. Also, flame

retardants such as hydrated aluminum oxide can be incorporated without a major loss of properties.

Vulcanization retarders are used to obtain sufficient induction time and a cure rate that is slow enough to allow the cells to grow and "blow-through" into the open structure. Cone rheometers, which measure "blow" pressure accumulation as well as cure-torque, are useful instruments to observe the relative rates of blow and cure in a compound. More recently developed instruments such as moving-die rheometers are now fitted with pressure transducers to satisfy this need.

Cure systems designed for "dense" rubber sometimes need significant adjustments for sponge, due to the interaction of the curatives with the high levels of fatty acids, acidic clays, retarders, nitrogen blowing agents and plasticizers.

Precise plasticity control is of extreme importance in the successful production of sponge rubber. Fortunately, in recent years the polymer manufacturers have developed processes to produce very uniform elastomers in almost any range of plasticity desired. Natural rubber (NR) can also be purchased in viscositycontrolled grades, but usually still requires mastication and peptizers. Natural rubber mastication requires careful control to hold the polymer to the required plasticity.

The firmness of sponge rubber is primarily related to the apparent density (specimen weight divided by volume) of the sponge rubber, and can be generally controlled by the amount of oil, the level of fillers, the amount of blowing agent, and the plasticity of the compound. Because of the complexity by which the "blow process" controls the apparent density, trial and error is generally required to zero in on a formulation. Designed experiments, especially response-surface methodologies, are very useful for sponge formula design and optimization.

Compression set and heat-aging of the sponge rubber, just like dense rubber, are mainly related to loading level, cure system type, base polymer, and stateof-cure as influenced by time, temperature and cure acceleration.

Sponge rubber can be molded into sheets, molded strips, or almost any shape. However, the molding of sponge rubber requires the venting of a tremendous amount of gas from the mold cavity. Since sponge expands into a porous matrix during curing, the cavity is initially only partially filled by the prep specimen and the remaining volume of air has to be vented. Also, excess "blow" gas that is necessary to properly create open cells and to fill the mold cavity, must be vented, even after the matrix has expanded. All of this gas increases the difficulty of molding complexly shaped sponge parts that are free from defects caused by trapped gas. Techniques that are used to solve this molding problem include the dusting of particulate (such as talc) on the prep surface, the insertion of fabric between mold cavity and lid, careful selection of prep shape, prep position in the cavity, mold venting, proper selection of mold parting line, and the optimization of cure temperature and pressure. The compound's cure/blow rates, and its ability to flow during expansion, are also critical. Molded sponge generally has a skin on its surface that has less porosity than the interior of the part. This skin (especially for sheet goods) may have a gnarled surface if it is molded against a fabric-coated surface to aid in gas venting. Some finished parts are produced by die-cutting sheets, so parts from these sheets will have the cell network exposed on all cut edges. Some finished goods such as cleaning sponges may require exposed cells on all sides, requiring the slitting of the top and bottom surfaces from the molded sheet prior to cutting individual parts.

Some open-cell sponge parts require a skin or coating that is more durable, water resistant, or weather resistant. Curing a dense skin around a cured sponge part, or conversely curing sponge rubber into a previously cured dense rubber skin, can meet this need. The latter method will not work well if the sponge has to be completely encapsulated, since this does not allow the "blow" gases to escape. A second method involves dipping the part into a suitably compounded latex, so that the latex coating can be built up to the required thickness through multiple dipping. A third method involves assembling a cured sponge part into a cured dense skin using adhesives.

Sponge rubber parts generally cannot be manufactured to the tighter tolerances of dense rubber parts. A good guideline for dimensional tolerances of open-cell sponge, as well as a discussion of defect types and tolerances, can be found in the Rubber Manufacturers Association's *Rubber Handbook for Molded, Extruded, Lathe Cut and Cellular Products.* 

#### **Open-Cell Sponge Compounds**

The following are selected formulations that produce different types of opencell sponge compounds:

Ingredients	phr	
Natsyn [®] 2210 Polyisoprene	100.00	
N990 Carbon Black	6.00	
Whiting	50.00	
Paraffinic Oil (Low Viscosity)	20.00	
Wingstay [®] 29	1.00	
Sodium Bicarbonate	4.00	
Zinc Oxide	7.00	
Stearic Acid	10.00	
Sulfur	3.00	
Salicylic Acid	1.00	
UNADS [®] Accelerator	1.00	
Total	203.00	

#### Firm Polyisoprene Sponge

Xtra-Firm EPDN
----------------

Ingredients	phr	
Vistalon™ 3666B	100.00	
Brown Factice	10.00	
N990 Carbon Black	40.00	
Whiting	80.00	
Paraffinic Oil (Low Viscosity)	38.00	
Sodium Bicarbonate	22.00	
Zinc Oxide	5.00	
Stearic Acid	5.00	
Sulfur	2.00	
CAPTAX [®] (MBT) Accelerator	1.00	
METHYL ZIMATE® Accelerator	0.70	
METHYL TUADS [®] (TMTD) Accelerator	1.25	
Total	307.95	

# Medium Chloroprene Sponge

Ingredients	phr	
Neoprene W	100.00	
80% Magnesium Oxide	4.00	
Cotton Flock	4.00	
N990 Carbon Black	40.00	
DIXIE CLAY [®] (Hard Kaolin Clay)	11.00	
Whiting	40.00	
Paraffinic Oil (Low Viscosity)	12.50	
Highly Aromatic Oil	35.00	
Wingstay 29	1.00	
Sodium Bicarbonate	13.00	
Zinc Oxide	5.00	
Stearic Acid	12.75	
75% ETU Dispersion	3.50	
METHYL TUADS (TMTD)	1.25	
Total	283.00	

# Soft Nitrile Sponge

Ingredients	phr	
NBE (Low Mooney, Med. ACN)	100.00	
N990 Carbon Black	50.00	
DIXIE CLAY (Hard Kaolin Clay)	150.00	
Whiting	54.00	
DOP	1.00	
Wingstay 29	10.00	
Sodium Bicarbonate	5.00	
Zinc Oxide	15.00	
Stearic Acid	3.00	
ALTAX [®] (MBTS) Accelerator	2.00	
Total	390.00	

### CLOSED-CELL SPONGE RUBBER

## by David Flood*

Derby Cellular Products Derby, CT *Retired

Closed-cell sponge rubber consists of individual, unconnected bubbles. The bubbles are created by the decomposition of a very finely divided blowing agent, and are separated by thin polymeric walls. The closed-cell sponge is unable to absorb water, even under an imposed vacuum. This is one of the primary characteristics of this type of cellular rubber.

Closed-cell products can be manufactured by three basic methods: low pressure molding, high pressure molding, and continuous extrusion.

Low pressure molding is performed by partially filling the mold cavity and relying on expansion to complete the fill. An initial charge is placed in the mold by hand, transfer or injection. Under preset curing conditions, the material is allowed to completely fill the cavity, thereby taking its shape. If the cavity is overfilled, the resultant part will be oversize or puffy and too firm. Too little material will produce non-fills, or the part will be overexpanded and too soft, or may even collapse.

High pressure molding requires the cavity to be completely filled. A two step curing and, in some cases, a two step expansion system is employed. High external pressure keeps the cavity closed while the compound partially cures, and either completely or partially activates the blowing agent(s). When the pressure is released, the pad expands beyond the confines of the mold. The pad is then postcured to normalize the dimensions and improve certain physical properties such as compression set resistance. With a two stage blowing agent system, this postcure allows the secondary blow to occur, which results in a much larger finished part. Pads up to 2 meters square by 10 cm thick (6 feet square by 4 inches thick) have been produced.

Continuously extruded closed-cell sponge is the culmination of the technology of sponge manufacture. Balancing the proper cure system with the correct amount and type of blowing agent will produce the desired finished part. These systems can be very sensitive and sometimes quite complex. The cure rate must be fast enough to retain the evolving gases and allow proper expansion. However, if the cure is too fast, poor expansion and an overly dense product will result. Ruptures within the cross-section, splitting or unnatural curling can also occur.

The blowing agents used in all three types of closed-cell sponge release nitrogen. Nitrogen has much lower permeability than carbon dioxide, so it normally results in non-interconnecting or closed cells. The three most important commercial blowing agents of this type are azodicarbonamides (AZO), dinitrosopentamethylene tetramine (DNPT), and various hydrazides such as benzenesulfonyl hydrazide. DNPT has lost favor due to its strong residual

odor. Hydrazides are used for low temperature, 110 to 165°C (230 to 325°F), expansion work. Azodicarbonamides work at high temperature, 175 to 205°C (350 to 400°F). The AZOs can be activated to produce gas at lower temperature through the use of finely divided treated ureas, ethylene glycol or zinc-bearing compounds. Blown densities of 100 to 750 kg/m³ (6 to 45 lbs/ft³) are easily attainable.

Choosing the correct type of polymer and filler system is also very important. Polymers with fast cure rates may be used individually or in blends to ensure good green strength and shape retention properties. Blending various types of semi-reinforcing blacks (FEF, SRF and GPF) with mineral fillers such as clay, whiting, talc or treated silica will produce a matrix that will expand readily to the desired parameters. Over-reinforcement will cause poor expansion and, frequently, rupture of the extrudate. Plasticizers are selected according to the nature of the base elastomer, and oils that impart special characteristics to the finished product may also be incorporated.

The mixing of these components is done in an internal mixer, normally using a two pass mix. Consistency of mixing is essential to ensure minimal fluctuations in the extrudate and the curing process. New machinery, such as internal mixers with four wing rotors, intermixers, and twin-screw extruders, have been developed to improve the consistency of mixing.

The type of curing apparatus used to vulcanize and expand the extrudate is as important as the proper compound. The heat sources used are circulating hot air, liquid curing media (salt bath), fluidized bed (Ballotini), microwave, infrared or any combination of the above. Extrusion speeds depend on the heat transfer efficiency of these media, and the type of cross-section being run. Sections with hollow areas usually require a slower speed because of the poor heat transfer inside the extrudate. A well-maintained extruder and properly tuned die will complete the process.

The finished extrusion must meet established specifications: ASTM D 1056 for general purpose parts, ASTM C 509 for architectural seals, SAE J18 for automotive use. Other very stringent specifications may require polymer-specific closed-cell compounds. Neoprene and nitrile rubber are used for oil resistance. EPDM, silicone or EPDM/silicone blends are used for high temperature resistance. Some plastics and the new TPEs, TPOs and TPRs are being extruded and expanded into numerous shapes. For most of these newer composites, specifications are developed by the customer with the close cooperation of the supplier. Typical properties for all closed-cell sponge products include compression deflection, compression set, density, load loss set, water absorption, ozone and flame resistance to algae and fungi through the addition of certain antimicrobials.

Closed cellular extrusions have found a multiplicity of uses, such as weather seals in automobiles, trucks, farm machinery, military and recreational vehicles; and architectural seals for doors, windows and garage doors in the home. Scuba divers use expanded Neoprene wet suits for underwater warmth and protection. Cellular PVC/Nitrile is used for pipe insulation in schools and all types of industrial and public buildings.

The following formulations are good starter compounds for their respective processing methods:

Ingredients	phr	_
Ultra Fast Curing EPDM	100.0	_
Stearic Acid	20.0	
Zinc Oxide	5.0	
AGERITE® SUPERLITE®	1.0	
DIXIE CLAY [®] (Hard Kaolin Clay)	80.0	
McNAMEE [®] CLAY (Soft Kaolin Clay)	80.0	
Whiting	100.0	
Azodicarbonamide	4.0	
BIK-OT	2.0	
Sulfur	2.0	
CAPTAX [®] (MBT) Accelerator	1.0	
METHYL TUADS® (TMTD) Accelerator	1.5	
Total	396.5	
Mixed Density, Mg/m ³	1.47	
Cured 10 min. @ 149°C, Postcure 20 min. @ 149°C		
Compression Deflection, kPa	90	
Blown Density, kg/m ³	440	
Water Absorption, Mass %	<1	

## Closed-Cell Sponge: High Pressure Molded, Low Cost Formulation

### Closed-Cell Sponge: Extruded, General Purpose

Ingredients	phr
Very Fast Curing EPDM	100.00
Stearic Acid	2.00
Zinc Oxide	5.00
N550 FEF Carbon Black	30.00
N774 SRF Carbon Black	60.00
Whiting	35.00
DIXIE CLAY	30.00
Sunpar [®] 2280	80.00
Celogen® AZ-199	10.00
METHYL ZIMATE [®] Accelerator	1.25
CAPTAX (MBT)	1.25
THIATE [®] U (DBTU) Curative	2.50
ETHYL TELLURAC [®] Accelerator	1.00
Total	358.00
Cured 4 min. @ 182°C, Postcure 4 min. @ 218°C	
Compression Deflection, kPa	100
Blown Density, kg/m ³	290
Water Absorption, Mass %	<1

## RUBBER-COVERED ROLLS

## by Ted Muzyczko

Finzer Roller Des Plaines, IL



## Applications

Rubber-covered rolls find application in many industries — notably graphic arts, paper manufacturing and processing, steel processing, textile processing, metal coating and leather processing. In graphic arts applications, they are usually called "rollers", but the two words are generally interchangeable. Rolls vary in size from very small, a few millimeters (fractions of an inch) in both diameter and length, to very large. Some paper mills now use rolls two meters (six feet) in diameter and more than 10 meters (33 feet) long. Hardness normally varies from 10 Shore A to "bone hard". As a class they are cylindrical and firmly bonded to a rigid core, usually made of metal.

Once the roll/roller application requirements are determined, the main design considerations are as follows:

- Core construction: material, overall length, body length, thickness, diameters, centers, shoulders, journal design, dead shaft configurations, keyways, gears, temperature controls, bearings and their placements, finishes and balancing.
- Loads, load distributions, surface speeds, driven or driving functions, nipping roller(s) and/or web contacts.
- Cover material(s), adhesives, construction and finishes, hardness and wall thickness.
- Environment, contact fluids, temperature and maintenance.
- Transport requirements, storage, and record keeping and training in proper handling.
- Economics: product/process value added, initial and maintenance costs, life expectancies, removal and replacement (down time) costs.



Figure 1: Roller Definitions for a Live Shaft/Journal Construction

The graphic arts industry is a major user of rubber-covered rollers. Rolls are used in most types of letterpress and offset printing presses to break down and convey the ink to the printing plate. These rollers are made of oil-resistant rubbers and generally run from 20 to 40 Shore A hardness. They are mostly in the small size range, i.e. less than 17 cm (7 in.) in diameter. Some printing occurs at very high web speeds, approaching a kilometer (3000 feet) per minute, so the compounds must be carefully designed to withstand severe dynamic conditions, even at these low hardnesses. Newer inks based on soy oils and acrylates (for ultra violet or other high energy curing) are getting more common, and require the formulation of special cover compounds.

The principal elastomers used for offset lithography are nitrile (NBR), PVC/nitrile, urethane (PU), EPDM and polyamide. Nitrile, Neoprene (CR), PVC/nitrile, EPDM, urethane and polyalkylene oxide (ECO) are commonly used for gravure. Nitrile, PVC/nitrile, EPDM, natural rubber and urethane are normally employed in flexography.

The *converting industry* often uses a hybrid combination of offset, flexo, letterpress and gravure printing in which a variety of drive and transport rollers are used. Rolls are also used for coating, laminating, corona treating, embossing, die cutting and spreading.

The *paper industry* employs the largest rolls. The hardness for couch rolls used in cylinder machines may be as low as 30 Shore A, but normal press rolls are in the range of 80 Shore A and higher. The hardnesses of paper mill rollers are normally specified in Pusey & Jones (P & J) rather than Shore A. Press rolls are designed to mechanically squeeze the water out of the newly formed paper web and compact it to the desired thickness. Some paper mill press rolls are bonded to the metal by the so-called hard rubber base method, often in addition to the chemical adhesion methods used on most other types of rolls. This is particularly true when cast iron cores are used. The most common cover materials are nitrile, EPDM, Hypalon[®] (CSM), SBR, Neoprene, natural rubber and urethane.
*Steel mills* require rubber-covered rolls in most of their strip-processing lines such as pickling, galvanizing, tin or chrome plating, and cleaning. Rubber coverings provide traction, wringing action between processes, corrosion protection for metal rolls, and reduction in noise levels. They are often grooved to provide better control of the web during processing. These rolls are usually of medium size, 15 to 90 cm (6 to 35 in.) in diameter and 1.2 to 1.9 m (4 to 6 ft.) long. Nitrile, Hypalon, Neoprene and urethane are the typical covers.

*Textile mills* use rubber-covered rolls in many processes. The smallest ones, (known as textile cots) are employed to pull the fibers through the yarn-spinning process. These are only about 2.2 cm (1 in.) in diameter and 2.2 to 15 cm (1 to 6 in.) long. Rubber rolls are also found in the slashers that apply the proper amount of sizing to the yarn before weaving, and then used again in the washing process to remove this sizing. They are also used in the padders to dye the fabrics, and in bleaching equipment. Most of these processes involve squeezing water or water solutions out of the cloth, and the rolls generally range from 60 to 85 Shore A hardness. Nitrile, Hypalon and urethane the most commonly used elastomers.

The *metal-coating industry* is another major user of rubber-covered rolls. Metal coating may be done on continuous coils or on pre-cut sheets. In both cases, the coating is applied by rubber-covered rolls usually in the 20 to 50 Shore A hardness range. These rolls must be very carefully formulated to resist the solvents in the coatings, as well as the cutting action of the metal edges. In the metal decorating industry, two-piece and three-piece cans are coated and printed. The covers for coater rollers are based mainly on urethane or EPDM compounds. Three-piece cans are printed by an offset process with cover compounds based on nitrile rubber. Two-piece cans are printed by a letterpress process with covers made from urethane, EPDM or Hypalon.

*Leather processing* also requires rubber-covered rolls to convey the leather through the various operations. These are normally made of oil resistant rubbers in the medium hardness range.

*Plastics processing* requires rubber-covered rolls to support (backup) calendering and embossing operations. These rollers may be made from nitrile, Hypalon, silicone or urethane.

Pulley lagging rollers are used in a number of industries. These look more like wheels than conventional rollers. The rubber cover is the "lagging." These rollers are used with belts to convey ore, rocks, grain, minerals or other particulate materials. They are used for cushioning, metal protection, damping or noise reduction. They can be idlers or may be the driving rollers. They may be built by standard roller manufacturing methods or may even be made by mechanically attaching or affixing cured rubber sheets to the base sheaves or cores. The compounds used are typically based on SBR, natural rubber, nitrile or urethane.

Finally, there are many dozens of specialty rollers that require unique rubber compounds. These include copier rollers; spreaders; high-release, traction or high-tack rollers; controlled electrical conductivity rollers; grooved and crowned rollers; very high-pressure rollers; specialty pulley coverings and waxing rollers.

Rubber roller covers are truly the "tires of industry." Virtually every base polymer "family" has been used depending on the application. Table 1 summarizes the more commonly employed elastomers, their typical Shore A hardness ranges and their applications. A variety of other rubber cover compounds are used to a lesser extent. These include carboxylated nitrile (XNBR), HNBR, TPR, blends such as silicone/EPDM, and specialty fluorocarbons and fluorosilicones. Plastics such as epoxies, polyamides are also used.

Elastomer	ASTM Designation	Hardness Range	Typical Applications
Acrylonitrile-butadiene Rubber, nitrile, Buna N	NBR	15 to 100	lithographic, letterpress, gravure and flexo printing, paper
PVC/Nitrile alloy (blend)		20 to 100	printing
EPR, EP(D)M, Ethylenepropylene (diene) Monomer	EPDM	25 to 90	coating, UV/EB printing rollers, nip rollers, paper processing
Natural Rubber, Polyisoprene	NR, IR	40 to 99	paper mills
Styrene-Butadiene Rubber, GRS, Buna S	SBR	40 to 90	idlers, pulley rollers, drive rollers
Chlorosulfonated Polyethylene, Hypalon	CSM	40 to 90	laminating, film, paper, extrusion, embossing, corona treating
Neoprene, Polychloroprene	CR	20 to 90	idler, flexo, gravure, paper, waxing, squeeze
Silicone, Polydimethyl siloxane	VMQ	30 to 80	laminating, extrusion, corona treating, release, waxing, copiers
Polyurethane (polyether, polyester)	AU, EU	10 to 99	idler, pull, feed, paper, metal/wood coating
Fluorocarbon	FKM	60 to 90	backup embossing, metal processing lines, nip rollers
Polysulfide, Thiokol®	Т	30 to 75	graining and coating
Polyacrylate	ACM	40 to 90	feed and idler rollers
Polyalkylene Oxide, Hydrin®	ECO, CO	80 to 95	ESA gravure

 Table 1: Rubber Roller Covers and Applications

# **Roller Design Factors**

The design of elastomeric roller covers for various applications depends on the following major factors:

- 1. Supporting Frame
- 2. Core Design
- 3. Bearings
- 4. Cover Characteristics/Specs
- 5. Economics

Virtually all rollers contact other rollers or other surfaces such as sheets or webs, which in turn are often supported by other rollers. Figure 2 shows the pressure factors experienced by the two main types of roller surface contacts.



Figure 2: Nipped vs. Unnipped Web Pressures

As can be seen, unnipped (web-wrapped) rollers generally do not experience the pressures that nipped rollers do. An exception would be heavy, high modulus webs.

Deflections should be minimized, for the best performances. Some very general examples of "Rules of Thumb" are:

- To <u>minimize deflection</u>:
  - Wrapped roller: L/D < 10
  - Nipped roller: L/D < 5
- To minimize drag issues:
  - Turning torque < (radius) (1% of tension)
- To <u>check balance</u>:
  - A spun roller should stop randomly (no heavy side)

The point of contact or common surface area created is called a nip. The socalled stripe, flat or footprint pattern observed (w) is probably the most important performance feature of a roller system. The pattern desired is usually a uniform stripe along the working face lengths of the contacting rollers as shown in Figure 3.

Nip widths or stripes (w) may be measured by inking or coating rollers, by the use of carbon paper, foils, photographic film or by special sensors. The axial (lengthwise) deflection or indentation of the hard roller into the soft roller affects the uniformity of the nip width.



Figure 3: Roller Nip Pattern or Stripe of Two Rollers in Contact

The effects of deflection on the elastomer surface contact pressure-profile curve are shown in Figure 4.



Figure 4: Nip Pressure vs. Width

As is apparent, nipped rollers generally experience higher loads than their wrapped counterparts. These systems have been researched to a great extent. Most studies are conducted using the model of a "rock-hard" roller nipped against an elastomer-covered roller. Two types of nips are of concern to roller designers and users:

- Static Nips
- Dynamic Nips

#### The Static Nip

When touching rollers are stationary, the nip created is called *static* nip. Static nip patterns are relatively easy to measure. The most common and most studied system is that of a hard roller (usually metal) pressing or penetrating into a soft roller. The stripe or footprint or nip width is a function of the impressed load, the contacting roller diameters, and the soft roller cover thickness, Poisson's ratio for the soft roller and the soft cover hardness or modulus. The depth of penetration, though complicated, is a function of the roller geometry. Equations for nip widths and contact penetrations as functions of impressed loads are available and are summarized in the section on Static Nip Equations.

A characteristic soft cover stress (pressure) versus nip width profile curve is often used to describe a two roller, soft/hard system. For the static nip, the curve is symmetrical about a point of maximum pressure,  $P_{M}$ , which is located in the center nip of the nip width or stripe and is shown as the peak in Figure 5 below.



Figure 5: Static and Dynamic Pressure vs. Nip Width

The nip force or load per linear (axial) distance (in kN/m or lbs/linear inch, pli) is the <u>key</u> value that describes the nip profile. This assumes equilibrium <u>static</u>, dry, constant-temperature conditions created by the uniform impression of an ideal hard roller (i.e. axially and radially undeflected) into a uniformly deflected soft roller. The curve is a symmetrical parabola/sine type. The average pressure ( $P_A$ ) and the maximum pressure ( $P_M$ ) can be computed using the following equations:

## $P_A = N/bw$ (Note when N = PLI, b = 1) and $P_M \approx 1.3$ to 1.5 $P_A$

 $P_{\rm M}$  is an important consideration for bond activation pressures in laminates, fluid transfer pressures in coating or printing and the distortion of sheets or webs. All stress (pressure) versus stripe (nip width) profile curves that have the same load (N/m or pli) also have the same areas under the pressure vs. nip width curve. In summary, at a given temperature, the static nip width or stripe

is a function of:

- Load. Increasing the load will increase the stripe (w) and both P_A and P_M. Loads vary from as little as 90 to 525 N/m (0.5 to 3 pli) for offset press rollers to 3.5 to 52 kN/m (20 to 300 pli) for gravure impression or laminating rollers and over 175 kN/m (1000 pli) for embossing or paper mill press rollers.
- The diameter(s) of the hard and soft rollers. Decreasing either or both decreases the stripe, increases the average pressure ( $P_A$ ) and increases the maximum pressure ( $P_M$ ).
- The thickness of the soft roller cover. Reducing it decreases the stripe (w) and increases both  $P_A$  and  $P_M$ . Cover nips can vary from as little as 1.6 mm (1/16 inch) to over 5 cm (2 inches) in thickness.
- The hardness or modulus of the soft roller. Increasing the hardness decreases the stripe and can increase both P_A and P_M. Hardness varies from 5 to 10 Shore A for some coating rollers to 80 to 100 Shore A for squeeze or laminating rollers.
- Recent studies have shown that although it is difficult to measure Poisson's ratio for roller covers, its value can have a significant effect.⁷
- If there is a sheet or web in the nip, the pressure-nip profile curve will be affected. Also, increasing the temperature will decrease the modulus and hardness (not linearly) and cause expansion of the elastomer, both of which will increase the stripe width – all other factors kept constant.

## **Static Nip Equations**

There are a number of static nip equations available in the literature. When using these it is important to be aware of the researcher's caveats. Two of the more interesting equations are shown below:



Note: Units in inches, pounds; P & J Hardness — 1/8 in. ball: check specific conditions and limitations at ref: Tappi Journal September 1986, page 66

The following equation was developed by Dr. J. K. Good⁸ and published as follows:

$$N = \frac{F_N}{w} = \frac{2}{3} \frac{(1-v)^2}{1-2v} \frac{E_o}{1-v^2} \frac{\sqrt{2r}}{t} \delta^{\frac{3}{2}}$$

According to Dr. J. K. Good this equation can be used for rubber strains up to 7 percent. *N*, *F*_N and *W* are explained below in Figure 6.  $\delta$  is the penetration or indention of the hard roller into the soft one.  $\nu$  is Poisson's ratio. *t* is the soft elastomeric cover thickness. *E*_o is Young's modulus without confinement effects. Note the average pressure, *P*_A = *N*/*b*.



Figure 6: Nip Force vs. Nip Width (N)

It is possible to solve for the indentation ( $\delta$ ) or the average pressure (P_A) with the appropriate rearrangement of the equation and within the limits of the study. All pertinent forces/weights, including the weight of the roller, should be included.



Figure 7: Footprint vs. Engagement

Note, Dr. J. K. Good has also established the following relationship between Young's moduli and Shore A hardnesses for a variety of elastomers. The Shore A hardness was considered to be equivalent to IRHD.

$$E_o(psi) = 20.97 e^{0.0564 (Shore A)}$$
$$E_o(kPa) = 145 e^{0.0564 (Shore A)}$$





Other static nip equations of interest are based on the work of Deshpande¹ and McPhee⁹.

*Nip/Load Measurements* — Whenever possible, it is desirable to measure nip-widths/footprints and then to establish correlations and conclusions. The techniques employed include: carbon paper, patterned aluminum foil, liquids, sticky notes, conductive inks, sensor films and direct reading sensors.

#### The Dynamic Nip

Rollers are made to "roll." They are driving or being driven, coating or being coated or perform other specialty functions such as web-spreading, beltaligning, squeezing or dewatering. The dynamic nip width or stripe is a function of the impressed load, the roller diameters, the soft cover thickness, the dynamic modulus of the soft cover and the surface velocity. The last two factors are related.

Pressing a soft roller into a rolling hard roller results in a larger "effective" diameter. This effective frictional drive diameter increases in proportion to the squeeze or penetration. In the nip, the elastomer is tangentially stretched. This phenomenon may be of concern if thick-walled soft covers are used under relatively high loads.



Figure 9: The Pressure Profiles of Two Rollers in Contact

Cover shear stresses are also an important consideration since they can lead to pitting and delamination failures. The maximum shear stress is located inward from the cover surface. One estimate is that this stress can be found about one nip width into the cover surface.

Most roller covers are viscoelastic. That is to say that the complex modulus of elasticity has a sizable viscous component. Dynamic mechanical test equipment can cycle an elastomer through strain cycle to generate an ellipse, whose area is proportional to the energy loss and the major axis is related to the dynamic modulus of the compound.

A common method of measuring loss factors is to look at an elastomer's response to sinusoidal displacement. The oscillating force leads the strain by a certain phase angle that is indicative of the size of the viscous component. Both dynamic modulus and phase angle ( $\delta$ ) change with temperature, test frequency, static deformation and dynamic deformation. These factors are compounded by friction, changing roll surface conditions, environmental (fluid, aging, etc.) effects and contact nips. The prediction of dynamic performance is challenging. Pilot testing is helpful, but the ultimate test is application performance. As will be appreciated, the dynamic nip is quite complex and is not easy to predict. It is best determined by actual measurements. Nevertheless, certain general qualitative relationships can be put forth. With higher roller speed, the following changes occur:

- Complex (E*) and viscous (E") moduli increase.
- Phase angle ( $\delta$ ) and tangent  $\delta$  increase.
- · More energy is lost per cycle, hysteresis or heat buildup are higher.
- · Rolling friction and rolling resistance increase.
- Nip width and nip width shortening from exit site (see Figure 3).
- P_M increases and shifts towards the entrance site (see Figure 3), and
- P_A increases.

In these simplified, ideal-model examples, the effects of additional friction due to windage, bearing drags, etc. are neglected. In the real world, heat build up causes modulus decrease, elastomer expansion and a larger nip. Nip research is continuing and the use of computer programs such as finite element analysis (FEA) is becoming more common among design engineers and researchers.

#### **Factors Affecting Roller Covers**

Some of the main factors that can affect roller covers are:

*Cores* — Regardless of the cover material chosen (or specified) or even the manufacturing process employed, good roller performances start with a correctly designed, installed and maintained core. The best cover material will not perform optimally if the core is inadequate. Special attention must be paid to performance criteria based on loads, deflections, balancing, centers, journal/bearing seat constructions, dead shafts and bearings. Support frame considerations should not be neglected.

Each time a roller is to be covered, the core must be examined and repaired or replaced as needed. As an example, poorly fitting or damaged bearings can lead to heat build-up, cover expansion and increased (often localized) pressure, all ultimately resulting in premature wear, uneven surfaces and failure.

Temperature – Elastomers can expand much more than steel under a comparable temperature rise (up to tenfold). Moduli also usually decrease as temperatures rise. Nip widths can increase. Solvent sensitivities and chemical reactions that can harden or soften rollers will be exaggerated at higher temperatures. End flare effects can be of concern. The interior roller cover temperature is usually higher than can be read at the surface and there are temperature gradients throughout the roller walls. Internal core heating or cooling is the most effective method to achieve maximum temperature control in critical processes. Surface cooling/heating is used but is not as efficient.

Surface finishes – These can affect friction, traction, slippage and release characteristics. Rougher surfaces can provide more effective surface areas for surface reactions. Irregular surfaces can mean different contact zones. Very smooth surfaces ( $R_A$  = 10 to 20) are sometimes required. Stress concentration sites should be avoided. Further, coefficients of friction between <u>all</u> contacting surfaces should be considered, especially for stresses that are imparted to sheets or webs.

Surface geometries – If the rollers are grooved, the contact areas will obviously be different. Excessive eccentricities can create variable nip profiles "around" the circumferences as well as along the face lengths.

*Compositions* — Some compounds dissipate heat more readily than others, have better thermal conductivities and/or dynamic properties and consequently expand less. Others are formulated for shock absorption, specific critical surface tensions, etc. Some elastomer covers are composed of layers such as hard bases, soft bases, and compressible surfaces or bases. These can generate very different nip profiles.

Environment – Oxygen, ozone, nitrogen oxides and other environmental gases or solvents will affect roller surfaces and overall characteristics. Many roller coverings exhibit selective absorptions of specific chemicals even though they may be present in very small quantities or concentrations. Also as the solubility parameter concepts have shown, the combination of several solvents can be very aggressive even though each solvent alone creates less of an effect. Of course, higher concentrations of environmental chemicals will increase penetration and rates of reactions. A lot of ingenuity is needed to develop elastomer compounds whose surfaces will be adequately wetted by the desired coatings, but that will not be progressively destroyed.

*Thicknesses* — Figure 10 depicts soft covered rollers nipped against hard rollers, with the static loads being the same in both directions. The pressure profiles (nips) vary as functions of diameter increases and/or hardness decreases and/or soft cover thickness increases.



Figure 10: Roller Cover Thickness, Diameter and Hardness Relationships

Soft Cover Thicknesses, T2 > T1; Soft Cover Roller Diameters, D2 > D1; Nip Widths, N2 > N1; Peak Pressures, P1 > P2; Soft Cover Hardnesses, H1 > H2; Impressed Loads (PLI), L1 = L2; Areas under the pressure profile curves, A1 = A2;

*End Effects* — Ends require special attention. Most of the time a hard roller is pressed into a soft roller by loading the journal ends; high load deflections can create an "hourglass" stripe. The resulting "family" of pressure profiles will be different along the loaded face length. These profiles are usually symmetrical. In extreme cases, the pressure and stripe in the center can be zero, while the ends will show high pressures and wide stripes. The <u>specific</u> pressures along the stripe will also be correspondingly different. (See the section on crowning.) Well-designed cores will deflect little, show uniform loading and indicate an even

stripe. Applying a uniform load to the journals is no guarantee that the stripe will be uniform. Either more details must be provided, or stripe measurements made. End beveling or dubbing is preferred whenever possible.



Figure 11: Typical Roller Cover End Trimming Geometers

Hardness - Soft roller hardness measurements are mostly made with Shore A, B, D, O, etc. durometer instruments or a P & J plastometer. These are related to modulus. The type "O" Shore and P & J instruments have reasonable correlations to modulus. Hardnesses and moduli generally decrease with increasing temperature, so temperature differences will result in different hardnesses. In general, the lower the cover's hardness, the greater is its sensitivity to environmental attack, and the poorer are the physical properties. Uneven hardnesses along the lengths or circumferences of rollers will show different pressure-stripe profiles. It does not matter if the source of variable hardness is due to compound variability, environmental attack or temperature, the result is the same. A good recommendation is: whenever possible use the greatest hardness roller cover consistent with the requirements of the application, i.e., pressure, fluid transfer, traction, release, etc. Increasing the hardness improves most physical properties and resistance to many solvents, but softer covers are more forgiving in their settings and transfer fluids more readily. Measuring roller hardness accurately with hand-held instruments is not an easy task. Because of this difficulty, an industry standard is plus of minus 5 points from a specified hardness and a range of 4 points within a cover (before installation) using the Shore A durometer scale. Note the relationship between Shore A hardness and Young's modulus shown earlier.⁷ A similar relationship has been shown to exist between P & J measurements and modulus.

*Poisson's ratio* — Some recent work, cited earlier has shown that the measurement of this factor is difficult, but can be significant.⁷

*Crowning* — Covered rollers are often "crowned" by creating a convex or concave roller surface, either linear or curved, as depicted in Figure 12. Hard rollers may be crowned in order to compensate for deflections or to track webs.

Crowning both the nipping soft and hard rollers will minimize nip contact area surface speed differentials. When excessive loads are applied to the journals or shafts of nipped rollers, axial deflection occurs that distorts the nip width or stripe.

The loads that cause deflection may be due to the roller weight(s) and/or impressed forces. The axial load deflection curve is approximated by a parabola or cosine function. Energy is expended in deflecting rollers. Uneven stripes can mean differential fluid transfers. If the contact length to diameter ratio of each roller is less than 5:1 for nipped rollers, then in general little if any crowning will be needed, depending on the applied load. The deflection problem can be addressed by using stiffer cores (materials, diameters, thicknesses, geometries, etc.), lighter settings, false crowning and crowning. The amount of crowning (C) needed in excess of given diameter(s), can be estimated from nip impressions.

A "false crown" is created when the two nipping rollers in question are skewed. This allows more fluid to pass through the ends. But a given crown configuration will only be good for one set of load conditions. The ends are usually dubbed or stress relieved in the "non-active areas".

Not all nipped rollers are vertically oriented, so deflections caused by screw, air or hydraulic source loads may be horizontal, while roller weight deflections caused by gravity would be vertical. Typically, the roll bends more in the center than at the ends. That is, core journals, shoulders and ends (due to header insertions) will usually deflect less than core bodies. There are many texts and computer programs that address this subject.



Figure 12: Concave and Convex Crowned Rollers

Crowning Concerns:

- 1. Cores alone may be crowned, depending on the cover type
- 2. Both contacting rollers may be crowned
- 3. Cover hardness has no effect on crowns, but
- 4. Softer covers can "forgive" crown irregularities

- 5. A crown is good for only one load condition
- 6. Use nip papers/foils to determine crown needs
- 7. PLI counts, not the psi of the gage
- 8. Thermal crowning can occur
- A uniform nip does not mean uniform pressure across the loaded face; crown diameters are not as important as different cover wall thicknesses so that the process may not be affected, but the roller cover life will be.



Table 2: Diagnosing Roll Stripe Patterns

Failure Analysis – Rollers can and eventually do fail. Sometimes the causes for rejection during manufacture are the same or similar to the causes for failure in the field. As an example, trapped air or gases generated either during vulcanization or with heat build-up in service are probably the number one enemy of roller covers, and can lead to rejection in manufacturing and/or problems in a given application. Table 3 summarizes the main causes for rejection in manufacturing

and modes of field failures.

Other factors to consider are specialty balancing (static and/or dynamic), alignments, drives, support frames, maintenance schedules, etc. These topics are best addressed by the machine equipment designers and manufacturers.

Type of Manufacturing Reject or Mode of Field Failure	Μ	S/T	Т	Α
Specifications, tolerances not met or not correct	Х	Х	Х	Х
Core, journal bearing faulty	Х	Х	Х	Х
Wrong cover material for manufacturing	Х	Х		Х
Contamination, cure system not optimized	Х			Х
Air (gas) trapped, blisters, ply separation	Х			Х
Constriction lines, bond failure, or surface finish incorrect	Х			Х
Environment too hostile for material	Х	Х	Х	Х
Insufficient protective wrapping, boxing or storage		Х	Х	Х
Installation incorrect			Х	Х
Maintenance not performed				Х
Installation incorrect Maintenance not performed			Х	X X

Table 3:	Possible	Sources	of Roller	Failures
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M = Manufacturing, S/T = Storage/Transportation, I = Installation, A = Application

## Summary of Roller Performance and Failure Factors:

- The equations and factors mentioned above are for the very important characteristics of covered roller surface contact stress/strain analyses and predictions. But much is also happening under the surface.¹²
- Cover surface contact stresses can be determined relatively easily for the two roller, hard/soft static conditions. Equations are available and measurements can be made. FEA can be used, but for small deflections the J. K. Good equations might be better. P_A and P_M and area distributions under the PLI/ nip width curves are important in analyzing laminating, coating, driving etc.
- Dynamic measurement on the fly are possible, but set ups are costly and any extrapolations made must be done with caution.
- Imbedded chips and other sensors along with FEA modeling techniques are being used in critical applications and for roller research.
- For running conditions the dynamic nip width shortening is factor. Also running moduli will be increased in amounts depending on the cover compound.
- Choose cover compounds wisely, noting mechanics, environments, and transports.
- Don't overlook appropriate bearings. Use cool running low friction types.
- Avoid stress concentration sites.
- Pay special attention to roller "ends" and end effects.
- Deflections are inevitable. Compensating core constructions or roller geometries are important for balancing, vibrations etc. Alignments must be considered. Solid supports are also important.

- Cover/core crowning can correct deflections. These can be + or and simple or compound. Skewing or "false crowning" is sometimes used as an expedient.
- Stripe patterns, though representing a sample of the circumference can be diagnostic. Actual nip width/load measurements are the most reliable and can be used in conjunction with nip/load equations.¹⁰ FEA modeling is becoming more popular.
- Rollers or roller assemblies must be installed properly to insure acceptable performances. Supports should be solid. Bearings in particular must be squarely and carefully inserted. Bearings that are incorrectly inserted or that are damaged can cause excessive rubber roller cover heat buildups, uneven stripes, and high local pressures — all leading to poor quality production and premature cover failures.
- In analyzing failures, remember that there can be multiple antagonisms involved.
- Covered roller surfaces do not always experience uniform running conditions in either the machine direction (MD), or the cross direction (CD) due to, material limitations, process variables – all of which are determined by economic factors i.e., cost/performance ratios. Even with good traction/ friction some slippage occurs and slippage under load means abrasion. In one study it was confirmed that higher rates of abrasion occur with irregular surfaces.
- Wrap webs around the harder roller, if possible.
- Surface energies are a consideration in fluid transfer applications.
- A leading contributor to roller cover failure begins about one nip width down from the surface as a maximum shear stress. A crack can begin parallel to the surface and angles up.
- The maximum heat build-up from hysteresis can occur about 1/3 in from the surface, according to some studies.
- Covers can expand with heat up to 10X that of steel per a °F rise. As cover temperatures rise, physical and chemical properties suffer.
- If rollers are reground, the effects of the new pressure profile of the new wall thicknesses should be considered.
- Layered roller covers are vulnerable to weaknesses or failures at the lowest modulus component.
- Poissons's ratio can be a significant but often overlooked factor.
- · Keep performance records.
- Which leads us to "The Golden Rule of Covered Rollers": Assuming that a well designed core and good bearings are used, and the assembly is securely mounted and well aligned, in general, regardless of the process or cover type, the best performance/life of a roller is usually experienced when the greatest appropriate hardness and best geometry cover is chosen and the roller is set as lightly as possible and is essentially running in traction and is maintaining a uniform nip in an acceptable environment.

#### **Roller Production**

Roller production begins with the selection or rebuilding of suitable cores/ spindles. Special attention must be paid to the journals and bearing seats. If necessary, the cores should be balanced. The base cover compounds must be formulated and tested to meet application requirements. The rubber compounds are usually mixed in internal mixers or two-roll mills.

Many small rollers are produced by ordinary compression and transfer molding processes. Some medium-sized rolls are produced by extrusion, either directly on the cores or by slipping cured extruded tubes over them. Most large rubber rolls, however, are produced from calendered stock or by hot-strip extrusion.

The core must first be properly prepared to receive the new covering. If the roll has been previously covered, the removal of the old cover is usually accomplished by mechanical means such as tooling in a lathe. New cores must be properly degreased. Chemical cleaning agents are often employed. The metal surface must then be thoroughly cleaned to bright metal. This may be accomplished by sand or grit blasting or by abrasive belts or discs. Once the metal is clean, appropriate primers and/or adhesives are applied. This part of the operation is highly critical, since the worst thing that can happen to a rubbercovered roll is an adhesion failure in service.

Next the elastomer cover compounds are applied by a variety of methods such as calender sheet (three roll) building, cold-strip application, hot-strip extrusion, crosshead extrusion, pre-engineered cured sleeve application, casting, doctoring or spraying.

The calendered sheet process is still popular. In this process a thin calendered rubber sheet from 0.76 to 2.3 mm (0.030 to 0.090 in.) thick is rolled around a suitably prepared core. This is accomplished with three roll building machines, as depicted in Figure 13, or by direct application on a lathe. Special care must be taken to prevent the incorporation of air into the roll, either between the plies or as blisters in the calendered stock. The roll is built up to a diameter size, which allows it to be vulcanized (cured), then ground to a smooth surface at the desired diameter. Overbuild is generally in the range of 1 cm (3/8") or less on the diameter, depending on the type of compound.



Figure 13: Three Roll Building of Calendered Sheet

Alternatively, an extruder building process may be used. Here a thin, narrow, hot rubber strip ribbon is extruded and helically wound around a suitably prepared core, as shown in Figure 14. Crosshead extrusion processes are also used. In this process, a core is passed through an extrusion crosshead device in which rubber is seamlessly applied. The built roll is then wrapped tightly with plastic, cotton or nylon tape for vulcanization in open steam or dry autoclaves. Curing cycles generally last between four to over twelve hours, depending on the core sizes and rubber thicknesses. The compounds must be carefully designed to prevent overcure of the outside layers or undercure of the inside layers and bond sites. After curing, the roll is removed from the autoclave, unwrapped, allowed to cool thoroughly and stress-relieved before proceeding with the finishing operation.



Figure 14: Hot-strip Extrusion Building of a Large Roll

Other building techniques include the casting of degassed liquid compounds (usually urethanes or silicones) into molds for oven curing; spraying; dispensing quick curing liquids onto rotating cores (moldless); doctoring liquids; and applying pre-engineered, cured sleeves.

The finishing operation (grinding) is carried out on cylindrical grinders or lathes, using either grinding wheels or abrasive belts. Rolls designed to serve under high pressures may be crowned (cambered) to compensate for bending (see the section on crowning). In any case, great care must be taken in the finishing operation to maintain uniformity of diameter and concentricity, as well as proper smoothness of the surface. Printing, coating, laminating and other specific industrial rollers undergo final finishing or polishing by automatic belt machines or by hand. The rollers are turned at high speeds and are normally progressively polished with 240 to 600 grit abrasives, in order to produce the desired finish.  $R_A$  values of 40 to 20 are possible, depending on the cover compound. If special surface geometries are required, such as diamond, lateral of spiral-shaped grooves, these may be configured by conventional mechanical machining or by lasers.



Figure 15: Summarizes the main aspects of roller manufacturing.

## **Quality Control**

Roller quality begins with meeting application specifications. In-process quality control is the next important step. The normal raw material checks, core preparations, adhesive applications, building, curing and finishing procedures vary according to the roller type. Some of the main inspection points before shipment are shown below:

- Journal Total Indicated Run out (TIR), in millimeters or inches.
- *TIR of elastomer surface* in cm or inches. Low pressure or non-contacting gauges are best.
- Outside Diameters are usually measured in three locations with diameter tapes, micrometers or laser devices. More measurements are sometimes required, especially if high precision crowning is specified.
- Hardness is measured with a calibrated Shore durometer gauge or equivalent, or a P & J plastometer. An average of 3 readings is usually taken at each of 3 sections, two inches from each end and at the center. If a hand-held Shore gauge is used, a standard weight is preferred to minimize biases. Drift is also determined. Thin walls will give "apparent" readings.
- Color is often confirmed by reviewing comparative standards.
- *Trim* must be at specified angles. The trim surface should be uniform, as compared with standards or specs.
- *The face surface* should be smooth and uniform, as compared with standards or profile measuring instruments.
- *The bond* of the elastomer to the core should be adequate for the application.
- The face length is usually measured with a standard tape measure or metal rule. If more precise devices are required, dial indicators, etc., should be employed.
- *Journals or bearing seats* should be in good condition. Bearing fit tests are suggested.
- Special requirements, such as materials, grooving, crowning, electrical characteristics, etc., should be confirmed.

## Roller Storage, Installation and Maintenance

Rollers, especially soft rollers, should never be stored or transported with their face sections supported on hard surfaces because flat spots can occur. Their journals or shoulders best support rollers as indicated in the Figure 16. Rollers, especially those with thick and hard covers, should not be transported or stored at low temperatures for prolonged periods of time.



Figure 16: Storage of Rubber-Covered Rolls

Special polyolefin black wrapping paper is suggested to maintain surface cleanliness, along with proper labeling. Storage should be in cool, dark locations, away from ultraviolet light sources and electrical equipment that produces ozone discharges. Large temperature and humidity changes should be avoided. Rollers should be brought to ambient temperatures prior to installation.

Appropriate boxing must be used. Clearances, especially of rubber cover to box surfaces of 5 cm (2 in.) for up to 75-90 cm (30-36 in.) diameters and 10 cm (4 in.) for over 75-90 cm (30-36 in.) diameter rolls are a common recommendation. Shoulder supports should be "locked" to prevent shifting in transit. Reinforcements should be placed where fork trucks may lift the box. Sling lifting strategies (in and out of boxes) should be considered. The contact areas of slings or belts should, clean, smooth and padded. Cables and/or ropes should never support the cover sections.

Rollers or roller assemblies must be installed properly to ensure acceptable performances. Bearings in particular must be squarely and carefully inserted. Bearings that are incorrectly inserted or that are damaged can cause excessive rubber roller cover heat build-ups, uneven stripes, and high local pressures, all leading to poor quality production and premature cover failures.

Roller maintenance should not be neglected. Proper, periodic cleaning and record keeping are important. Rollers should be cleaned, wrapped, labeled and well supported when returning them to inventory/storage. Rollers with large, soft covers that must be maintained at critically close tolerances are sometimes rotated periodically, 60° every sixty days or 90° every ninety days, to avoid possible surface run-out irregularities from sagging.

## **Typical Roll Compounds**

Rubber rolls serve under a wide variety of conditions. Virtually all commercial polymers have been used in their manufacture. As with any rubber product, the compounder must formulate to meet application specifications. In general, printing rollers are made from nitrile rubber. Paper mill rolls are made from either natural rubber or synthetics such as nitrile or Neoprene or urethane. Steel mill rolls are made from Neoprene, Hypalon or EPDM. Textile rolls are made from nitrile or EPDM. Leather processing rolls are made from Neoprene. Plastics processing rolls are

made from high temperature resistant materials such as EPDM, Hypalon or silicone.

Although the referenced formulas (see General References) are general representations for a variety of roller types, all specific formulas must be adjusted as needed to fit specific processing equipment and tested to ensure end-use performance. Typical tests include modulus, tensile, tear, compression set, flex fatigue, static and dynamic fluid immersions, oxidation resistance, heat resistance, hysteresis, bond integrity, static and dynamic nip properties, load bearing capability, electrical resistance and conductivity, friction and release performance, abrasion resistance and a host of other specific pilot, pre-production and plant evaluations.

Although rubber rollers have had a storied past, they are truly the "Wheels of Industry." New needs are expected to be met with new rubber compositions and processes.

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#### by Christopher D. Favreau

Quabaug Corporation Vibram[®] North Brookfield North Brookfield, MA

#### Introduction

The last few decades have seen many changes in the design and manufacturing of footwear, as well as many footwear industry changes through mergers, acquisitions, bankruptcies, and global sourcing. Many companies have been changing their business models as the global economies fluctuate in an effort to manufacture their products while achieving a reasonable profit margin. Because of this the technologies that are involved have also changed. The shift from North American and European manufacturing to Taiwan, China, and Vietnam has resulted in changes pertaining to raw materials, mixing, preforming, molding, finishing, adhesive machinery and other processes.

The increase in globalization since 1978 has led to many changes for footwear in general, and in the recent years of 2006, 2007, and 2008 it has led to an unprecedented global raw material demand. As a result, material prices are at an all-time high.

Modern footwear is performance-driven, requiring specific technology to support specific performance. The various types of footwear can be assigned to such categories as: Athletic, Casual/Fashion, Industrial, Outdoor Sports, and Military. Within these categories are various types of shoes – each with a price point range based on the complexity of the shoe itself, and the quality of the components used.

As you will read in the next few pages, the demands of the footwear chemist are high. Their ability to interact across a multitude of operations within their own factory, subcontractor's factories, and outside shoe factories is critical to their success. Their role demands knowledge both inside and outside of rubber chemistry, and they need to be able to determine the effects of extreme environmental conditions. This can lead to an exciting role that will most likely never present the same tasks on a daily basis.

#### Footwear Sole & Heel Design

Rubber still offers a demonstrable advantage over other materials in particular footwear markets. Even in tough economic times an industry such as *Asphalt Paving* still demands high-performance outsoles, and vulcanized rubber is still the preferred material. Rubber, being a vulcanized thermoset, has superior heat-resistance compared to a thermoplastic urethane. Asphalt paving boot soles and heels are designed to spread the weight of the user over the entire foot print to diminish the possibility of leaving depressions in the asphalt before it cools and hardens. This boot requires a series of large, wide, flat and non-patterned lugs to provide maximum surface area. Even the heel breast requires a softened or beveled edge to prevent indentations.

Since footwear is used in diverse environments it is often necessary to blend different polymers in order to obtain the unique characteristics of each. Studies have been done of many types of compounds, and polymer hybrids have been created to combine the heat-resisting qualities of a Neoprene with the oil resistance of nitrile. This type of hybrid compound combines the best of both materials into a very reliable and lasting product.

Similar types of hybrids have been developed for markets such as Wildland Fire Fighting where heat, oil, and tear resistance are important to the lifespan of the outsoles. The user may encounter very hot surfaces while ascending rocky slopes full of sharp edges capable of tearing the lugs off of a typical outsole. Pure nitrile compounds will not have the heat resistance necessary for the sole to survive, while SBR compounds will not have the oil resistance required by the NFPA specifications. The National Fire Protection Association (NFPA) was established in 1896 as an International, non-profit association. They are an authority on fire, electrical, and building safety and provide and advocate consensus codes and standards, research, training and education). For the Wildland Firefighter the lug design requires wide outer lugs for stability while on uneven terrain, center lugs with leading edges in all directions for traction while ascending or descending, a deep/sharply defined heel breast for traction when braking and/or climbing ladder rungs, and deep thick lug depths for heat and tear resistance. The design should also be self-cleaning so each step provides optimum traction.



Structural Firefighting does not demand long-term heat resistance, but does demand extreme traction on ice covered surfaces, with flame resistance a given in both environments. Since oil resistance is also required, a hybrid compound is necessary for optimal performance. Vibram has invented a formula called Fire & Ice[™], which has been identified as an industry leader in this market segment (see Table 1). For the Structural Firefighter the lug design should have wide outer lugs for stability on uneven terrain/debris, center lugs with large flat surfaces for improved traction on ice, channels cut off the edges of the sole to disperse fluids and prevent hydroplaning, and sharp leading edges on all lugs to increase the coefficient of friction. The design should also be self-cleaning so each step provides optimum traction.





### **Compound Quality and Testing**

When performance compounds are being produced there are many factors that come into play for the rubber chemist, such as consistent high-quality raw materials, controlled manufacturing processes, and constant laboratory testing to verify intended attributes. A performance compound is developed under controlled conditions, then lab tested. It is also *"tested where it matters",* in actual field conditions. Test results are tracked and once the compound has met all of the necessary criteria it is introduced into production. The scale-up of the formulas and processes are critical to ensure that the production trials will match the characteristics of the lab trials. A standard protocol of repeating all tests of production lots to demonstrate consistent results should be followed.

In addition to the aforementioned "actual field conditions", there are other physical properties and tests to be considered by the compounder to make a high quality outsole:

 The National Bureau of Standards Abrasion test is a measurement of wear resistance for footwear compounds, whereby rubber samples are tested by being put into contact with a small drum covered with a 40 grit garnet paper rotating under a known speed. The test continues until a certain amount of rubber is abraded away, then the number of cycles is counted and compared to the number of cycles necessary for a known control compound. A good number for a high quality outsole would 120 NBS minimum (ASTM D 1630).

- The Ross Flex is a test used to measure the cut growth resistance of a compound. Vulcanized samples are punctured in the center with a 0.100" awl and mounted in the flexer, which bends the samples at 90 degrees over a round mandrel. The compound is considered to be acceptable if the cut growth where the sample was punctured fails to grow to 5 times it's initial size (ASTM D 1052).
- Volume Swell is a test to determine how resistant a compound is to certain solvents or oils. It is achieved by taking a sample of the subject rubber, and placing in a liquid medium, usually Fuel B or an ASTM reference oil, for the desired time (usually 46 hours) and calculating the amount the compound has swelled by finding the difference between the weight of the sample (in water) before and after testing. The difference in weight is then divided by the original weight to determine swell, as a percentage (ASTM D 471).
- The Bata Flex is a test to check for cracking in the forepart of a sole. The forepart is cut off from a unit sole and mounted to a fabric belt that has been bonded to itself to form a continuous loop. This loop is then mounted in a machine with mandrels to spread the loop. The mandrels should have different diameters, with one of them being the powered or drive mandrel. The belt is then rotated around both mandrels for a total of 50,000 revolutions, while stopping every 10,000 revolutions to record any visible cracks.
- A good heat resistance test to perform on soles that will be subjected to extreme temperatures can be done in a lab oven set at 480°F. This test requires samples of the sole be placed in a sand bath inside this oven, and left there for 40 minutes. After 40 minutes the samples are taken out and given a visual observation. The test sample has passed if there is no ignition and no cracking of the rubber when flexed.

One area in footwear that needs to be considered is that of "marking", e.g., when you sole leaves a black mark on the floor. As a result of this need for non-marking most sole formulations utilize a reinforcing package of mineral fillers. For less demanding physical requirements clay or talc is often used, for high performance applications a system of amorphous silica and silane is used to achieve the desired tensile and abrasion needs. The key attribute of silica that needs to be considered is the particle size: typically surface areas above 150 m²/g will yield the best balance of physical properties and processing. When working with Silica you need to note that cure rates will be slower when compared to a similar compound that is filled with carbon black, so cure rate adjustments will be necessary.

#### Sole & Heel Production

There are many different types of machinery for each stage of the sole and heel production process. The process usually begins with Banbury[®] mixing since high-volume compound production is required. Once the compound has been mixed it may need to be preformed to a specific size, shape, thickness, and weight of material before being molded.

Several different types of preforming machines are described in the following

paragraphs and figures. Figure 1 is a picture of a gear-pump extruding operation. The extruder is cold-fed by a continuous strip of rubber compound staged on a transport skid. It feeds into a short extruder, then through a set of meshed gears. As the compound moves through the extruder, it is blended and continually folded over. It is then forced into the narrow space between the meshed gears and is further blended and folded. As a result of these two actions, the compound achieves a high level of homogeneity. The compound is then forced through a custom designed die to create the final shape, and is then cut by a fly-knife spinning and cutting at set intervals.



Figure 1: Gear-Pump Extruder Preforming Operation

Figure 2 is a picture of a standard hot-fed rubber extruder being fed with a continuous strip of rubber from a 64" mill. The 64" mill is being fed by another 64" break-down mill where the cold rubber is "broken-down", heated up, and becomes pliable. The operation is continuous throughout the given cycle until the planned number of outsole pairs has been preformed.



Figure 2: Hot-Fed Extruder Preforming Operation

A typical compound may not process well in both extruders, so the rubber chemist needs to understand the heat-history/rheology of the compound before and after being processed through each machine. Because the compound goes directly from mixing to preforming there is no additional milling of the compound, so increased mixing time or a two-stage mix cycle may be required.

Rubber chemists must understand the rheology of production compounds and have the ability to alter the cure package to accelerate or retard the rate of cure as needed. This is true for both current and compounds under development.

The third type of preforming operation produces large-scale preforms for sheet goods up to 36" X 36". This is accomplished through a series of machines where the uncured rubber slabs are broken down on a 64" mill, then fed into another 64" mill, which then feeds a small strip into a large extruder. The extruder then feeds a large ribbon of compound into a roller-head die extruder to form a continuous thin sheet of rubber, as shown in Figure 3, which is then conveyed through a cooling tunnel to an automated cutting system.



Figure 3: Roller-Head Die Extruder Preforming Operation

All of the various preforming operations require the rubber chemist to have the ability to alter the tackiness of the compound. Internal tack of the rubber is critical for processing. If the rubber is too tacky it can stick to the mill rolls, which can slow down both the mixing and preforming processes. If the rubber does not have enough internal tack it poses problems such as "bagging" on the mill, which will also slow down the process. Solutions to either may be a change in the sequence of raw materials being introduced into mixer, the mixing time, the mixing temperature, or the use of a tackifying agent.

## Molding

For the molding operation there are also several types of machinery, with the most common being the vertical compression molding press such as the ATR

brand pictured in Figure 4. This is a special model of molding press with multiple decks. As shown in the picture there are two decks, each capable of containing molds with up to five pair of sole cavities. These presses are installed to create a line of press that can be controlled by one operator.

The ATR presses are unique in that the top deck comes out of the press and rotate towards the sky to reveal the top plate of the mold to the operator. This allows for specially designed outsoles to be produced, and also gives flexibility to over-molded components such as nylon plates in rubber outsoles.



Figure 4: Preforms Loaded for Compression Molding in ATR Press

More efficient molding is accomplished with the rotary-table injection molding machine shown in Figure 5. It contains 16 stations configured in a circular rotating layout, requiring only one operator. The rubber is milled into a continuous strip about 2" wide and wig-wagged into a Gaylord container. From the Gaylord the strip is fed into a short extruder located next to rotary molding machine.



Figure 5: Extruder Strip-Feed of the Rotary Table Injection Press

The molding machine will cycle the mold next to the extruder front. The extruder will draw in the rubber strip, forcing it through a custom die to deposit the rubber as thin spaghetti-type strands into the mold. The extruder head will travel back and forth to dispense the strands appropriately into the different sections of the mold, as shown in Figure 6. Then the mold will close and the rubber will soften, flow, fill, and cure all within approximately 6 minutes.



Figure 6: Extruder Fed Rotary Injection Press Mold

The rubber chemist is responsible for the compound's rheology and the mold flow, fill, and quality of the finished molded product. If, for example, the stock cures too quickly it may mold out within the anticipated timeframe, but will give the finished product a scorchy appearance with a wrinkled surface, and be of poor quality. Special attention needs to be given to the cure system, providing enough scorch safety to allow for preforming, but also an economical rate of cure for molding. This type of molding machine also allows for multiple colored inserts to be easily placed within the mold.

## **Finished Product**

It is very important for the rubber chemist to take into consideration the external factors which may lead to changes to the cured rubber compound prior to its being put into the field. These factors include:

- · extreme temperature exposure (cold and/or hot) during transit
- · shoe assembly operation solvents
- · shoe assembly operation heat activators/ovens
- · shoe assembly operation special adhesive systems
- · shoe assembly operation stitching processes
- shoe assembly operation co-molding processes such as PU direct attach or autoclaving
- shoe assembly operation autoclaving

All of these factors should be considered and documented in the early stages of compound development so the end product that reaches the consumer will perform to expectations.

Ingredients	phr
SBR 1502	80.0
DIENE 645	15.0
SBR 1606	5.0
High Styrene Resin	5.0
Silane TESPT	3.0
Naphthenic Oil	7.0
Precipitated Silica	50.0
Zinc Oxide	2.0
Stearic Acid	1.3
PEG	1.5
ALTAX [®] (MBTS)	1.0
METHYL TUADS®	0.4
Sulfur	1.3
Process aid	0.8
PE Wax	0.7
Total	174.0

# Typical SBR Sole Formulation

# **Typical NBR Heel Formulation**

Ingredients	phr
NBR DN 219	95.0
SBR 1606	5.0
Precipitated Silica	50.0
High Styrene Resin	20.0
Hydrocarbon Resin	10.0
Silane TESPT	2.0
DOA	5.0
Antioxidant	2.0
Zinc Oxide	3.0
PEG 3350	2.0
Stearic Acid	1.0
AMAX® Accelerator	1.1
ALTAX (MBTS)	0.8
METHYL TUADS	0.1
Sulfur	2.0
Total	199.0

Typical Sole & Heel Formulations

#### WIRE AND CABLE

#### by Vipin M. Kothari

Therm-O-Link, Inc. Garrettsville, OH

#### INTRODUCTION

Electrical Cables are designed to supply the flow of electricity from the power source to its destination without any leakage, failures, or interruptions. This, in general, is accomplished by covering the metal conductors such as copper, aluminum or iron with a coating of materials that are highly dielectric resistant and act as nonconductors of electricity. These materials, which exhibit superior electrical properties, are usually referred to as the insulations or insulating materials.

Historical records show that the earliest insulations were fibrous materials such as cotton and jute dipped in water-resistant materials like waxes, shell oil or tar. Cellulose was also the material used for the electrical insulation in early days. Paper impregnated with high grade of a mineral oil, applied to the conductor, was introduced as the power cable in 1894, and carried a large amount of power over a long distance. Charles Goodyear's discovery of the sulfur vulcanization of natural rubber in 1839 eventually resulted in a more durable elastomeric coating or insulation. Since the discovery of the vulcanization process, with the passage of the time and the advent of the technology, there has been a rapid progress in the types and the quality of insulation materials.

From the early days of natural rubber (polyisoprene), styrene-butadiene and butyl rubber as insulations, the wire and cable industry has come a long way. Today, the insulating materials, derived from resins such as polyethylene and polyvinyl chloride and high performance elastomers such as EPDM, Neoprene, CPE, EVA, Hypalon[®], Silicone and Fluoroelastomers are much more intricately composed. They are tailor-made by compounding with ingredients such as fillers, plasticizers, antidegradants, processing aides, flame retardants and curatives to meet the required heat, fluid, and flame resistance, electrical properties, and other specifications designed by organizations such as SAE and OEMs for automotive cables, and NEMA, UL, CSA, ANSI and IEEE for industrial cables.

All solid insulations are applied by the extrusion process. Most insulations are continuously extruded, and vulcanized (except thermoplastics) in a process that is referred to as continuous vulcanization or the "CV process". This process causes a rapid cure at high temperature in presence of steam. Other vulcanization techniques that have been used to some extent are Radiation (Electron Beam) Curing and Moisture Curing. All Vulcanization Processes will be discussed later in more detail.

#### CABLE CONSTRUCTION

Today, the application of insulation to wire and cable construction has become a lot more complex. As a result, we have not only the primary insulation but also the jackets, sheaths and separators that go into the manufacture of wires and cables. A few examples of basic cable construction with various insulation coverings are shown in Figure 1.



Figure 1: Some Cable Constructions

Any material that supports the flow of the current is called a conductor. The best practical conductors are metallic conductors because of the free flow of the electrons. Some metals such as copper and aluminum are better than carbon which is nonmetallic.

Insulation is primarily designed to meet a cable's electrical (Dielectric Strength and Insulation Resistance) requirements. Separator, such as paper and Mylar polyester, generally is applied between the conductor and insulation in order to strip the cable for smooth and clean termination. In large cables, the role of the separator is to keep the multi-stranded conductor free of insulation contamination. Sheath and Jacket are used to protect the insulation coverings and are also designed to protect the cables from handling, wear, and environment.

The diversity of materials, processing, service, and numerous specifications and requirements by various organizations tend to make the wire and cable a specialized field of study.

Table 1 shows a wide range of wire and cable applications. Generally, the insulated wires bigger than 8 AWG (gauge) are popularly referred to as Cables.

1. Automotive, primary wires, low voltage (<60V)	12. Machine Tool Wiring
2. Battery Cables	13. Submersible Pump Motor Wiring
3. ABS Cables	14. Marine Cables
4. Telecommunication Cables	15. Heavy Truck Refrigeration Units' Cable
5. Appliance Wiring	16. Heater Cables (Temperature Sensitive)
6. Recreational Vehicle Cables	17. Military Cables
7. Switchgear, Switchboard and Control Panels (Building Wires)	18. Mining Cables
8. High Medium Voltage Power Cables	19. Instrumentation Cables
9. Ballast Leads (Fixture Wires)	20. Flexible Cords
10. Welding Cables	21. Flat Cables
11. Motor Lead Wires	22. Hermetic Wires

Table 1: Wire and Cable Applications

### **INSULATION PROPERTIES**

The electrical properties of the wire and cable insulation materials, that are of the most concern to the rubber and plastics compounders, are the Dielectric Strength, Dielectric Constant, Insulation Resistance, Dielectric Loss and Power Factor. Other important properties of Cable are the Mechanical Properties (original and aged Tensile, Elongation and Hardness), Flammability, low Temperature Resistance, Fluid Resistance, Pinch, Abrasion and Ozone Resistance and Environmental Cycling.

#### **Dielectric Strength**

The dielectric strength of rubber or plastic insulation is the electric stress required to puncture the sample. It is measured by applying a voltage across a sample of the known thickness and raising the voltage until the breakdown occurs.

Dielectric strength (D) is expressed by the equation,

D = V/t

where V is the applied voltage when the breakdown occurred, and *t* is the sample thickness in mils.

The dielectric strength of the insulation is affected by the rate of the rise of the applied voltage. A slower rate of rise will cause insulation breakdown at a lower voltage than with a rapid rate of rise, whereas, the insulation may withstand relatively high voltage for a short time before the breakdown occurs.

The dielectric strength can be measured on the insulation material plaque or insulated wire. The test most frequently used is performed by placing the sample sheet between two electrodes and starting at zero, and increasing the voltage at a uniform rate until breakdown occurs. For many rubber compounds the rate

of rise is 500 volts per second. The choice of electrode depends on the material being tested. For thin, flat sheets of rubber, the electrodes are usually cylindrical with rounded edges. The diameter of the electrode generally is from 2.5 to 5 cm (1 to 2 inches), depending on the specifications of the particular product.

Dielectric strength test on the insulated wire or cable is a must test to make sure there are no voids or leakage in the insulation. In this case, the test is performed per SAE or UL specification. For many rubber and plastic cables, a 2' cable sample with 1" at each end stripped of insulation is submerged in water containing 5% salt by weight at room temperature such that not more than 5-6" of each end of the sample protrudes above the solution. After being immersed for 5 hours, and while still immersed, a 1 kV (1000 Volts) voltage is applied between the conductor and solution, and insulation shall withstand the application of voltage for 1 minute without rupture or failure. A meter indicates the voltage applied to the sample and a circuit breaker will open when the failure of wire occurs. Proper safety precautions of not touching the wire must be observed while the test is in progress because of the high voltage circuit when the current is on. Dielectric strength tests are often used to check for the contamination, voids or deterioration of insulation prior to or during the use.

A further discussion of dielectric strength test methods may be found in ASTM D 149-64 published by the American Society for Testing and Materials. Typical values for the dielectric strength of pure gum stocks obtained by this test method are shown in Table 2.

Elastomer	Dielectric Strength (volts/mil)
Natural Rubber	600 to 800
SBR	500 to 700
Silicone	500 to 600
Fluorocarbon	500 to 600
Butyl	400 to 600
EPDM	500 to 1100

Table 2: Typical Dielectric Strength Values of Various Elastomers

It should be noted that the values of the observed dielectric strength are often less than the theoretical values due to the impurities that cause early breakdown. Dielectric strength (volts/mil) of the same material also varies depending upon the thickness of the sample. A thin test specimen on the average will show a higher dielectric strength than the thick one.
# **Resistivity and Conductivity**

### Resistivity

The resistivity of the insulation material to oppose the passage of the electric current is its intrinsic property and it is expressed as:

$$\rho = RA/L$$

- $\rho$  = Specific Resistivity in ohm-cms
- R = Resistance of the sample in ohms
- A = Cross-sectional area in circular mils
- L = Length of the sample in cms

Specific Resistivity is also referred as the Volume Resistivity  $\rho v$ . Most insulation materials have the resistivity in the order of  $10^6$ - $10^{18}$  ohm-cms. Surface resistivity measures the current across the surface and it changes considerablely with the change in the humidity.

The resistivity of a material is determined by measuring the resistance of the sample of known dimensions. It is measured by placing a sample between two electrodes, applying a voltage between them and measuring the current flowing through the sample in accordance with ASTM D 257. Resistivity measurements are used often in determining the uniformity of insulation materials.

# Conductivity

Conductivity is the reciprocal of resistivity and is expressed as:

 $\gamma = 1 / \rho$ 

 $\gamma$  is conductivity in ohm-cms and  $\rho$  is resistivity in ohm-cms

By definition, a conductor, generally, a metallic in state, is a material that conducts electricity and the insulator is the one that does not. However, there are no perfect conductors or insulators. Hence every material will have some value of resistivity. The range of resistivity values between a good conductor and a good insulator is extremely large. A conductor such as copper will have a resistivity of about  $1.7 \times 10^{-6}$  ohm-cm, while the resistivity of a good insulator like polyethylene will be in the order of  $1 \times 10^{15}$  or more ohm-cms. Therefore, the resistivity measurements determine the degree to which a material is a conductor or insulator.

# **Dielectric Constant**

Dielectric Constant is a specific property of the insulating material and is a measure of the capacitance of the insulation and its ability to store electrical energy. Dielectric constant value is measured in accordance with ASTM D 150. A typical low dielectric constant value in the range of 2.2 to 3.3 is desired for insulations. Dielectric constant test is often used to determine if the electrical properties of the insulation, such as capacitance or impedance, are within the required specifications. The dielectric constant of the insulation material increases considerably if it absorbs a small amount of moisture. Hence the cable insulation, particularly for high performance communication cables, must have

dielectric constant as stable as possible in the presence of water or moisture.

### Dielectric Constant Calculations

The Dielectric Constant of a rubber or plastic material may be measured on the press cured slabs and electrodes are used similar to those used in the resistivity tests. The dielectric constant is calculated as:

# K = Ct/0.885A

- K = Dielectric Constant
- C = Capacitance of the sample in micromicrofarads
- t = Thickness of the sample in centimeters
- A = Electrode area in square centimeters

Dielectric constant of the insulation on a cable is measured by immersing a known length of cable in a conducting medium such as water or mercury. The commonly used length of wire sample for this is 10 feet immersed.

# K = .0136C Log (D/d)

- K = Dielectric Constant of the insulation
- C = Capacitance in micromicrofarads for a 10 ft. sample
- D = Diameter over insulation
- d = Diameter over conductor

### **Dielectric Loss**

The Dielectric Loss of an insulation material is caused partly by the insulation resistance and partly by an electrical stress, or hysteresis, which is characteristic of each material. The operating temperature of any cable depends upon the rate at which the heat is generated and upon the rate at which the heat is dissipated. The higher the dissipation of heat, the higher the dielectric loss. Hence the dissipation factor tan  $\delta$  determines the degree of dielectric loss.

Insulation materials should have low tan  $\delta$  value to avoid excessive loss. Dielectric Loss of Polyethylene (PE) insulations is lower than most solid insulation materials. With some materials such as PVC, the dielectric losses increase with an increase in the temperature. The presence of any small concentrations of polar groups and the presence of the antioxidants and pigments in PE insulations may also contribute to the dielectric loss.

#### **Power Factor**

Power Factor of the sample insulation is measured by the ratio of power loss in insulation expressed in watts to the volt ampere, a product of the applied voltage and resultant current. In order to achieve the maximum performance of the cable, it is necessary that the power factor of insulation be kept as low and as uniform as possible. A perfect insulation would hence have a power factor of zero. Polyethylene insulation probably comes closest to the perfect insulation with a power factor not exceeding 0.0005 or 0.05%. Many rubber insulations such as EPDM have the power factor of 0.1-1.0%. Addition of pigments and increase in the temperature and voltage also tend to increase the power factor of insulation.

#### Insulation Resistance

The measured resistance of the insulated wire and cable is called the Insulation Resistance.

# Method of Measurement

The equipment for measuring the insulation resistance of the wire consists of a tank for immersing a coil of wire sample in water. The resistance is measured between the conductor and the water after the wire has been immersed for a specified period of time. The results of the insulation resistance test are expressed in ohms. In case of the insulated wire, the resistance is expressed in ohms per unit length. The length of wire chosen in the laboratory testing can be 50 or 100 feet. The formula used in determining the insulation resistance of a given length of wire is:

$$R = rL_1/L_2$$

R = Insulation Resistance in ohms per unit length

r = Resistance of the sample

L₁ = Length of Sample

 $L_2$  = Limit length (1000 ft. in most cases)

In many cases, UL has a table of values of minimum insulation resistance requirements for various types and size of wires that are used in switchgears, switchboards, control panels and underground utilities applications. Some of these wires require the long-term (12 weeks or more) insulation resistance at elevated temperatures per UL specification. Resistance measurements, often, are affected by temperature, humidity and surface conditions of test specimen.

# **Other Cable Properties**

#### Flammability

All wires and cable require some degree of flame resistance. Automotive wires are governed by the flammability test requirements per SAE specifications as well as the internal standards of OEMs. Many industrial wires have to meet, UL flame resistance requirements of horizontal or stronger vertical flame and horizontal tunnel testing with an 87870 watt high powered methane flame. In some applications, wires must also meet IEEE's cable tray flame test. Many switchgear, switchboard, control cables are required to meet UL's vertical VW-1 and IEEE's cable tray tests where as some plenum and riser communication cables require tunnel tests in which both the flame resistance distance and smoke generation are measured.

# Heat Aging

The effect of temperature on cable is profound, so the cable insulation compound must be formulated to meet heat aging requirements which vary in temperature and duration, depending upon the application. There are two major obstacles with heat aging. First is the increase in the conductivity as the temperature rises, which can inhibit the insulation from protecting the cable. Second is the deterioration of the insulation material in the presence of heat and oxygen, resulting in the loss of flexibility (elongation and hardness properties). Many cables have to meet various continuous operating requirements at 60°C, 90°C, 105°C, 125°C, 150°C and 200°C temperatures. SAE and UL have time and temperature aging specs for wires depending upon the application. Auto primary wires governed by SAE specs are rated from 80°C/100°C for PVC wires for interior applications and battery cables to 125°C/150°C rated XLPE and EPDM under-the-hood primary wires and battery cables. PVC based wires are also used in 105°C machine tool and appliance wiring, whereas crosslinked PE, and rubber based Neoprene, Hypalon[®], and EPDM insulated wires are used in appliance wires, motor leads, fixture wiring, switchgears, control panels etc. up to 150°C applications and Silicone and Fluoroelastomers based insulations are used in applications of 200°C and above.

# Other Cable Tests

Other important tests that are performed on cable are the physical properties (stress/strain tests), fluid resistance, cold bend, pinch, abrasion and ozone resistance, impact strength and environmental cycling. The stress/strain tests are performed on the insulation (after removing the conductor) per ASTM D 412, while the other tests are performed on the cable itself per UL, CSA and SAE, and other approving agencies. In addition to the electrical, thermal aging and flammability requirements described above, these tests are designed to meet the mechanical and chemical properties of the cable. Although we have listed in Table 3 all the possible tests for UL, SAE, ICEA, ANSI, and CSA approvals, not every one of these tests are neither needed nor required on every category of wire.

Table 3:	Cable	Insulation	Tests
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Cable Service Temperature Range -50°C to 200°C (-70°F to 400°F)
Original and Aged Physical Properties (Stress/Strain)
Dielectric Strength, original, after heat aging, and at elevated temperature
Abrasion Resistance and pinch properties
Impact Test
Insulation Resistance (IR), long- and short-term @ RT and elevated temperature
Ozone Resistance
Sunlight Resistance
Flame Tests - Horizontal, Vertical, Cable Tray, Tunnel, 45° Angle
Cold Bend @ -10°C to -60°C
Crush Resistance
Fluid Resistance (ASTM oils and other fluids)
Weatherometer or Environmental Cycling for Cracking

# **INSULATION MATERIALS**

While the earliest cables used wax, oil, or tar impregnated cotton and paper, the polymeric materials such as rubber, crosslinked polyethylene (XLPE), PVC, and thermoplastic elastomers (TPE) are now the basis of the insulation and/or jacket in cable constructions. This chapter will discuss in detail the role of most rubbers and XLPE in wire and cable applications. Table 4 lists some important

Polymer Properties			Resistance*					
Polymer	Spec. Gravity	Dielectric Strength (kV/mm)	IR**	Flame	Heat	Oil/Gas	Ozone	Weather
Neoprene	1.2-1.7	5.9-23.6	1x10 ¹³	G	G	G	G	G
Hypalon	1.4-1.7	11.8-23.6	1x10 ¹⁴	G	G	G	E	E
Silicone	1.1-1.6	19.7- 23.63	1x10 ¹⁴	F	E	Р	E	E
EPDM	1.1-1.4	35.4-41.3	>1x10 ¹⁶	Р	G-E	Р	E	E
FKM	1.9-2.0	19.7-23.6	1x10 ¹²	E	E	E	E	E
PVC	1.9-2.0	19.7-23.6	1x10 ¹⁶	G	F	G	G	G
XLPE	0.9-1.3	21.7-98.4	>1x10 ¹⁵	Р	G-E	G	E	E
* P = Poor, F = Fair, G = Good, E = Excellent; **IR = Maximum Volume Insulation Resistance (ohm-cm)								

electrical and other properties of some common insulation materials.

Table 4: Properties of Some Common Insulation Materials

For a long time, rubber was recognized for its insulation properties but wasn't practical to use since it was soft, sticky, and needed to be hardened. With the discovery of the vulcanization process, the sticky and gummy rubber was transformed into a stable and tough electrical insulation material. Early on, vulcanization brought into focus various polymers such as natural rubber, styrenebutadiene rubber, butyl, nitrile-butadiene rubber, and Neoprene for insulating applications. All of these rubbers were suitable for sulfur-vulcanization. However, except for Neoprene, these rubbers became obsolete as manufacturers moved on to the current improved performance polymers such as EPDM, Hypalon, CPE, EVA, Silicone, Fluoroelastomer, Crosslinked Polyethylene (XLPE), thermoplastic elastomers (TPE), thermoplastic vulcanizates (TPV), and engineered resins, to meet the mechanical, chemical, thermal and environmental requirements for cables. XLPE and PVC, because of their low cost, still remain in the majority for many industrial, automotive and communication cable applications. Neoprene, with over a 50 year history, is still being widely used in jacketing applications. Both prior and current polymers are listed in Table 5.

Prior Polymers	Current Polymers
Natural Rubber (NR)	EPDM
Isoprene, Synthetic (IR)	Hypalon (CSM)
Styrene Butadiene Rubber (SBR)	CPE
Butyl (IIR)	EVA
Neoprene (CR)	Silicone (FMQ)
Nitrile (NBR)/PVC	Fluoroelastomer (FKM)
PVC	XLPE
	TPE/TPV
	Engineered Resins

**Table 5: Insulation Materials** 

The following is a presentation of the "historical" rubbers, and the "current" high-performance rubber and XLPE, along with their application as insulations.

### Natural Rubber

Natural rubber (polyisoprene based on the  $C_5H_8$  unit), when compounded properly was used in the past as insulation rated up to 25kV for power cables, portable cords, and building wires. After synthetic polyisoprene was developed it eventually replaced natural rubber. Polyisoprene rubber became obsolete because of its poor thermal stability above 60°C, and its poor resistance to oil and other fluids due to the high level of unsaturation in the polymer matrix. It was replaced by other rubbers, particularly the ethylene-propylene elastomers which offered better heat and ozone resistance, with excellent electrical properties.

# SBR Rubber

Styrene-butadiene rubber, a copolymer of randomly polymerized styrene and butadiene, is an amorphous rubber. The low temperature (5°C) polymerized cold SBR offered improved tensile and insulation properties over polyisoprene, and was used in low voltage (under 600V) applications as insulation and jacketing material. Wires had good electrical properties, excellent flexibility and resistance to tear and abrasion, but also had poor aging and flame resistance. Like natural rubber, it was replaced by EPDM.

### **Butyl Rubber**

Butyl Rubber is a synthetic copolymer of isobutylene and a small amount of isoprene. The isoprene affords the site for sulfur cure. Butyl Rubber, because of its saturated backbone, provides good ozone, corrosion, aging and moisture resistance. It is suitable as an insulation for application up to  $85^{\circ}$ C (an improvement over isoprene and SBR rubber), and during 1940 and 1950 found applications in medium and high voltage power cables, and shipboard cables with rating higher than 25kV. Butyl rubber was replaced in many applications by EPM rubber because of its ease of processing and improved performance. Table 6 lists some cable applications of NR, SBR, and Butyl Rubber.

Table 6:	Cable	Applications	of NR,	SBR,	and But	yl Rubber
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Power Cables (NR, Butyl)
Portable Cords (NR)
Building Wires (NR, SBR)
Low Voltage Insulation & Jacket (SBR)
Shipboard and Power Cables rated to 85°C (Butyl)
High Voltage Cables (Butyl)

# Nitrile and Nitrile Blends

Nitrile rubber, a copolymer of acrylonitrile and butadiene monomers, finds limited application as insulation for its oil resistance properties. A blend of nitrile and PVC improves ozone, abrasion and weathering resistance. Nitrile/PVC blend insulations are used in some UL jacketing applications. Nitrile/PVC Blend cables are more flexible than PVC alone because of the presence of the nitrile rubber.

#### Neoprene (Polychloroprene)

Polychloroprene, a polymer of chlorinated butadiene (chloroprene), was the first successful synthetic rubber. It was introduced by DuPont in 1932 under the trademark of Neoprene. Properly compounded Neoprene is still widely used as a flexible jacketing material in shipboard and mining cables, and in the internal wiring of appliances. The vulcanization system for Neoprene compounds includes thiourea, metal oxides, sulfur, and thiuram accelerators.

Neoprene's advantages over natural rubber and SBR are improved weathering, oil, flame, ozone and corona resistance, along with mechanical toughness owing to its crystallinity. Neoprene may be compounded to give the wire a thermal rating of -40°C to 90°C. Some Neoprene cable applications are listed in Table 7.

Table 7: Cable Applications of Neoprene Rubber

Cable and Cord Jackets
UL ZMAY Welding Cable Jacket (90°C, 600V or 100V)
Heater Cord (HPN)
Mining Cable Jacket
90°C Rated Appliance Wiring Material (AWM)

# Hypalon (CSM) and CPE (CM)

Hypalon (CSM), a chlorosulfonated rubber, was introduced by DuPont in 1951. It is polymerized by a simultaneous chlorination and chlorosulfonation of polyethylene in an inert solvent with chlorine and sulfur dioxide. Sulfonyl chloride (SO₂Cl) groups provide the cure sites. Hypalon compounds can be crosslinked at the sulfonyl chloride groups with sulfur and thiuram accelerators. However, sulfur and thiuram based formulations have a slow rate of cure and inferior physical properties when compared to peroxide-cures. Metal oxides, such as magnesium, in presence of moisture also have a slow rate of cure. Peroxide-cured Hypalon provides very good heat resistance and compression set, but peroxide by itself has a slow cure rate. For a faster rate of cure, coagents such as triallyl cyanurate (TAC) or vinyl silane may be added to the peroxide system. The addition of plasticizers on a large scale, particularly aromatic petroleum oils, should be avoided as they may interfere with the cure system.

Hypalon is widely used as insulation and a jacketing material because of its toughness, colorability and good electrical properties. Some of the important applications of Hypalon are in RHH-RHW insulations for control cables, HPN cords, appliance wires up to 105°C rating, power cables, locomotive and military cables, and jacketing of mining cables. Hypalon insulated cables are also used in nuclear power stations because of their excellent resistance to degradation by radiation.

CPE (CM) was initially developed as chlorinated polyethylene by DuPont, but was made commercially successful by Dow Chemical in 1970s using an aqueous suspension chlorination of high or low density polyethylene thru the "Slurry Process". Controlled chlorination can yield a wide range of CPE polymers, with chlorination ranging from 25% to 42%. CPE compounds can be processed in both the thermoplastic (uncured) and thermoset (crosslinked) form. CPE can be cured with peroxide/coagent, as well as amine accelerator/sulfur donor-type (thiadiazole) cure systems. CPE insulation is used in welding cables, locomotive cables, military wires, HPN cords and appliance cord jackets.

Both Hypalon and CPE have good oil, ozone, flame and chemical resistance and can easily be pigmented. They can be made heat resistance up to 105°C with proper compounding. Cable applications of Hypalon and CPE are listed in Table 8.

Hypalon	CPE
90°C / 105°C Appliance Wiring Material (AWM)	Appliance Cord Jackets
Heat Cord (HPN)	Heater Cord (HPN)
Power Cables	Welding Cables
Mining Cable Jackets	Mining Cable Jackets
Shipboard, Locomotive, Oil Platform Cables	Locomotive Wires
Military Wires	Military Wires
Nuclear Control Cable Jacket	
Submersible Pumps	
RHH / RHW Insulation for Control Cables	

Table 8: Applications of Hypalon and CPE

# Ethylene-Propylene Rubber (EPM/EPDM)

With the discovery of polymerization of ethylene and propylene using transition metal (Titanium, Vanadium) catalysts by Ziegler and Natta in the 1950's, two new classes of polymers were developed – a saturated copolymer of ethylene and propylene, and a another class of terpolymer called EPDM from ethylene, propylene and a diene monomer. EPDMs have been manufactured by various US and overseas chemical producers (DuPont, Exxon, Lanxess, DSM, Dow) using 1,4 hexadiene, dicyclopentadiene (DCPD) or ethylene norbornene (END) the third monomer as a cure site.

Both peroxide and radiation cured ethylene-propylene elastomers have excellent corona, ozone and heat resistance and superior electrical and low temperature properties (down to -50°C). They can be compounded to get the desired flame resistance using halogenated flame retardants and antimony trioxide or with non-halogenated aluminum trihydrate and/or magnesium hydroxide.

Ethylene-propylene elastomers are the fastest growing rubber for a wide range of wire and cable applications. These elastomers have replaced butyl rubber as the choice material for power cables and they compete with XLPE for cable rated up to 35kV. The low-unsaturation EPDM polymer has been compounded for insulation in UL approved appliance wiring, fixture wires and motor lead wires, for temperature resistance up to 150°C when used in non-flex applications.

Metallocene catalyzed EPDM elastomers were commercialized over fifteen years ago. Metallocene catalysts allow higher reactor temperature and improved

catalyst efficiency to yield cleaner polyolefins (EPM, ethylene-octene, ethylenebutene) and EPDM elastomers with properties similar to those produced using Ziegler-Natta Catalysts. EPM and EPDM based insulations are used in a wide range of wire and cable applications as shown in Table 9.

#### Ethylene Vinyl Acetate Rubber (EVA)

Ethylene copolymers containing 9 to 18 percent vinyl acetate are used in a wide range of appliance, motor lead, fixture wires and switchboard cables. When EVA polymers are properly compounded they perform similar to crosslinked polyethylene (XLPE), but with improved flexibility. EVA polymers with 40% and higher vinyl acetate content can be compounded like a typical rubber, and be peroxide or radiation cured. EVA insulation compound with vinyl acetate content of 50% or higher can be formulated for continuous operation up to 125°C. Increasing vinyl acetate content from 40% to 70% EVA improves the oil and flame resistance, but decreases the low-temperature flexibility. EVA elastomers find application in battery, welding, and mining cables.

### Silicone Rubber

Silicone polymers contain alternate silicone and oxygen groups in combination with methyl, ethyl or phenyl groups, providing elastomers with a wide operating temperature range of -80°C to 250°C. Silicones have outstanding heat resistance, dielectric strength, and excellent ozone, corona and weathering resistance, and can be compounded for good flame resistance. Silicone elastomers generally are filled with silica fillers for reinforcement, and with aluminum trihydrate for arc resistance. When exposed to fire, silica is converted to silicone carbide, forming an insulated char layer that maintains the integrity of the insulation.

Wire and cable insulated with extruded silicone rubber compounds are cured by either hot air or continuous steam vulcanization. Benzoyl peroxide (VAROX[®] ANS) and Bis(2,4-dichlorobenzoyl) peroxide (VAROX DCBP-50 Paste) are the most commonly used peroxides for curing. Silicone compounds are softer and thus have inferior mechanical properties of abrasion resistance and cut-thru resistance. Therefore, many of the insulated silicone cables have either polyester glass fiber or nylon braiding to protect the insulation layer from rough surface pass thru abrasion. Silicone insulated cables find wide range of application in heavy duty wiring of heat pumps, self cleaning ovens, clothes dryers, room cooler, refrigerators, motor lead wires and control cables.

# Fluoroelastomers (Fluorocarbon Rubber)

Fluoroelastomers are very expensive, and are considered the "Cadillac" of insulation materials because they can be compounded to resist temperatures up to 250°C, and can also provide excellent flame, oil and weather resistance. The best known fluoroelastomer, Viton[®], is a dipolymer of vinylidene fluoride and hexafluoropropylene.

Because of their high cost, Fluoroelastomers find limited application in appliance wires of self-cleaning ovens, aircraft wires, and catalytic converter and automatic transmission cables. Fluoroelastomers are also used in the sheathing

application when good oil resistance is required at high temperature. Blends of polyolefin and fluoropolymer, such as ethylene tetrafluoroethylene (ETFE), are used in high frequency plenum cables. Because of their excellent properties, the insulation wall thickness may be lowered to compensate for the cost without sacrificing the performance.

# Polyethylene (PE) and Crosslinked Polyethylene (XLPE)

Low and high density polyethylene (PE) and crosslinked polyethylene (XLPE) are used extensively in wire and cable applications because of their low cost and good to excellent mechanical, thermal, and chemical properties. XLPE has become a workhorse in under-the-hood automotive primary wires and battery cables, and is widely used in industrial control and power cables, switchboard cables, underground service entrance (USE) cables, appliance and motor lead wires, and for ballast leads in fixture wires. Many of the XLPE formulations may also contain a small amount of vinyl acetate (9 to 18 percent) to make the insulation smooth and flexible.

Crosslinked polyethylene can be compounded with high grade fillers, antioxidants, and both halogenated and non-halogenated flame retardants, to provide the insulation with up to 150°C continuous performance, and meet the flame resistance requirements of UL, CSA, and IEEE's horizontal, vertical and cable tray flame tests. XLPE also has excellent dielectric and insulation resistance, good to excellent moisture, oil absorption and abrasion resistance, along with very good weathering properties. XLPE can be cured by peroxide, radiation, or moisture in the presence of silane (these curing processes and mechanisms will be covered in more detail in the crosslinking section). Wire and cable applications of XLPE are numerous and some of them are listed in Table 9.

XLPE	EPR/EPDM
Appliance Wires	Appliance Wires
Motor Lead Wires	Motor Lead Wires
Ballast Leads (fixture wires)	Fixture Wires
Switchgear, Switchboard	Battery Cables
Underground Service Entrance Cable	Welding Cables
Power and Control Cables in Wet and Dry Locations up to 90°C	Power Cables
Submersible Pumps	

Table 9: Wire and Cable Applications of XLPE and EPR/EPDM Rubber

# Polyvinyl Chloride (PVC) and Thermoplastic Elastomers

Polyvinylchloride (PVC) and Thermoplastic Elastomers (TPE) and Thermoplastic Vulcanizates (TPV), are also used in wire and cable. PVC, in particular, is a choice material for low voltage (60 volts) and low temperature (80°C-105°C) automotive applications such as under the dashboard and lighting cables. PVC formulated compounds provide low cost insulation with excellent mechanical properties, and good chemical, corrosion and flame resistance. PVC compounds can be made more flame retardant with an addition of 5 to 10 parts of antimony trioxide. PVC material, though rigid, can be compounded to provide good low temperature flexibility by adding a wide range of plasticizers to the formulation. PVC insulation has good electrical properties, and can match the capacitance value of polyethylene cable with a thicker insulation wall. PVC is used as insulation or jacketing material for many UL approval wires and cables such as machine tool wires, building wires, appliance wires, flexible cords, power distribution and coaxial cables.

Thermoplastic Elastomers (TPE), Thermoplastic Vulcanizates (TPV) and Thermoplastic Olefins (TPO) are relatively new classes of materials that find application in building wires, power cables, appliance wires, and flexible cords. The new engineered resins, such as polyamides (nylons) and polyester TPEs, are tough and are being used in jacketing applications. Many of the thermoplastic classes of insulation provide properties similar to thermosetting rubber or XLPE, but offer the advantage of not having to be cured.

# COMPOUNDING OF INSULATIONS

Wire and cable insulation and jacketing materials are compounded using the basic ingredients shown as a typical formulation in Table 10. Using this generalized formulation as the matrix, a rubber chemist or a compounder can develop a specific insulation compound that will fit the need of a particular cable. Elastomers or resins, which constitute the main ingredient of the formulation, were previously described. Fillers and other additives are discussed in more detail below.

Ingredients	phr
Elastomer or Resin	100
Fillers	30-80
Flame Retardants	10-50
Plasticizers	2-10
Stabilizers	2-10
Process Aids	1-3
Colorant	1-2
Accelerators*	2-5
Curatives*	2-5

Table 10: Typical Insulation Compound Formulation

* Needed for Crosslinking

# Fillers

Fillers serve multiple purposes in the insulation system, including lowering the cost of the compound. Most of the white fillers such as clays, and talcs (VANTALC[®] 6H) are used as extenders and/or reinforcement to improve the mechanical and electrical properties of the insulation. Hard clays, like DIXIE CLAY[®], yield higher modulus, higher tensile and abrasion resistance. Whereas the soft clays, like McNAMEE[®] CLAY, yield lower modulus, lower tensile and higher elongation. Calcined and silane treated clays and talc, are recommended

for further improvement in the mechanical and electrical performance of the insulation compounds. Precipitated silicas, like Hi-Sil[®], provide excellent reinforcement to rubber, particularly, EPDM, SBR, NR, butyl, and Neoprene compounds. Whiting (calcium carbonate) serves as color enhancer, and as filler in most insulations, and also acts as a smoke suppressant in FR compounds. Talc may not only serve as a extender, but also as a viscosity modifier in butyl and EPDM compounds. For black insulation to be fed as a strip in the extruder, carbon blacks, particularly the Thermal Process type, like N990, are used as reinforcing fillers for most rubber insulations that require good physical and electrical properties.

#### Flame Retardants

Both halogenated and non-halogenated flame retardants (FR) are used in the insulation formulation to improve the flame resistance performance of the cable. The degree of the flame resistance requirement depends upon the cable application. Many of the switchgear/switchboard cables, and control cables in nuclear power plants require UL's VW-1 Vertical flame test and IEEE's cable tray tests. Some appliance wires are required to pass only UL's less stringent horizontal flame test. Other cables, such as auto primary wires, are required to pass SAE 45° angel flame test.

Ingredients like aluminum trihydrate, magnesium hydroxide and zinc borates are used in non-halogen FR systems. Halogenated flame retardants are used for the more stringent applications. They include brominates, biphenyl oxides, chlorinated plasticizers and chlorinated paraffins. Halogenated flame retardants generally are used with antimony trioxide (20%-35% by wt. of FR), which acts as a synergist. Other newer type flame retardants include molybdates, phosphates, and melamines.

#### **Protective Package**

This package includes antioxidants, antiozonants, waxes, metal oxides and stabilizers.

Antioxidants - are used as protective ingredients for the polymer chain. They provide protection from oxidative attack during service life. The oxidation of the rubber insulation increases with time and temperature, and the role of the antioxidant is to slow the degradation process by scavenging and destroying oxyradicals before they have a chance to attack the rubber polymer chain. Classes of antioxidants include aromatic amines, phenolics, phosphites, thioimidazoles and thiocarbamates. Amine based antioxidants are "discoloring and staining", while the phenolics are non-discoloring. Phosphites, mercaptotoluimidazole and sulfides are secondary antioxidants, added as synergists. Some examples of antioxidants are AGERITE® RESIN D®, VANOX® ZMTI, Wingstay® L and Songnox® 1010. Without antioxidant or with an insufficient amount of antioxidant, the insulation becomes less flexible, brittle, and hard and will crack over time.

Antiozonants - provide protection from atmospheric ozone attack. Ozone directly reacts with rubber, cleaving the double bonds. Most common antiozonants

are polyphenylenediamine (PPD) derivatives that are used to improve resistance to the ozone attack on the insulation compound. However, because of their staining nature they are not widely used in cable insulations. Instead of them, waxes may be added in most insulation formulations to provide protection from ozone. Waxes are also added to lower viscosity and improve processing during extrusion. Wax added in excess of its solubility in the compound will bloom to the surface after vulcanization and form a film that provides protection from corona and ozone related atmospheric cracking as long as the film remains intact. Paraffins, microcrystalline waxes, and various pre-blended combinations of waxes are used for the purpose of the surface protection. Paraffin waxes (VANWAX[®] H Special) bloom quickly and form a barrier film. Microcrystalline wax (VANWAX OZ) blends bloom slowly.

*Process Aids* - include oils, waxes and internal lubricants. These materials help both the mixing and extrusion of the insulation compound. VANFRE® AP-2 is used as a processing aid in filled compounds to lower heat build up during mixing, and for a smoother extrusion operation.

*Metal Oxides* - such as zinc oxide, are added for better heat resistance. An ester type stabilizer, like Evanstab 18, may also be added to provide secondary oxidative protection.

#### Acceleration and Cure Systems

Sulfur - a sulfur based acceleration system consists of sulfur, and sulfur based accelerators like thiuram (METHYL TUADS®,) dithiocarbamate (BUTYL ZIMATE®), mercaptobenzothiazole (CAPTAX®), and cure modifiers such as VANAX® MBM. All these accelerators should obviously be evaluated in the proposed compound for scorch safety and dispersion.

*Metal Oxide* - compounds of chlorinated polymers, such as Neoprene and Hypalon, may also be cured by a divalent metal oxide such as magnesium oxide to produce ionic crosslinks.

*Peroxide* - A peroxide-based cure system consists of VAROX DCP or VAROX VC-R peroxide and Triallyl Cyanurate (TAC) and/or TMPTMA type coagents. Other cure systems may be amine or resin based. A peroxide cure system is preferred over the sulfur, amine or resin based cure systems whenever possible in wire and cable compound formulations because it is cleaner, non-discoloring, and produces no foul odor during mixing and/or extrusion.

# WIRE and CABLE COMPOUND PROCESSING

# Mixing

Insulation compounds can be mixed in both the Banbury or on a two-roll mill. For polyethylene and certain rubber polymers requiring more efficient breakdown, Banbury mixing is the preferred operation. Compounding areas, along with mixing areas and mixing equipment, should be kept clean and free of contaminants to safeguard any electrical failures in the final cable product. Sulfur and sulfur-based accelerators, or peroxide and coagents, are added at

the end of a second pass, or in an all together separate operation to avoid scorch and any cured lumps in the mixed compound.

An extruder straining operation is commonly performed on the mixed compound. This serves to remove any extraneous matter and also provide further plasticization. A 30 to 40 mesh wire screen, backed with a 10-12 mesh coarser screen, is used in the strainer. The mixed compound can be converted to strips or pellets, and either diced or pelletized using an underwater extruder prior to its extrusion as insulation on the metallic conductor.

#### Extrusion

The extruder's function is to apply the plastic or rubber compound on to the conductor, in what is known as the extrusion process. The extruder's heated barrel and revolving screw, combined with friction and the generated pressure, forces the molten insulation compound through the crosshead and coating die, where it engulfs the solid or stranded bunched conductor. The wire or cable, with the extruded compound, discharges directly from the extruder head into a steam tube through which it is conveyed under tension. Steam pressure in excess of 250 psi is generally used in a steam tube with a minimum length of 200 feet. The typical residence time (cure rate) for thin walled (0.045" or less insulation) wire is from 200–800 feet/ min. Thicker walled high voltage 760 cms power cables, with steam at 200°C plus and 250 psi pressure, will take several minutes to cure. The insulated wire will then pass under pressure through a waterseal, and be air wiped prior to the take up spool for packaging in a drum or on the reel.

# Crosslinking

Two commonly used crosslinking techniques used to optimize the physical properties of the insulation are peroxide-cured continuous vulcanization (CV) in a steam tube, and radiation (electron beam) curing. The third, and more recent crosslinking method, used primarily for polyethylene (PE) insulation, is the silane based moisture cure. Table 11 shows the crosslinking techniques for a variety of insulation compounds.

Material	CV	E-Beam	Moisture
PE (LD, HD, Low VA)	Х	Х	Х
Rubber	Х	Х	-
PVC	-	Х	-
TPO/TPE	no curing required	no curing required	no curing required

Table 11: Crosslinking Techniques

# Peroxide Vulcanization (CV)

Of the three crosslinking techniques, continuous vulcanization (CV), using a peroxide catalyst in the presence of steam, is the most common and widely used curing process. However, care must be taken that premature crosslinking (scorch) does not occur in the extruder, since this will cause small lumps on wire and make the wire unacceptable by the customer, or may affect its properties.

Peroxides of different decomposition temperatures are available for tailor-made

crosslinking. For example, VAROX DCP (dicumyl peroxide) decomposes at a lower temperature, while VAROX VC-R [di-(t-butylperoxy)diisopropylbenzene] requires a higher decomposition temperature. The CV method generally results in a high degree of cure. Line speed, insulation wall thickness, steam pressure and the length of CV tube will all determine the final crosslink density. A three step mechanism of peroxide curing process is illustrated in Figure 2.



Figure 2: Peroxide Vulcanization Mechanism

# Radiation (Electron Beam) Curing

The use of radiation is an effective crosslinking technology (shown in Figure 3), especially for polyethylene since radiation cured polyethylene is used widely in many industrial cables, but it is also a costly method. Radiation, like peroxide, also causes the formation of free-radicals under the electron bombardment, followed by carbon to carbon bonding. It is a fast process, but the cure is determined by the radiation dosage of megarads (Mrads) and insulation wall thickness, and is designed for curing thinner insulation walled wires. Generally, the state of cure is lower than that obtained by the CV process.



Figure 3: Radiation Curing Mechanism

The radiation process can also be used for crosslinking other polyolefins, as well as some rubbers and PVC. Listed below are advantages and disadvantages of radiation curing.

Advantages	Disadvantages
Fast	Limited to thinner wall insulations
Clean	May interfere with antioxidant system
	Health concerns

Table 12: Advantages and Disadvantages of Radiation Curing

# Silane Moisture Cure

Silane based moisture cure is a relatively new crosslink technology for polyethylene. It involves the base PE polymer that is fed in the extruder simultaneously with the master batch containing a vinyl-silane and organic peroxide such as dicumyl peroxide (VAROX DCP). The two step process involves the radical formation, and grafting of the vinyl-silane onto PE, followed by the hydrolysis of the silane alkoxy groups to silanols which condense to form siloxane bonds and the crosslinked structure. After extrusion, the reel of wire is placed in a hot water bath for a number of hours for crosslinking to occur. An alternative ambient temperature curing process may take up to two weeks for crosslinking to occur.

Table 13: Advantages and Disadvantages of Silane Curing

Advantages	Disadvantages
Inexpensive Curing Process	Longer cure time
	Lower crosslink density
	All materials must be kept dry

# CABLE REQUIREMENTS AND APPROVAL PROCESS

Automotive and industrial wire and cable users require approval of one or more the independent testing agencies described below to validate that their wires meet safety and performance requirements:

- American National Standards Institute (ANSI)
- American Society for Testing and Materials (ASTM)
- Canadian Standards Association (CSA)
- Insulated Cable Engineers Association (ICEA)
- Institute of Electrical and Electronics Engineers (IEEE)
- National Electrical Manufacturers Association (NEMA)
- Society of Automotive Engineers (SAE)
- Underwriters Laboratories (UL)
- Original Equipment Manufacturers (OEM), GM, Ford, Toyota, etc.

Some agencies, like UL, have their identification or logo printed on the wire. This has required the manufacturers of wire to submit their products to UL, CSA, ANSI and other agencies, which perform the prescribed tests, at a significant cost, for product approval. Automotive wires have to meet both SAE (which establishes the performance specifications for primary wires and battery cables) and OEM's internal specs.

In the case of UL, once a product is approved the UL field representative makes unannounced visits to the manufacturing plant once or twice a week to randomly sample UL marked wires for onsite testing of such things as physical properties, insulation resistance and flame tests. The UL representative also sends samples to the UL Laboratory for testing of aged physicals or any other properties he cannot perform in the manufacturer's facility.

If a wire fails to pass either the inspector's or the UL Lab specification test requirements UL will put a hold on the entire lot of wire for nonconformance, and request the manufacturer's comments and a corrective action plan. Usually nonconformance can be resolved by redoing wire testing in the presence of the UL field representative. Generally, wires will pass the test requirements upon sitting as the gaseous byproducts escape with time, and permit UL to release the product. If the wires cannot meet the requirements at this point, wires may have to be scrapped. UL approval may be withdrawn or modified if wires continuously fail to meet UL requirements.

OEMs, and the harness makers who supply wire harnesses to OEMs, also normally require wire manufacturers to test wires periodically to make sure they meet the originally established specifications.

#### JACKET and INSULATION FORMULATIONS

Wire and Cable jacket and insulation formulations, along with some of their test data, are listed on the following pages for a beginning compounder to use in developing new wire & cable formulations to met required specifications.

Polymer (Poting)	SBR		Butyl
(Raung)	(КПУУ)		(КПП, КПУУ)
Ingredients	phr		phr
SBR 1502	45.0		
SBR 1018	25.0		
Pliolite [®] S6-F [®] Resin	30.0		
EXXON [™] Butyl 065			100.0
Stearic Acid	1.0		1.0
Zinc Oxide	20.0		5.0
AGERITE RESIN D	1.0		
VANOX ZMTI	2.0		
VANWAX H Special	2.0		2.0
Mineral Rubber	30.0		
NYTAL [®] 400 Industrial Talc			50.0
Calcined Clay			100.0
Sulfur	1.0		
p-Quinonedioxime (GMF)			2.0
Litharge (PbO)	5.0		
Red Lead (Pb ₃ O ₄ )			6.0
ALTAX®	1.0		4.0
BISMATE®	3.0		
Totals	166.0		270.0
Mooney Scorch @ 121°C			
Minutes to 5 pt. rise	19	5	
Original Physical Properties, Cured in Steam	@ 198°C		<u>Required</u>
Cure Time,	30 sec.	45 sec.	
Tensile, MPa	9.4	5.2	4.8 min
Elongation, %	490	600	300 min
Physical Properties After 20 hrs. in Air Bomb	@ 127°C, 550	kPa Air Pres	ssure
Tensile, % Retained	97	81	50 min
Elongation, % Retained	73	95	50 min

Heat and Moisture Resistant Insulation (	UL Dual Rated
------------------------------------------	---------------

# Heavy-Duty Neoprene Jacket

Ingredients	phr
Neoprene W	100.0
VANPLAST® PL	12.0
VANFRE AP-2	6.0
Magnesium Oxide	4.0
Wingstay 100 AZ	1.0
AGERITE STALITE® S	2.0
N770 SRF Carbon Black	25.0
N550 FEF Carbon Black	25.0
Whiting (water ground)	35.0
Zinc Oxide	5.0
VANAX CPA	1.5
SULFADS®	1.5
DOTG	0.5
	010 5

872

33
15
1.2
16.1
490
80
76
106
72

# Extra Heavy-Duty NBR Mining Cable Jacket

· · · · · · · · · · · · · · · · · · ·	
Ingredients	phr
NBR/PVC (70/30)	100.00
Stearic Acid	1.00
Zinc Oxide	3.00
Paraplex G-33	10.00
Dioctyl Sebacate	10.00
AGERITE STALITE	1.00
AGERITE SUPERFLEX® SOLID	0.50
Wingstay 100	0.50
Titanium Dioxide	5.00
Hydrated Silica	35.00
DIXIE CLAY	15.00
PVC Stabilizer	1.25
Sulfur	0.20
ALTAX	2.50
METHYL TUADS	2.00
ETHYL TUADS®	1.00
Total	187.95
Mooney Scorch @ 121°C	
Minimum Viscosity	33
Minutes to 5pt. rise	40
Original Physical Properties. Cured in steam 60 seconds @ 198°C	
200% Modulus MPa	29
Tensile Strength, MPa	12.4
Elongation. %	620
Physical Properties After Heat Aging 20 hrs @ 127°C 3.8 Air Pressure	
Tonsile % Retained	08
Flongation % Retained	84
	04
Physical Properties After Heat Aging in Test Tube, 70 hrs. @ 135°C	100
Tensile, % Retained	100
Elongation, % Retained	78
Physical Properties After Aging in ASTM No. 2 Oil, 18 hrs. @ 121°C	
Tensile, % Retained	104
Elongation, % Retained	90

Ingredients	phr
Hypalon 4085	30.0
Hypalon 40	70.0
Magnesium Oxide (high activity)	4.0
Ti-Pure R-902 Titanium Dioxide	5.0
Precipitated Silica (Hydrated)	25.0
Stearic Acid	1.0
Polyethylene (Low MW)	1.0
VANWAX OZ	20.0
Ester Plasticizer	20.0
METHYL TUADS	2.0
Sulfur	0.5
Total	178.5
Mooney Scorch @ 121°C	
Minimum Viscosity	20
Minutes to 1 pt. rise	13
Minutes to 5 pt. rise	19
Minutes to 10 pt. rise	22
Original Physical Properties	
200% Modulus, MPa	5.6
Tensile Strength, MPa	23.4
Elongation, %	560
Physical Properties After Heat Aging in Air 168 hrs. @ 100°C	
Tensile, % Retained	79
Elongation, % Retained	78
Physical Properties After Aging 18 hrs. in ASTM No. 2 Oil, 18 hrs. @ 121°C	
Tensile, % Retained	108
Elongation, % Retained	87

Extra Heavy-Duty Colored Hypalon® Mining Cable Jacket

# Low-Smoke Flame Retardant AEM Cable Jackets

Ingredients (phr)	Α	В	С	D
VAMAC [®] G	100.0	100.0	100.0	100.0
Stearic Acid	0.5	0.5	0.5	0.5
Cab-O-Sil M-7D	10.0	10.0	10.0	15.0
Nipol [®] 1411	10.0	10.0	10.0	10.0
Multiwax [®] 180-M	3.0	3.0	3.0	3.0
Atomite Whiting	70.0	35.0	135.0	30.0
Hydral [®] 710		35.0		70.0
VANOX CDPA	2.0	2.0	2.0	2.0
VAROX DCP-40C	7.0	7.0	7.0	7.0
VANAX MBM	2.0	2.0	2.0	2.0
Totals	204.5	204.5	269.5	239.5

Original Physical Properties, Press Cur	ed 20 min. @	2 177°C		
Hardness, Shore A	64	64	75	71
100% Modulus, MPa	2.2	1.9	4.1	4.1
Tensile, MPa	6.0	6.7	5.9	7.1
Elongation, %	540	590	480	490
Oxygen Index (Minimum Oxygen Conce	entration)			
Volume percent	25	26	26	27
Vertical Strip Burning (152 x 6 x 2 mm)				
Burn length, mm	152	152	152	152
Number of Ignitions, (N1)	1	1	1	1
Total Burn Time (Tt), sec.	66	79	66	80

# EPDM Cable Insulation- Medium Voltage

Ingredients		phr
Vistalon™ 1703P		100.0
Zinc Oxide		5.0
Paraffin Wax		5.0
Red Lead (90% dispersion in EPM)		5.0
Low Density PE (2.0 M.I.)		8.0
Treated Calcined Clay		65.0
Vinyl Silane		1.0
AGERITE RESIN D		1.5
VAROX DCP		2.6
Total		193.1
Density, Mg/m ³		1.2
Mooney Scorch @ 121°C		
Viscosity, MS		13
Minutes to 10 pt. rise		30+
		IPCEA
Original Physical Properties, Press Cured 20 min. @ 177°C		<u>S-68-516</u>
200% Modulus, MPa	8	
Tensile Strength, MPa	12	4.8 min.
Elongation, %	340	250
Physical Properties After Heat Aging in Air, 168 hrs. @ 121°C		
Tensile, % Retained	100	75 min.
Elongation, % Retained	94	75 min.
Physical Properties After Heat Aging in Air, 336 hrs. @ 150°C		
Tensile, % Retained	102	
Elongation, % Retained	91	

# Heat, Flame and Moisture Resistant EPDM Insulation (UL Dual Rated, 75-90°C)

Ingredients	phr
Vistalon 1703P	90
LD PE (Melt Index-2.0)	20
Zinc Oxide	5
Litharge (90% Dispersion in EPDM)	5
Paraffin Wax	5
VANOX ZMTI	2
	1
Iranslink 37	60
Vinyi Silane	1
Antimony Trioxido	33 12
VAROX DCP	3
Total	237
Sample: 0.76mm wall on No. 12 AWG Solid conductor, Steam Cured 60 psi Steam	0 sec. in 250
Original Physical Properties	
Tensile Strength, MPa	11.2
Elongation, %	300
VM-1 Flame Test (UL)	Pass
Electrical Properties Water Immersion at 90°C	
SIC (60 Hz)	
1 Day	2.74
7 Days	2.86
14 Days	2.76
180 Days	2.9
Power Factor, 60 Hz, %	
1 Day	0.45
/ Days	0.48
14 Days	0.48
180 Days	0.48

# Ethylene Vinyl Acetate (EVA) Automotive Wire Compound

Ingredients	phr
Elvax [®] 40L-02	100.0
SRF Carbon Black	0-3.0
Stearic Acid	1.0
VAROX VC-R	2.5
VANAX MBM	1.0
Hydrated Alumina	75-90.0
Silquest [®] A-172	1.0
Songnox 1010	2.0
Songnox DLTDP	1.0
Total	183.5-201.5

Mooney Viscosity ML 1+4 @ 100°C	17
Original Physical Properties	
Hardness, Shore A	70
Tensile, MPa	9.4
Elongation, %	360
Tear Strength, kN/m	6.2
Dielectric Strength, ASTM D149, kV/min	14.5
Physical Properties After 18 hrs. @ 121°C in ASTM No. 2 Oil	
Tensile, % Retained	70
Elongation, % Retained	60
Retained Physicals After Heat Aging in Air, 72 hrs. @ 177°C	
Tensile, % Retained	106
Elongation, % Retained	92
Retained Physicals After Heat Aging in Air, 168 hrs. @ 150°C	
Tensile, % Retained	100
Elongation, % Retained	95

# Chlorinated Polyethylene in General Purpose Flexible Cord Jackets 90°C

Ingredients	phr
Tyrin [®] CM 0136	100.0
Trimethylolpropane Trimethacrylate (TMPTM)	5.0
VAROX 802-40KE	5.0
N550 Carbon Black	35.0
Calcium Carbonate	150.0
Diisonyl Phthalate	38.0
Paraffin Wax	2.0
Magnesium Oxide	5.0
Total	340.0
Original Physical Properties	
100% Modulus, MPa	4.3
200% Modulus, MPa	5.9
Tensile, MPa	9.7
Elongation, %	457
Physical Properties After Heat Aging in Air, 240 hrs. @ 110°C	
Tensile, % Retained	111
Elongation, % Retained	86

# Crosslinked Polyethylene Integral Insulation Jacket

Ingredients	phr
Polyethylene (DYNH)	100.0
AGERITE MA	0.5
N990 Carbon Black	60.0
VAROX DCP-40KE	7.0
Total	167.5

Original Physical Properties, Press Cured 20 Minutes @ 171°C	
100% Modulus, MPa	11.0
Tensile Strength, MPa	16.1
Elongation, %	310
Physical Properties After Air Bomb Aging 20 hrs. @ 127°C, and 550 kPa Air	
Tensile, % Retained	97
Elongation, % Retained	94
Physical Properties After Oxygen Bomb Aging 168 hrs. @ 80°C, and 2.1 MPa	Oxygen
Tensile, % Retained	97
Elongation, % Retained	80

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# ELASTOMERIC SEALS

## by John J. Carr

JnC Consulting Laconia, NH

One of the larger non-tire applications for elastomers is sealing components, where all of the commercially available natural and synthetic materials are currently used. A seal can be defined as a device intended to eliminate or control the passage of liquids and/or gases, while preventing the entrance of dust, dirt and other external contaminants. Sealing elements are classified as either static or dynamic, depending on their specific function. Static seals are those where sealing is accomplished between two mating surfaces with no relative motion between them. Typical examples are automotive engine cylinder head gaskets and oil pan gaskets. Dynamic seals, examples of which are automotive crankshaft seals and hydraulic cylinder rod seals, include those where relative motion, either continuous or intermittent, exists between adjacent parts.

Historically, gaskets, U-packings, V-packings, cup packings and O-rings have been used as general purpose sealing devices. More recently, customdesigned seals have supplanted their traditional counterparts, primarily to satisfy the demand for increased sealing efficiency and extended service life. This is particularly true for devices such as radial shaft seals and mechanical face seals, where many proven performance proprietary design components are available. Custom-designed seals incorporating proprietary design features and/or special purpose elastomeric materials have enjoyed exponential growth in the past, a trend that is likely to continue.

#### Seal Design Considerations

Design is critical to the success of any sealing application, particularly where proprietary components are involved. The design engineer and material technologist must consider a variety of interdependent variables to achieve the required end product performance. These include:

- The chemistry of the medium or media to be sealed.
- The anticipated high and low temperature operating range.
- The pressure range and frequency of application.
- The clearance between mating components.
- The degree of lubrication present.
- The frequency and speed of relative motion.
- · The surface finish on adjacent components.
- The method of handling and installation.

The choice of elastomer is governed by the medium or media to be sealed and the anticipated temperature range in service. High pressure applications may cause the elastomeric sealing element to elongate or extrude into prevailing clearances. This is frequently compensated for by reducing clearances, modifying the physical properties of the elastomer and/or a basic modification of the seal design. Normally, high pressure operating environments require a high modulus/ high durometer formulation. In many cases, rigid plastic or metallic devices provide additional support. Inadequate lubrication in dynamic applications can lead to frictional heat generation and premature seal failure. Graphite, Teflon[®] and other dry lubricants can be added to the formulation to impart the required lubricity.

Optimum seal performance is to a large degree dependent upon the proper design of mating components, and installation procedures which are quite often not within the control of the seal supplier. In dynamic applications particularly, the seal contact surface should have a finish between 10 and 20 micro inches. Coarser finishes cause excessive wear, while finer ones inhibit the formation of a lubricant film on the shaft, which is necessary to reduce friction and lower temperatures at the contact interface. Care must be taken to select the appropriate shaft finishing technique in order to prevent machine "lead" or spiral grooving that can lead to leakage. Scratches on the shaft surface, particularly at the seal contact point, inevitably lead to leakage and can not be tolerated. High pressure seals such as those used on hydraulic cylinders should have a smooth finish at the low end of the recommended range, to prevent the ingestion of dirt into the system. Hard chrome plating or corrosion resistant alloys are frequently used when environmental conditions require them.

Many sealing devices are precision-molded, highly engineered products. As such, they must be handled and installed properly to satisfy the required performance level in service. In the case of shaft seals, any assembly procedures that could damage the rubber sealing element and/or dislodge springs or other support devices must be avoided.

#### Seal Failure Modes

If appropriate design considerations are taken into account, precision-molded elastomeric seals will perform satisfactorily throughout their useful life. Heat or prolonged exposure to high temperatures beyond the recommended limit of the base elastomer is a major factor limiting longevity. Thermal hardening is caused by a progressive crosslinking of the base elastomer, in many cases catalyzed by oil additives used in most proprietary hydraulic and lubricating fluids. The materials ultimately lose their elastomeric properties and assume a permanently distorted configuration. Surface crazing and hardening is the initial indication of thermal degradation, followed eventually by total embrittlement of the sealing element. Heat sources are not always obvious and are quite often overlooked. Temperature surges can come from sources external to the seal and/or from the seal itself. Examples are inadequate air circulation and heat generators such as a car's catalytic converter or an adjacent exhaust pipe. Finishing operations performed by the seal user, including painting and subsequent hot air drying, are another potential source of heat. The seal assembly itself is a common cause of frictional temperature increases. In dynamic applications, lack of lubrication in the area where the seal contacts the mating metal surface can produce a temperature increase. The seal will ideally be completely covered by oil, although this is seldom the case. Oil cools and provides lubrication to the seal while excluding oxygen, a catalyst of thermal degradation. Newer seal designs often incorporate hydrodynamic pumping features to reduce frictional heat buildup. High pressure invariably means that more rubber will contact the adjacent metal sealing surface, creating another generator of frictional heat.

Prolonged exposure to temperatures in excess of 150°C can break down petroleum-based hydraulic and lubricating oils to form hard carbon-like particles. These accelerate heat buildup and quite often abrasion of the elastomeric sealing element. Severe seal wear and thermal degradation can be caused by the so-called "Joule effect." The phenomenon occurs when the elastomeric component is heated while stretched. One would expect it to thermally expand, when in reality it contracts. Many dynamic seals are used under "Joule effect" conditions, which can increase the load or force at the seal contact point and further elevate the temperature, unless appropriately compensated for.

### **Types of Seals**

Cross-sectional views of the five general purpose sealing devices are shown in Figure 1. They are quite often available in standard sizes and materials. Simplicity of design, ease of installation and relatively inexpensive maintenance make them ideal for a wide variety of applications.



Figure 1: General Purpose Sealing Devices

*Gaskets* are typical examples of the basic compression sealing concept. They are manufactured from a wide variety of materials, including elastomers and elastomeric composites. Combinations of cork and elastomers have been popular for many years in the automotive and allied industries, where the compressibility of cork and the resilience of rubber combine to provide an ideal composite in applications such as automotive engine gaskets. Gaskets can be molded, die cut from a flat sheet to a desired geometry, or formed in place using liquid silicone or other commercially available compositions. They are installed between two adjacent surfaces with the compressive sealing force exerted by a bolting or clamping action. Molded automotive engine gaskets have supplanted FIPG (formed in place gaskets) and cork/rubber composites as the preferred sealing method (Figure 1). Currently they are fabricated from a variety of materials, including silicone (VMQ), polyacrylate (ACM), ethylene/acrylic (AEM), and in some cases fluoroelastomers (FKM).

*O-rings*, candidates for most any general purpose application, are the simplest and most universal elastomeric sealing device. With proper design and installation, they are capable of sealing extremely high pressures in the static mode. Their ability to withstand dynamic pressure depends largely on groove design and clearances. The primary mode of failure of a dynamic O-ring seal is material extrusion into prevailing clearances. Backup rings are rigid support members made from plastics or metal that serve as anti-extrusion devices. O-rings are used extensively in automotive steering and brake systems, "off the road" heavy equipment, aircraft and a wide variety of industrial and household applications.

*U-packings* are pressure-actuated sealing elements used very effectively in low to moderate dynamic pressure sealing applications. Their thin walls or sealing surfaces provide very little friction, but this friction increases proportionately to the pressure applied. The friction at low pressure can be adjusted somewhat by modifying the mechanical properties of the elastomeric composition principally hardness and modulus. Most U-packings are used on reciprocating hydraulic and pneumatic rod seal applications. Their use allows more liberal tolerances on mating components. A pneumatically or hydraulically actuated door opener is a typical U-packing application.

*V-packings*, sometimes called Chevron seals, are normally used in high pressure dynamic applications at relatively low speeds. They accommodate axial and radial loads much better than U-packings. High pressures normally require the use of 3 or more seals. A composite of fabric impregnated with an elastomer will substantially increase pressure-bearing capabilities. Quite often, V-packings made from tetrafluoroethylene compositions are used in combination with rubber counterparts to reduce friction, without compromising pressure-bearing capabilities. V-packings are used extensively in heavy duty hydraulic cylinders for "off the road" earth moving equipment and other general purpose hydraulic cylinders.

*Cup-packings* are used almost exclusively as piston head seals. Originally made from leather, almost all low pressure smaller size cups are now made from elastomeric compositions, while their high pressure counterparts incorporate elastomer-fabric constructions or tetrafluoroethylene compositions. When used alone, they are unidirectional seals, although two mounted back to back will provide bidirectional sealing capabilities. Cup-packings are considered to be very good general purpose hydraulic piston seals. They can be used where clearances between mating parts are excessive, or rough metal sealing surfaces will be encountered in service.

Radial lip seals are normally used in dynamic, relatively low pressure sealing applications. Shaft movement can be rotating, reciprocating or a combination of the two. While many are available in standard sizes, the trend is toward custom-designed components available in a variety of proprietary, application-specific configurations.

Radial lip seals feature a stationary flexible elastomeric sealing lip, frequently bonded to a rigid metal or plastic support ring. Many designs incorporate a spring mounted behind the sealing lip to maintain contact between the lip and shaft, while others eliminate the spring and simply rely on the resiliency and modulus of the rubber to provide the required sealing force. A secondary wiper or dust lip is frequently incorporated to exclude contaminants. Figure 2 illustrates these three basic geometrical concepts.



Figure 2: Radial Lip Seals

Proprietary designs are available for higher pressure service. These normally incorporate thicker flex sections at the base of the sealing lip, reduced seal lip height and a higher tension spring. In some cases, rigid plastic or metal support devices are used immediately behind the seal to further enhance pressure bearing capabilities and resistance to extrusion.

Many rotating shaft applications employ custom designed seals with hydrodynamic pumping aids that significantly improve seal life and reliability by lowering operating temperatures and improving seal lip lubrication. Typical examples are shown in Figure 3. A series of raised ribs or other proprietary shapes that function as pumping aids are molded into the inner side of the sealing lip. Any oil leaking past the seal lip while the shaft rotates is returned to its point of origin. A molded annular lip provides sealing in the static position. Depending upon the type, shape and placement of the pumping aids, seals are available for both unidirectional and bidirectional shaft rotation.



Figure 3: Hydrodynamic Seal Designs

Mechanical Face Seals, as illustrated in Figures 4 and 5, are multicomponent sealing devices used to provide a leakage-free seal between a rotating shaft and a member through which the shaft passes. Sealing is accomplished through continuous relative contact between two flat radial sealing surfaces located in a plane perpendicular to the shaft center line. Sealing faces are made from plastic, metal or other corrosive and abrasion resistant compositions. One face is attached to the shaft and rotates with it while the other is stationary, mounted in the housing. Unlike the more conventional seals, there is no direct contact between the rubber and the shaft. Mechanical face seals are more expensive than most other seals; consequently they are used in more demanding applications involving corrosive and abrasive environments, high pressures and/ or shaft speeds. These include automotive water pump seals and a wide variety of applications in the chemical process industries where their high reliability and efficiency justify the cost premium.







Figure 5: Mechanical Face Seal Components

#### Polymer Selection and Formulation Design

Proprietary elastomeric seal materials are available to satisfy most current sealing challenges. The experienced rubber technologist uses the appropriate polymer and additives in the design of a formulation to satisfy specifically defined application requirements.

Criteria for base polymer selection include temperature extremes and the chemical composition of the medium or media to be sealed. Of equal importance, and not to be overlooked, are factors external to the seal that can influence performance. For example, seals operating in close proximity to electric motors should contain a suitable antiozonant such as 6PPD to prevent ozone attack, unless the polymer is inherently resistant.

Sealing elements exposed to water and/or high humidity conditions are vulnerable to corrosion where pitting of the metal sealing surface adjacent to the seal lip can accelerate lip wear. Appropriate choices of base polymer(s), along with careful selection of compounding materials, will minimize this concern.

Polymers low in water-soluble ash are preferred. Some mineral fillers used in seal formulations, either alone or in combination with carbon black, absorb water readily. Including polyglycols and/or organosilanes in the formulation is an effective and practical technique to reduce water absorption.

Table 1 and Figure 6 show the relative performance properties of a variety of properly formulated seal materials. This information is intended as a general guide to material selection since, quite often, maximizing performance in selected areas requires compromise in others. For example, silicone is considered to be one of the most thermally stable elastomers available. However, when exposed to automotive brake fluids at temperatures in excess of 125°C, severe softening and loss of mechanical properties can occur.

Nitrile rubber (NBR), Styrene-butadiene rubber (SBR), Polyisoprene and Neoprene are the traditional elastomers of choice for most conventional sealing applications. While resistance to thermal and oxidative degradation is marginal when compared to other special purpose elastomers, careful selection of compounding ingredients can significantly enhance end product performance and extend service life.

NBR, for example, is the most popular of the general purpose elastomers used in seals. It combines excellent oil resistance and reasonable thermal stability with moderate cost. Ideally, formulations should contain low levels of elemental sulfur in the curing system. Sulfur donor, peroxide or sulfur/peroxide systems are preferred in many applications for optimum thermal stability. Blends of antioxidants such as AGERITE® RESIN D®, AGERITE STALITE® S and VANOX® ZMTI initially enhance heat resistance, although some are frequently extracted by oils in service. Some NBR polymers contain a non-extractable antioxidant system, and merit consideration where this is a concern. Mineral fillers used either alone or in combination with carbon black are preferred in thermally stable NBR seal compounds. Treatment with organosilane coupling agents and/or polyglycols is effective in improving water resistance, minimizing the cure inhibition frequently experienced with some mineral fillers, and upgrading resistance to wear and abrasion. A carboxylated NBR should be considered for use in applications requiring maximum abrasion resistance.

		Lube	Hydraulic	Brake	Syn.	FR	
	Fuels	Oils	Fluids	Fluids	Lubes	Fluids	Abrasion
Epichlorohydrin	Yes	Yes	Yes	No	Ltd	No	Good
Ethylene-acrylic	No	Yes	Ltd	No	No	No	Good
Ethylene-propylene	No	No	Yes	Yes	No	Yes	Good
Fluorocarbon (FKM)	Yes	Yes	Yes	No	Yes	Ltd	Good
Fluorocarbon (FEPM)	No	Yes	Yes	yes	Yes	Yes	Good
Fluorosilicone	Yes	Yes	Yes	No	Yes	No	Poor
NBR	Yes	Yes	Yes	No	Yes	No	Good
NBR (Carboxylated)	No	Yes	Yes	No	Yes	No	Exc
NBR (Hydrogenated)	Yes	Yes	Yes	No	Yes	No	Exc
Neoprene	No	Yes	Yes	Yes	No	No	Good
Polyacrylate	No	Yes	No	No	No	No	Fair
Polyisoprene	No	No	Yes	Yes	No	No	V. Good
SBR	No	No	Yes	Yes	No	No	Good
Silicone	No	Yes	Yes	Ltd	No	No	Poor

#### **Table 1: Seal Material Properties**

*Notes*: Yes = Elastomer has satisfactory resistance; Ltd = Limited compatibility; No = Elastomer is not compatible and should not be used.

Fuels Lube Oils	<ul> <li>Gasoline and high swell petroleum-based hydraulic oils</li> <li>Engine and transmission oils, greases and lubricating oils</li> </ul>
Hydraulic Fluids	= Water, alcohols and water based hydraulic fluids
Brake Fluids	= Glycol-based automotive brake fluids
Syn. Lubes	= Diester oils and greases
FR Fluids	= Fire resistant phosphate ester oils

High performance special purpose elastomers including Ethylene Propylene (EPDM), Epichlorohydrin (CO, ECO, GECO), Fluorocarbons (FKM & FEPM), Hydrogenated Nitrile (HNBR), Polyacrylates (ACM), Ethylene/Acrylic (AEM), Silicone (VMQ) and Fluorosilicone (FVMQ) continue to supplant their general purpose counterparts in a wide variety of sealing applications. Although initially more expensive, they offer cost-effective solutions to requirements for upgraded performance, reliability and longevity. As with most elastomeric seal compounds, the formulation must be carefully designed to ensure optimum product performance in a specific environment.

As an example, sealing elements in today's passenger car brake systems normally require EPDM-based compounds. To satisfy the temperature demands, they should be cured with an organic peroxide such as VAROX[®] DBPH-50 and stabilized with a suitable antioxidant such as AGERITE RESIN D. Most EPDM polymers provide outstanding resistance to traditional glycol-based brake fluids, although the ethylene content of the polymer must be carefully selected to provide the required balance of low temperature performance with thermal stability. Compounds should contain a minimum of extractable materials in order to prevent volumetric shrinkage after exposure to the brake fluid.

Hydrogenated Nitrile Rubber (HNBR) is frequently the material of choice in many applications where conventional NBR compounds fail to provide the required thermal stability and/or resistance to prevailing hostile environmental conditions. The technology involves a reduction of double bonds or unsaturation in the polymer backbone by hydrogenation of conventional NBR. HNBR compounds are characterized by dramatically improved thermal stability, resistance to oxidative and ozone degradation along with superior tensile, tear, abrasion and general dynamic properties.

HNBR is equivalent to NBR in oil and fuel resistance and can be cured with either sulfur or peroxide, depending on the level of unsaturation in the base polymer. Seal compounds designed for optimum thermal stability are ideally based on polymers with low levels of unsaturation. A peroxide/coagent cure system, such as VAROX[®] 802-40KE and VANAX[®] MBM, is used with a combination of antioxidants such as VANOX MTI, AGERITE STALITE S and VANOX CDPA. Mineral fillers either alone or in combination with carbon black provide good reinforcement and excellent overall seal performance, particularly in rotating shaft seals. Plasticizers are used at fairly low levels in thermally stable HNBR compounds, mainly to improve low temperature performance.

Special grades of HNBR modified with zinc oxide and methacrylic acid are available, offering exceptionally high physical properties, toughness and abrasion resistance with some sacrifice in compression set resistance. The materials can compete with polyurethane in selected applications by offering improved thermal stability and water resistance.



Figure 6: Practical Temperature Ranges for Seal Elastomers

*Fluorocarbon Elastomers (FKM)*, copolymers of hexafluoropropylene and vinylidene fluoride and terpolymers that include tetrafluoroethylene (TFE) are generally recognized as the ideal materials for long term exposure to hot oils and gasoline. Although high cost limits their consideration in many seals, FKM

remains the material of choice for many automotive drive train applications, where it has proven to provide cost-effective solutions to chronic seal failures, notably in the engine and transmission.

Traditional general purpose FKM compounds can be adversely affected by engine and transmission oil additives, manifested by a substantial reduction in physical properties, along with visually apparent surface crazing and cracking. The process occurs in a relatively short period of time at elevated temperature, and is believed to be caused by dehydrofluorination of the elastomer surface. A change in base polymer and/or curing system will frequently eliminate or minimize the condition. Base polymers with higher fluorine levels or TFEcontaining terpolymers are optional alternatives.

Fluorocarbon copolymers based on tetrafluoroethylene and propylene (FEPM) offer outstanding resistance to aggressive engine oils and corrosive chemicals, making them viable alternatives for sealing devices used in the automotive and chemical process industries, as well as oil field installations. Unfortunately, peroxide cure systems, poor mechanical properties at high temperature and rubber to metal bonding concerns combine to create processing problems.

Tetrafluoroethylene/propylene/vinylidene fluoride terpolymers represent some of the latest technology in the fluoroelastomer field. Advertised as Base Resistant Elastomers (BRE), they combine excellent resistance to aggressive amine-containing engine, transmission and gear oils with good processing characteristics quite similar to the FKM types. An incorporated bisphenol cure system replaces peroxide to further enhance processing and improve rubber to metal bond quality. In contrast to their FKM counterparts, both the copolymers and terpolymers are adversely affected by high aromatic gasolines.

Fluorocarbon formulations are fairly simple compositions normally containing a base polymer, metal oxide(s), carbon black and/or mineral fillers and a curing system. Some polymers contain proprietary curatives, while others require the addition of diamines or peroxides. The base polymer is the most critical component governing end product performance. Mineral fillers are the preferred loading materials for shaft seal compounds.

*Polyacrylate Elastomers (ACM)* provide outstanding resistance and long term stability in hot oils. The automotive industry is the largest consumer of polyacrylate for sealing applications; they are used mainly in static or low speed dynamic applications. They have operated for years in automatic transmission seal applications, although their use in relatively high speed dynamic seals has declined. Inadequate low temperature flexibility and relatively poor wear resistance, along with sensitivity to moisture and water, have virtually eliminated them from consideration as an engine seal material.

There is a wide variety of commercially available ACM polymers offered under the HyTemp[®] trade name by Zeon Chemicals. Compositional differences include the monomer used to form the polymer backbone and the cure site monomer incorporated for crosslinking, the more popular being chlorine-containing types.

Depending on the specific polymer, a variety of cure systems can be used, including soap/sulfur, ammonium benzoate, blocked diamines and thiourea, among others.

A soap/sulfur cure system with a chlorine-containing cure site is a popular, easy processing choice for many successful seal formulations. An antioxidant such as AGERITE RESIN D, Wingstay[®] 29 or VANOX CDPA should be included for sustained high temperature performance. Plasticizers are available to improve low temperature performance, although the more effective types will volatilize during the post cure operation or be extracted by fluids encountered in service, making their long term viability questionable. ACM compounds respond well to carbon black and mineral fillers. Graphite is used in selected applications to improve wear resistance. Hydrophilic fillers should be treated with a glycol and/or an organosilane to reduce water absorption. Stearic acid is an effective process aid, as is the metallic soap when a soap/sulfur cure system is used.

Ethylene Acrylic Elastomers (AEM), based on ethylene and methyl acrylate, are among the most recent innovations in polyacrylate technology. Carrying the ASTM D 1418 designation "AEM", a wide range of products, marketed under the trade name Vamac[®] by DuPont Performance Elastomers, is available as both copolymers and terpolymers. The former grades respond exclusively to peroxide/coagent crosslinking, while the latter can be cured with either peroxide/ coagent or diamine systems. Ethylene/acrylic elastomers traditionally exhibit a fairly high volume swell in automatic transmission fluids and engine oils. Newer grades with higher levels of methyl acrylate offer reduced swell.

Ethylene/acrylic seal compounds are available for gaskets, O-rings and radial shaft seal applications. Generally, their wear resistance and low temperature flexibility, as well as their performance in hot water and low pressure steam, are superior to traditional ACM compounds. Compounding techniques for AEM and ACM compounds are quite similar, although peroxide cured AEM copolymer compounds normally do not require postcuring. ACM polymers do not respond well to peroxide crosslinking. In most cases, ACM and AEM terpolymer seal compounds require a post cure of 3 to 5 hours at 177°C (350°F) to develop optimum properties.

*Epichlorohydrin (CO, ECO, GECO)* elastomers currently find limited application as seal materials. They are mainly used in O-rings, gaskets and other custom seals for fuel management systems. Homopolymers (CO) offer an excellent balance of heat, oil and fuel resistance, along with the very low gas permeability and ozone resistance inherent in the polymer. Copolymer (ECO) grades contribute excellent low temperature flexibility, while the terpolymers (GECO) can be blended with a variety of other elastomers to achieve intermediate performance. Cure systems for CO and ECO include thiourea types and diamines. GECO grades can be crosslinked with peroxides such as VAROX DBPH-50, as well as conventional sulfur systems.

Silicone (VMQ) and Fluorosilicone (FVMQ) compounds have been used in a wide variety of seal applications for many years. O-rings, shaft seals,
gaskets and many custom-designed components made with these polymers provide outstanding thermal stability with unmatched low temperature flexibility. However, VMQ grade silicone polymers are at best only moderately resistant to oil. Oil resistance can be dramatically improved by using high vinyl-containing base polymers and additives to produce a very high crosslink density or state of cure. A further reduction in volume swell is achieved by incorporating very high filler levels to dilute the polymer content.

The high fluorine content of FVMQ polymers permits the design of compounds that are highly resistant to petroleum oils and gasolines, without any major sacrifice in thermal stability or low temperature performance. Unfortunately, their high cost, and the difficulty in bonding compounds to steel and other substrates, has hindered their use in many potential applications.

In most cases, both VMQ and FVMQ are marketed as finished compounds by raw material suppliers or custom mixers, requiring only the addition of an organic peroxide prior to use.

Seal performance and long term viability rely totally on the successful marriage of an appropriate product design geometry with a properly selected and formulated compound, which must be put together under precisely controlled manufacturing conditions to produce a high quality finished component. Technology is available to solve most any sealing concern if these fundamental criteria are satisfied.

Appended to this section are selected formulations for seal compounds based on polymers commonly used in the industry. Each will probably require minor adjustments, or even major modifications, to satisfy specific operating criteria. In any event, thorough end product testing is strongly recommended prior to use.

### Acknowledgements

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- · John C. Dahlheimer Engineering Manager, Mechanical Face Seals
- Roger O. Gagne Vice President of Engineering (now retired)

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Ingredients (phr)	Fluorocarbon (FKM)	Fluorocarbon (FEPM)
Viton [®] A-401C	100	
Viton TBR-605C		100
N990 Carbon Black	20	30
Amlok [™] 321 Kaolin Clay	10	
Calcium Hydroxide	6	
Magnesium Oxide (High Activity)	3	8
Totals	139	138

### **Typical Formulations for Seal Applications**

Press Cure 10 min. @ 177°C			
Postcure 16 hrs. @ 200°C			
Original Physical Properties			
Hardness, Shore A	75	75	
100% Modulus, MPa	4.2	7.0	
Tensile, MPa	14.2	15.9	
Elongation, %	280	245	

Typical Formulations for Seal Applications			
Ingredients (phr)	Ethylene/Acrylic (AEM)	Ethylene/Acrylic (AEM)	Polyacrylate (ACM)
Vamac [®] DP	100.00		
Vamac G		100.00	
HyTemp [®] AR-71			100.0
Stearic Acid	0.50	1.00	1.0
Armeen [®] 18D	0.50	0.50	
VANFRE® VAM		1.50	
N550 Carbon Black	50.00	55.00	25.0
Graphite		20.00	20.0
Amlok 321	15.00	20.00	
Zeolex [®] 23			25.0
Plasticizer 759	5.00	10.00	
VANFRE AP-2	1.25		
AGERITE RESIN D	1.25		
VANOX CDPA		2.00	1.5
Wingstay 29			1.0
VANAX MBM	2.00		
VAROX 802-40KE	4.50		
VANAX DOTG		4.00	
Diak [™] 1		1.25	
Sodium Stearate			3.0
Potassium Stearate			1.0
Spider Sulfur			0.4
Totals	180.00	215.25	177.9
Press Cure 10 min. @	177°C		
Postcure @ 177°C	none	5 hrs.	5 hrs.
Original Physical Prope	erties		
Hardness, Shore A	68	74	69
100% Modulus MPa	4.2	5.1	5.4
Tensile, MPa	12.7	13.3	9.8
Elongation, %	390	225	330

Ingradiante (nhr)	Ethylene-propylene	Polyisoprene	Styrene-butadiene
ingreaients (pnr)	(EPDM)	(IK)	(58K)
Vistalon [™] 2504	100.00		
Nipol [®] IR 2200		100.00	
SBR 1502			100.00
Zinc Oxide	5.00	5.00	5.00
Stearic Acid	0.50	1.75	1.50
N550 Carbon Black	45.00		55.00
Amlok 321	15.00		
N110 Carbon Black		45.00	
N990 Carbon Black		20.00	
VANTALC [®] 6H			15.00
Light Process Oil			5.00
AGERITE RESIN D	1.25	3.00	1.50
VANOX ZMTI			1.50
VANFRE AP-2	1.25		
SR-350 Coagent	1.75		
Spider Sulfur		0.25	0.25
VAROX DBPH-50	4.50		
ALTAX [®]		2.00	
METHYL TUADS [®]		1.25	2.50
VANAX A		1.25	
VANAX NS			2.00
Totals	174.25	179.50	189.25
Press Cure @ 177°C	10 min.	5 min.	10 min.
Original Physical Prope	erties		
Hardness, Shore A	73	68	70
100% Modulus MPa	3.4	3.1	4.6
Tensile, MPa	15.1	23.3	19.1
Elongation, %	420	510	445

# **Typical Formulations for Seal Applications**

	Nitrile	Carboxylated	Hydrogenated
Ingredients (phr)	(NBR)	Nitrile (XNBR)	Nitrile (HNBR)
Nipol 1032	100.00		
Nipol NX-775		100.00	
Zetpol [®] 2010			100.00
Zinc Oxide	5.00	5.00	
Stearic Acid	1.00	2.00	0.50
AGERITE RESIN D	0.75	1.00	
AGERITE STALITE S	0.75		
VANOX CDPA			1.50
VANOX ZMTI	1.50	1.50	
VANOX MTI			1.50
N550 Carbon Black	45.00	50.00	
N330 Carbon Black			30.00
VANTALC 6H	35.00		15.00
Paraplex G-50	5.00		
Plasticizer TP-759	5.00		7.50
Dioctyl Phthalate (DOP)		7.50	
VANFRE AP-2	1.50	1.50	
METHYL TUADS	2.50	0.25	
ALTAX	3.00		
UNADS®		1.25	
Spider Sulfur	0.40	1.50	
VANAX MBM			3.00
VAROX 802-40KE			7.00
Totals	206.40	171.50	166.00
Press Cure 10 min. @ 177°C (No F	Postcure)		
Original Physical Properties			
Hardness, Shore A	73	77	75
100% Modulus, MPa	4.8	4.4	5.0
Tensile, MPa	18.0	24.6	26.1
Elongation, %	420	445	355

**Typical Formulations for Seal Applications** 

	Neoprene	Epichlorohydrin
Ingredients (phr)	(CR)	(GECO)
Neoprene W	100.00	
Hydrin [®] T3000LL		100.00
Stearic Acid	1.00	1.00
Magnesium Oxide	4.00	
Dyphos		2.00
AGERITE STALITE S	2.00	
VANOX NBC		1.50
N774 Carbon Black	40.00	
Calcium Carbonate	60.00	
N550 Carbon Black		45.00
N326 Carbon Black		20.00
Dioctyl Sebacate (DOS)	7.50	
Plasticizer TP-95		5.00
VANFRE AP-2		1.00
VANWAX [®] OZ	1.50	
Zinc Oxide	5.00	
DOTG	0.75	
UNADS	0.75	
Spider Sulfur	0.40	
THIATE [®] EF-2	0.75	
VAROX DPC-40C		1.75
SR-350 Coagent		2.50
Totals	223.65	179.75
Press Cure 10 min. @ 177°C		
Original Physical Properties		
Hardness, Shore A	66	64
100% Modulus, MPa	3.1	2.1
Tensile, MPa	14.3	11.3
Elongation, %	310	430

**Typical Formulations for Seal Applications** 

### by R. H. Parker, PhD

Assistant Professor of Chemistry LaGrange College, LaGrange GA

Rubber has been used as a coating material to modify the properties of fabrics for hundreds of years. In the seventeenth century, Juan de Torquemada¹ reported that the "juice" of the Ulagahil tree could be painted onto linen fabric to protect the user from rain. Indeed, one of the earliest British patents², in the eighteenth century, describes the waterproofing of fabric by coating it with a solution of rubber in turpentine.³

The means of application of the rubber (coating) to the fabric (substrate) is usually determined by the desired amount of coating to be applied (add-on). The application of dry coatings in amounts of approximately (4 to 20 mils) in a single pass is usually done on a calender. As depicted in Figure 1, a stock, compounded in the usual manner, is softened on a set of heated rolls and is applied to the fabric by passing both through a gap (nip) of desired dimensions between another pair of rolls.





Smaller add-ons can be achieved by applying the coating to the stock from solution or dispersion. After the stock has been compounded, it is sheeted or chopped into small pieces and dispersed in a suitable solvent. The dispersion takes place in a device known in the trade as a churn. It may be as simple as a paddle-type stirrer in a mixing tank, or may contain one or several devices to further reduce the size of the particles as mixing progresses.

The most common method of applying a coating of this type is by the creation of a gap under a knife, suspended perpendicularly to the direction of travel of the substrate on the coating machine. As depicted in Figure 2, the coating is applied to the substrate, prior to the knife, in excess of the desired add-on. The excess is removed by the shearing process of passing through the gap. This method allows for the addition of a constant volume of coating dispersion in a rapid manner. The penetration of the coating into the substrate and many other parameters can be determined by the shape of the edge of the knife and the angle it presents to the moving substrate. This technique can also be used to apply single or multiple layers of coating to a release medium, with the subsequent transfer and lamination under pressure of the coating to the desired substrate.



Figure 2: Typical Knife-coating of Fabric

The rubber dispersion may also be applied to the fabric by transfer from an engraved roll (gravure), passing under a wire wound rod, transfer from a coated roll (reverse roll), extrusion of the coating from a slot, or by spraying. In some cases, the fabric is immersed in the coating dispersion and the excess is removed by squeezing the fabric between two rolls.^{4, 5}

The solvent is removed in a drying step by passing the fabric through an oven, which typically consists of one or more chambers in which the temperature can be carefully controlled and the expelled vapors removed. The manipulation of the temperature in each of these chambers is necessary so that the solvent can be removed safely and without detriment to the coating. Improper or incomplete removal of the solvent can lead to the formation of bubbles (blisters) or discontinuities in the coating (pin holes). The solvent must also be removed at a rate that does not allow an explosive concentration of vapors to collect in the oven. The ability to properly remove the solvent may define the amount of coating that can be applied in a single pass, or the speed at which the coated fabric can be processed. Environmental concerns may dictate that the solvent be recovered and recycled, or it may be required that the solvent be destroyed, as it is removed, by incineration. These requirements may also affect the economic efficiency of the coating process.

Various methods exist by which the dried fabric can be cured. The fabric may pass directly into another oven where it may pass over many rollers in a serpentine manner (or it may be festooned in large loops) to allow for the necessary exposure time to complete vulcanization. In some cases, the fabric may be wound on a roll and cured in an autoclave. If the cure rate allows, the same effect may be achieved by passage of the coated fabric over one or a series of drums, heated, typically, by hot oil.⁶ The cure system for a potential coating formulation must be devised with the requirements of the available curing equipment in mind.

No mention has been made, until now, of the choice of polymer systems for the coating. The compounder is familiar with a variety of sources (this volume being one) to determine the choice of a polymer, its cure system and auxiliaries, in order to meet a series of desired performance parameters. Some additional particulars concerning coating systems, which require consideration, are mentioned below.

The coating must be an adhesive. Regardless of the final use of the coated product, the coating must adhere to the substrate and remain on it during the service life of the product. This means that the compounder must understand the nature of the material that is to be coated and how the coating will interact with that material, chemically and mechanically, to achieve adhesion. It may require the use of additional ingredients, or the possibility of multiple passes (primers) with different compounds. It may also require the modification of the intended cure system.

Materials such as diisocyanates or silanes can act as bridging agents between the coating and the substrate, and will markedly improve the adhesion of some coatings that have difficulty bonding to synthetic fabrics. Diisocyanates are commercially available, and can be used either as adducts to the coating formulation or as primer coats. Caution must be used with these materials because of their noted toxicity and potential for sensitization. Blocked diisocyanates, which are not as toxic, are also available, but require additional heat and time during processing to remove the protective group before they become reactive. Silanes⁷ can also be used as primers, after hydrolysis to remove protecting alkoxy groups, or, less frequently, may be used as adducts to the formulation.

Adhesion to the fabric can be maximized by the use of primer coats of materials such as resorcinol-formaldehyde resin permeated latex systems (RFL)⁸, with a potential loss, however, in composite flexibility and appearance.

Coated fabrics can usually be placed into one of two groups. When the mass of coating exceeds the mass of the fabric, the role of the fabric is typically to reinforce the composite (e.g. conveyor belts, hoses, V-belts etc.). These materials are covered in detail in other chapters of this volume. When the mass of the coating is a smaller percentage of the composite weight, the coating is usually intended as a modifier of the fabric properties. In this case, the finished composite is typically recognized as a textile, with the latter's properties.

The tensile strength of a compounded rubber is rarely fully used in a coating of the textile type. Because of the inelasticity of the fabric, the critical elongation of a rubber is seldom approached. The desired tensile properties of the cured compound are commonly those that do not detract from the nature of the fabric. For instance, it is usually highly desirable that the composite be flexible and "drapes" like an uncoated fabric. In this case, the compounder should be very aware of the tensile stress of the cured stock at low extension (e.g., 50% modulus), as an indicator of how the coating might affect this property. A high stress value, and any tendency of the coated film to contract under cure, can cause an undesirable condition in which the composite curls toward the coated side, when cut, to form a tube.

Many coated fabrics are required to possess some degree of resistance to burning. The compounder is aware of the types and amounts of flame retardants that are required to achieve the desired effect in the compounded polymer. It should be noted that the mass of the coating, being a small percentage of the mass of the composite, may require that a more efficient flame retardant package be used to achieve the same effect on the coated fabric.

A series of typical coating formulas, previously reported in this volume, is listed in the following tables.⁹

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- For a short review of this subject, the reader is referred to Wake, W.C. and Wootton, D. B., *Textile Reinforcement of Elastomers*, Applied Science Publishers, Ltd., London, 1982, p. 4.
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- 5. See also "Coating and Processing Techniques" contained in Satas, D. (ed.), *Coatings Technology Handbook*, Marcel Dekker, Inc., New York, 1991, p.101.
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- A review of RFL technology is available in Takeyama, T. and Matsui, J., *Rubber Chem. Technol.*, 42, 159, (1969), updated in Solomon, T.S., *Rubber Chem. Technol.*, 58, 561, (1985).
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	Heater-Cured	Self-Cu	iring
Ingredients (phr)		Calendered	Spread
Smoked Sheet	100.00	100.0	100.0
VANPLAST® R	3.00	3.0	3.0
Stearic Acid	1.00	0.5	0.5
Zinc Oxide	3.00	3.0	3.0
AGERITE® STALITE® S	0.50	0.5	0.5
N774 Carbon Black	4.00	4.0	4.0
Calcium Carbonate, (pptd.)	75.00	75.0	75.0
McNAMEE [®] Clay	50.00	50.0	50.0
Sulfur	0.75	1.5	1.5
ROTAX®	1.00	-	-
ALTAX®	1.00	-	-
METHYL ZIMATE®	0.25	-	-
BUTYL EIGHT®	-	3.0	4.0
RODO [®] 0	0.10	0.1	0.1
Totals	239.60	240.6	241.6
Density, Mg/m ³ (calc.)	1.46	1.46	1.45
Note: Heater-cure spreading.	d compound can be pr	ocessed by either calen	dering or

# **Natural Rubber Clothing Formulations**

Suggested Cures: Heater-cured compound, 1 hour rise and 1.5 hours at 132°C (270°F). Self cure, 24 to 48 hours in warm room.

# **SBR Clothing Formulations**

		Heater-Cured	Self-Cu	uring
Ingredients (phr)	)		Calendered	Spread
SBR 1006		100.00	100.0	100.0
VANPLAST R		7.00	7.0	7.0
Stearic Acid		2.50	0.5	0.5
Zinc Oxide		3.00	3.0	3.0
AGERITE STALIT	ES	0.50	0.5	0.5
Cumar MH		20.00	20.0	20.0
Calcium Carbona	te (pptd.)	75.00	75.0	75.0
N774 Carbon Bla	ck	4.00	4.0	4.0
McNAMEE Clay		75.00	75.0	75.0
Sulfur		2.50	2.5	3.0
AMAX®		1.75	-	-
METHYL ZIMATE		0.50	-	-
BUTYL EIGHT		-	5.0	6.0
RODO 0		0.10	0.1	0.1
Totals		291.85	292.6	294.1
Density, Mg/m ³ (c	alc.)	1.48	1.47	1.46
Note:	Heater-cured (knife-coatin	d compound can be p g).	rocessed by either calen	dering or spreading
Suggested Cures:	Heater-cured cure, 24 to 4	d compound, 1 hour ri 8 hours in warm room	se and 1.5 hours at 132° n.	°C (270°F). Self

Ingredients (phr)	Butyl	EPDM
EXXON [™] Butyl 068	100.0	
Vistalon [™] 2504		100.00
Stearic Acid	1.0	1.00
Zinc Oxide	5.0	5.00
VANFRE [®] AP-2	2.0	
Whiting	20.0	60.00
ULTRASIL [®] 150 Precipitated Silica	35.0	
DIXIE CLAY®		20.00
Titanium Dioxide	5.0	5.00
N774 Carbon Black	2.0	2.00
Sunpar [®] 2280 Oil		50.00
Sulfur	1.5	1.50
METHYL TUADS®	1.5	0.75
CAPTAX®	1.5	
ETHYL TELLURAC®	0.5	
BUTYL ZIMATE®		2.00
Totals	175.0	247.25

### **Butyl and EPDM Proofing Compounds**

*Note:* Compounds can be processed by either calendering or spreading.

Cure: 20 minutes rise and 1.5 hours @ 141° (285°F).

	Hypalon®	Neoprene	
Hypalon 40	100.00		
Neoprene W		100.0	
Stearic Acid	1.00		
Magnesium Oxide	10.00	4.0	
AGERITE RESIN D [®]	2.00		
VANOX [®] NBC	2.00		
AGERITE STALITE S		2.0	
VANWAX® H		3.0	
DIXIE CLAY	50.00		
Titanium Dioxide	15.00		
N774 Carbon Black	2.00		
N990 Carbon Black		60.0	
Di(2-ethylhexyl) Azelate	20.00		
VANPLAST PL		5.0	
Litharge	20.00		
SULFADS®	0.75		
VANAX® CPA		1.5	
UNADS [®]		0.5	
VANAX DPG		0.5	
Sulfur		0.5	
Totals	222.75	177.0	
<i>Note:</i> Compounds can be processed by either calendering or spreading. In the Hypalon compound, a synthetic hydrotalcite can be substituted for the litharge to maintain low water swell without using lead.			

# Hypalon & Neoprene Proofing Compounds

Cure: 20 minutes rise and 1.5 hours @ 141° (285°F).

### by William F. Barham

### Firestone Building Products Company Prescott, AR

Repeating information from my predecessor in this chapter, F. W. Doherty of DuPont de Nemours and Company¹, "Flexible polymeric membranes for waterproofing industrial flat and low slope roofing and for the ground containment of liquids and dry waste, evolved from their use for foundation waterproofing in Germany in the 1930's".² Approximately 66% of the present day 320 million square meter (3.5 billion square feet) market for non-residential roofing utilizes single-ply roofing membranes (SPRM) with approximately 1/4 of that being based on EPDM rubber.

Soil-supported polymeric membranes and barriers for the solids (landfills), liquids, and gases presently constitutes a market for an estimated 45 million square meters (500 million square feet), if not larger, of flexible membrane liners, also known as geomembranes.³ Some of the synthetic rubbers used are, Hypalon[®] (CSM), Neoprene (CR), CPE, Epichlorohydrin (ECO) and Ethylene-Propylene Terpolymer (EPDM), along with PVC and thermoplastic elastomers (TPOs), and their selection is based on the type of chemical, environmental or radiation attack possible. Some specific uses are industrial ponds, aquaculture ponds for fish farms, potable water reservoirs, golf course and other aesthetic (homeowner) ponds, closed landfill covers, and waterproofing of parking decks.

General requirements for the SPRM and geomembranes, again quoting my old friend Mr. Doherty, "are imperviousness to water, certain chemicals and effluents; flexibility; strength and weather resistance." Different additives and blends can modify the compounds to obtain other specific properties such as fire resistance, wind uplift resistance.

### Single-Ply Roofing Membranes

BUR (built-up roofing) was the primary roofing system for many years for industrial buildings. This system consists of hot asphalt (bitumen) and bitumensaturated felts applied in multiple layers on the roof. As long as the roof had some pitch (i.e. incline) to allow water to drain rather than puddle on the roof and these roofs were located in the Northeastern part of the United States, they were acceptable. As new and larger buildings with very little or no pitch to them became the norm, and these spread into the South and West, the BUR systems were found to have major problems with weather and sunlight deterioration.

This allowed an emerging technology, the single-ply roof membrane (SPRM) to become prominent. The first membrane used was of Butyl rubber, followed soon after by EPDM, in the late 1950's and early 1960's under development programs. In the mid-1960's, these became commercial roofing systems with EPDM becoming the dominant polymer. Two primary reasons for the success of the EPDM for weathering and ozone resistance is due to (1) the diene

crosslinking sites are pendant to the saturated polymer backbones and (2) carbon black is an excellent UV absorbent. The UV energy is converted to heat at a temperature which has little effect on the rubber.

In the early 1970's, there was a worldwide petroleum shortage, which led to the refineries learning how to make more gasoline and other fuels from a barrel of crude. This left little "bottoms" from which the majority of the asphalt (bitumen) of the day was made, and which was also of lower quality and more expensive. This shortage made building owners aware of the need for new roofing systems, including energy efficiency to reduce energy costs to the owner (insulation), less costly to put down and generally more weather resistant.

By this time there were several roofs made of rubber membranes, as noted above, which had at least ten years of actual weather exposure. This was sufficient to entice roofers, building owners and architects to try the new membranes, particularly in light of generally superior performance. This performance included retention of flexibility over many years of exposure to hot and cold weather, wind, water, etc. Another enticement was the ability to put down a membrane roofing system over an existing roof, including the thermal insulation, due to the low weight of the new systems, with little affect on the snow load rating of systems in the North.

With time, the roofing systems evolved to three types: <u>ballasted</u> where approximately 10 pounds per square foot of rounded rock or other ballast are placed on top of the membrane and insulation to hold it in place; <u>mechanically attached</u> where long screws (to penetrate to the decking) and batten bars are placed around the periphery of the membrane to hold the system in place; and finally, the <u>fully adhered</u> system where the back side of the membrane has adhesive applied and is then applied to the top of the insulation or other decking. As can be deduced from the different systems, the membrane must have abrasion, penetration and tear resistance; ability to adhere; good tensile and elongation properties, besides the weathering (UV) and heat aging resistance.

With time, the membranes used in the above systems were either <u>reinforced</u> or <u>non-reinforced</u>. The <u>reinforced</u> membrane is used primarily in areas of high foot traffic on the roof or roofs with equipment requiring high levels of maintenance with the possibility of sharp objects dropping to its surface. This reinforcement can be added at the calender between the plies (generally using 1000 denier polyester with 9 ends per inch in both the machine and cross machine direction) or as polyester backing similar to a thin mat. This membrane is normally put down using either the mechanically attached or fully adhered systems. Breaking strength and penetration resistance increase dramatically with the use of reinforcement in or on the membrane.

Generally, rubber membrane is made of EPDM currently. A generic compound is formulated as noted in Table 1.

Ingredients	phr
Vistalon [™] 5601	100.0
Zinc Oxide	5.0
Stearic Acid	1.0
Paraffinic Process Oil	8.0
N650 Carbon Black	130.0
Sulfur	1.2
BUTYL ZIMATE® (ZDBC)	1.0
ALTAX [®] (MBTS)	1.5
Total	319.7
Density, Mg/m³	1.15
Original Physical Properties (Typical)	
Hardness, Shore A	65
300% Modulus, MPa	1.0
Tensile Strength, MPa	12.6
Elongation, %	400

### Table 1: EPDM Roofing Compound

The membrane compound can be modified dramatically with the addition of mineral fillers, halogenated oils, fire retardant materials, and different cure systems, to increase fire resistance to meet UL-790 specification burn requirements, enhance tear resistance, reduce costs, and improve wind uplift resistance.

This compound is mixed in the internal mixer, as are other similar compounds. The compound is then sent to the calender. Generally, roofing membrane consists of two equal plies separately calendered or extruded through a roller die system, then laminated together. The reason for this is that, statistically, it is almost impossible to have two defects to line up and give a hole in the sheet. These sheets can be made in any width up to 3.0 m (10 feet), relative to the calender's or roller die's working face on the rolls. They can be assembled to form panels up to 15.2 m (50 feet) wide by over 132 m (400 feet) in length, dusted with a partitioning agent (to improve stripping and is normally a talc or mica dust) and rolled up onto large curing mandrels. The panels are then cured either by autoclave (steam or hot air) or Rotocure (though this technology is primarily used in Europe). After curing, the membrane is stripped from the mandrels, slit to the customer's requirements (generally in multiples of 3.0 m [10 feet] widths and 33 m (100 feet) lengths, packaged for shipment, and then shipped per customer orders.

The properties required of the membrane are dictated by ASTM D 4637, which is found in Volume 04.04. The minimum gauge of the finished membrane is 1.0 mm (.040 inches), though the customer may request membrane of different gauges. In fact, the two industry standards are 1.1 mm (.045) and 1.5 mm (.060 inches) in thickness, though gauge thickness of 3.0 mm (0.120 inches) has been made for special applications.



Figure 1: EPDM Installation

Notably, the above information has covered only black EPDM membrane. White and colored membrane has been made and used successfully, but is considerably more expensive due to the use of white fillers such as precipitated silica and titanium dioxide, along with other ingredients, such as Carbowax 3350, to enhance the mineral fillers ability to "wet" into the polymer matrix for good physical and processing properties. With the proper filler loadings and polymer, a white sheet can be made which has at least 15 years of service life, though it will "chalk" as the rubber breaks down with UV exposure. Also, with the proper compounding, the membrane will have very high reflectivity, which can reduce the cost of cooling in the summer and may reduce urban temperatures, according to Environmental Protection Agency studies. Unfortunately, as noted above, these rubber compounds are relative expensive, particularly when compared to the white thermoplastic (TPO) materials and the difference in cost of putting the systems down (heat welding for TPO's to seal sheet edges together versus adhesives for rubber membrane).



Figure 2: Meadowlands Building

Along with the roofing membrane, there are additional materials used to make the roofing system a successful, long lasting roof. These are:

*Flashings* - These are uncured, non-reinforced sheet from 2 to 18.9 cm (5 to 48 inches) in width and 30.5 m (100 feet) in length. This product contains a special cure system to allow it to vulcanize after placement on the roof with just sunlight. The uncured sheet of EPDM is easily formed around any roof protrusions or up parapet walls, due to lower compound viscosity to allow ease of forming, and is held in place with adhesive, as described in ASTM D 4811. Neoprene or Epichlorohydrin (ECO) flashing is occasionally used. These materials may or may not be cured and are generally used as a barrier between the main membrane and the grease or oil generator (i.e. a fast food restaurant vent-pipe). Typical compounds are shown in Table 2.

Ingredients	Neoprene	EPDM
Neoprene W	100.0	
Vistalon 3708		100.0
N762 SRF Carbon Black	75.0	
N650 GPF-HS Carbon Black		100.0
Sundex 790T	25.0	
Sunpar 2280		60.0
Maglite D	4.0	
Novazone AS	2.0	
AC-617 Polyethylene	4.0	
Stearic Acid	3.0	2.0
Sulfur	1.0	1.0
ALTAX (MBTS)	0.4	3.0
Zinc Oxide	4.0	5.0
Total	218.4	271.0
Density, Mg/m³	1.30	1.11
Original Physical Properties (Typical)		
Hardness, Shore A	60	55
300% Modulus, MPa	10.0	11.0
Tensile Strength, MPa	11.7	12.6
Elongation, %	500	600

Table 2:	Typical	Neoprene	and EPD	M Flashing	Compounds
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Seam Tape - a solid adhesive made with EPDM or butyl as the carrier for the other ingredients, such as polybutene, that give the tape its adhesive capability. The seam tape compound must be designed to resist "creep" where the forces on the sheet act to open a gap in the splice, hence an area where a leak may occur. These polymers also impart extraordinary weathering resistance.

*Walkway Pads* - are typically made from reclaimed rubber and placed on the roof to prevent foot traffic damage to the membrane.

Perimeter Strip - is made from reinforced sheet and is mechanically attached, as well as adhered around the perimeter of the roof to stop the forces on the

membrane (due to wind or building shifts) from pulling rubber from the parapet walls, as examples.

Liquid Adhesives - are made with Neoprene or Butyl rubber to adhere the membrane or flashing to the substrate of the roof. These may be fiber or insulation boards. Butyl adhesive has proven to be more water resistant in ponded water areas, but the Neoprene adhesive is still used in application areas where grease or oil may come into contact with the main membrane.

### Liquid-Applied Roofing and Waterproofing

Neoprene and Hypalon are two polymers used to formulate compounds which can be made into a liquid for ease of application on roofs. These are normally either spray-applied or manually spread on a substrate, which may be a new roof, or over an existing one. As the solvent dissipates, the layer of rubber hardens, then eventually vulcanizes in place. The membrane surface is solvent and oil resistant to some degree, but the down side is that original solvent of the liquid system is released into the air. The specification for these materials is found in ASTM D 3468.

### Geomembrane

As noted in the introduction, this term covers a wide variety of membrane uses, from land fill covers and liners to decorative ponds for individuals and golf courses. Some of the uses are listed below with examples of polymers used in the rubber compounds:

- Pond liners are used for private fishponds, golf course ponds. The pond liner compound must be fish-friendly for decorative fish such as Koi. EPDM is used for long lasting UV resistance.
- Canal liners are primarily used in Europe for recycling agriculture-use water. EPDM is used for long lasting UV resistance and easily designed compounds which must be very fish-friendly, to the microscopic aquatic life level.
- Landfill liners depending on their application, may require compounding with Neoprene, ECO, CPE, or Hypalon polymers for solvent and oil resistance.
   EPDM would be used for resistance to radiation, minor oil resistance and primarily for water resistance.
- Landfill covers have generally been made from EPDM since only water resistance over a very long period is required. Because these liners are buried, soil resistance is also required. The rubber type will change relative to the need for oil and solvent resistance, etc.
- Above ground sewage treatment for areas which are swampy and can't have normal septic systems, as the raw waste migrates to the surface with potential health hazards. A new system has been developed by the University of Arkansas extension in Hope, AR., using membrane-lined sewage laden streams around homes with native plants in them. Between the plants and the bacteria on the plant roots, the sewage is transformed into nutrients for the plants while cleaning the water.

Examples of Hypalon compounds are shown in Table 3.

Ingredients	phr	phr
Hypalon 45	100.0	100.0
Maglite D	4.0	4.0
N762 SRF Carbon Black		50.0
McNAMEE® CLAY		50.0
N990 MT Carbon Balck	100.0	
SULFADS®	1.0	1.0
VANAX® MBM	1.0	1.0
ALTAX	1.0	1.0
Carbowax 3350	1.0	1.0
Total	208.0	208.0

Table 3: Starting-point Compounds for Hypalon Geomembranes

The liners and covers use the same basic compound structure and technology of roofing from the standpoint that the sheets are laid out on the ground, then the edges adhered together to make a continuous membrane with water resistance.Obviously, the membrane follows the contour of the pond, landfill, stream or canal. Those areas above the water line that are exposed to sunlight have the same UV resistance as seen in the roofing membrane. Typical pond liner applications, in both cases for reservoir use, are shown in Figure 3 and Figure 4.



Figure 3: Reservoir Lining



Figure 4: Snow Reservoir

Please contact the appropriate polymer suppliers for specific compounding and technical data for the intended end use.

### Other Uses of Rubber Polymers in Roofing

Modified bitumen is basically an asphalt which has been modified with mineral fillers and polymers such as SBS or polypropylene, along with a fiber mat between plies to enhance its ability to be torch-applied to a substrate on the roof. The addition of the SBS allows the membrane to resist flow in hot weather, as well as improve weather resistance, particularly low temperature cracking. Other rubber polymers have been explored, but haven't been as successful as this one or some of the thermoplastic elastomers.

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# CHAPTER 7 General Information

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# Standard Classification System for Rubber Products in Automotive Applications

This specification system has been devised jointly by the ASTM Committee D 11 on rubber and rubber-like material and the Society of Automotive Engineers (SAE). It is of sufficient interest and importance to warrant its reproduction in part and to show how it may be used. The following may be considered an abbreviated course on how to interpret a typical "line call-out" or specification using the example outlined in the D 2000 publication.

An example line call-out may comprise the following letters and numbers:

# 2BC 510 A14E034

The first portion of the call-out is called the basic requirements. This consists of the *2BC 510*. The basic requirements may be interpreted as follows:

- 2 = *Grade* number. This defines the performance level for the suffix requirements.
- B = The material *type*. This defines the aging temperature requirements. B type materials are aged at 100°C (212 °F).
- C = The material *class*. This determines the oil swell requirements. C class materials have a 120% maximum volume swell in ASTM IRM 903 Oil.
- 5 = The target hardness,  $50 \pm 5$  Shore A.
- The minimum tensile strength, 1000 psi. If the line call-out starts with the letter M (for metric), the tensile is given in MPa. (Since 1000 psi = 7 MPa, the equivalent metric call-out is M2BC 507).

The letters and numbers following the basic requirements are called the suffix requirements. These are added only as needed to meet specific end-use requirements. For example, the *A14E034* suffix requirements may be interpreted as follows:

- A = Special heat resistance, -15% maximum tensile change and -40% maximum elongation change. Without the A14 suffix, the basic type materials are permitted  $\pm$  30% tensile change and -50% elongation change after heat aging.
- 1 = The test method for heat resistance, ASTM D 573 for 70 hours.
- 4 = The test temperature for heat resistance, 100°C (212°F).
- EO = Fluid resistance (oils and lubricants). As the case for heat resistance, this suffix allows less change in properties after ASTM IRM 903 Oil immersion than the basic C class material.
  - 3 = The test method for fluid testing, ASTM D471 in IRM 903 Oil for 70 hrs.
  - 4 = The test temperature for heat resistance, 100°C (212°F).

Тур	e by Ter	nperature	Cla	ss by Volume Swell
Α	70°C	(158°F)	A	no requirement
В	100°C	(212°F)	В	140% maximum
С	125°C	(257°F)	С	120% maximum
D	150°C	(302°F)	D	100% maximum
Е	175°C	(347°F)	E	80% maximum
F	200°C	(392°F)	F	60% maximum
G	225°C	(437°F)	G	40% maximum
Н	250°C	(482°F)	Н	30% maximum
J	275°C	(527°F)	J	20% maximum
Κ	300°C	(572°F)	K	10% maximum

The following tables show the basic types and classes that have been established for the ASTM D 2000/SAE J 200 nomenclature system.

As shown below, Table X1.1 of ASTM D 2000 provides the polymers most commonly used to meet the *Type* and *Class* requirements, and the table following it lists the meaning of the *Suffix Letter* requirements.

Type &			
Class	Polymer Commonly Used	Mear	ning of Suffix Letter
AA	NR, IR, SBR, IIR, EPDM, BR	А	Heat Resistance
AK	Т	В	Compression Set
BA	EPDM, high temp. SBR, IIR	С	Ozone or Weather Resistance
BC	CR	D	Compression-Deflection
BE	CR	EA	Fluid Resistance (aqueous fluids)
BF	NBR	EF	Fluid Resistance (fuels)
BG	NBR, AU, EU	EO	Fluid Resistance (oils and lubes)
BK	NBR	F	Low-Temperature Resistance
CA	EPDM	G	Tear Resistance
CE	CSM	Н	Flex Resistance
CH	NBR, ECO	J	Abrasion Resistance
DA	EPDM	K	Adhesion
DE	CM, CSM	Μ	Flammability Resistance
DF	ACM (low temperature)	Ν	Impact Resistance
DH	ACM, HNBR	Р	Staining Resistance
EE	AEM	R	Resilience
EH	ACM	Z	Any special requirement, as
EK	FZ		jointly agreed to buy producer
FC	MQ (high strength)		and customer
FE	MQ		
FK	FVMQ		
GE	MQ		
HK	FKM		
KK	FFKM		

The *first suffix number* following each suffix letter may be interpreted from the following table. Only 4 first suffix numbers are listed, but up to 9 first suffix numbers are available in the complete D 2000/J 200 system. The cell defined by each letter and number combination shows the ASTM test method and time in hours that are to be used.

Suffix	First Suffix Number					
Letter	1	2	3	4		
A, Heat	D573, 70 h	D865, 70 h	D865, 168 h			
B, C/S	D395, 22 h	D395, 70 h	D395, 22 h	D395, 70 h		
	B molded	B molded	B plied	B plied		
C, Ozone(a)	D1171, A	D1171(a)	D1171, B			
D, C/D	D575, A	D575, B				
EO, Oil	D471, 70 h	D471, 70 h	D471, 70 h	D471, 168 h		
	IRM, 901 Oil	IRM 902 Oil	IRM 903 Oil	IRM 901 Oil		
EF, Fuel	D471, A, 70 h	D471, B, 70 h	D471, C, 70 h			
EA, Aqueous	D471, water	D471, 70 h				
		water-glycol				
F, Low temperature	D2137, 3 min.	D1053	D2137, 22 h	D1329, 10%		
G, Tear	D624, die B	D624, die C				
H, Flex	D430, A	D430, B	D430, C			
J, Abrasion	as specified					
K, Adhesion	D429, A	D429, B				
M, Flame	as specified					
N, Impact	as specified					
P, Staining	D925, A	D925, B				
R, Resilience	D945					
Z, Special Requirement						

(a) = 6 week weather test used in suffix C2; ozone cabinet for C1 and C3 Note: Test method A, B or C generally specified after the main method number. (Fuel A, B or C specified in suffix EF; IRM 901, 902 or 903 Oil in suffix EO.)

The second suffix number indicates the test temperature and, for all but low temperature testing, increases with the number:  $1 = 23^{\circ}C$  (74°F);  $2 = 38^{\circ}C$  (100°F);  $3 = 70^{\circ}C$  (158°F);  $4 = 100^{\circ}C$  (212°F), etc. Temperature increments are 25°C (45°F) per suffix number for temperatures above 100°C. This progression continues up to a second suffix number of 11 at 275°C (527°F). A second suffix number of zero indicates ambient outdoor testing conditions.

For low temperature testing (suffix requirement F), the test temperature decreases as the second suffix number increases:1 =  $23^{\circ}C$  ( $74^{\circ}F$ ); 2 =  $0^{\circ}C$  ( $32^{\circ}F$ ); 3 =  $-10^{\circ}C$  ( $26^{\circ}F$ ); 4 =  $-18^{\circ}C$  ( $0^{\circ}F$ ); 5 =  $-25^{\circ}C$  ( $-13^{\circ}F$ ). Below 25°C, temperature decrease in 5°C ( $9^{\circ}F$ ) increments down to  $-80^{\circ}C$  ( $-112^{\circ}F$ ) at a second suffix number of 12.

In order to develop a particular specification or line call-out, a current ASTM D 2000 or SAE J 200 publication should be consulted to determine what available suffix grades and requirements have been developed for each type and class of material. Where blank spaces occur in the tables of suffix requirements, it signifies currently unavailable properties. Sample tables for BC materials are shown on the following pages.

Purporter tesponeStrong by painUtimate painHeat Age ASTM DotsoDiamenetion ASTM DotsoAvailable ASTM Dotso3034353002,53010145050002,53014203150002,54007101540002,54007101540002,54007101540002,540014203150001,540014203150001,540014203150001,540014203150002,540014203150002,550010145035002,550010145035002,550011203130002,550012304645002,650021304650002,650014203135003,550014203135003,550014203135003,550014203135003,550014203135003,550014203135003,550014203135003,550014203135003,550014203135003,550014203135003,5500142031<	Basic Requirements						
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Durometer Hardness ±5 Points	Te <u>Strenc</u> MPa	nsile g <u>th, min.</u> psi	Ultimate Elongation, min. %	Heat Aged ASTM D 573 70 h at 100°Cª	Oil Immersion ASTM D 471 IRM 903, 70 h at 100°C⁵	Available Suffix Numbers
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		Grade	Grade	Grade	Grade	Grade
	Suffix Requirements*	2	3	4	5	6
A14	Heat resistance, ASTM D573, 70 h at 100°C:					
	Change in hardness, max points	+15	+15	+15	+15	+15
	Change in tensile strength, max, %	-15	-15	-15	-15	-15
	Change in ultimated elongation, max, %	-40	-40	-40	-40	-40
B14	Compression set, ASTM D 395,					
	Method B, 22 h at 100°C, max, %	35	35	35	35	35
C12	Resistance to ozone ASTM D 1171	100	100	100	100	100
012	Resistance to ozone, ASTIN D TITT	100	100	100	100	100
EO14	Fluid resistance, ASTM D 471, IRM					
	901 Oil, 70 h at 100°C:					
	Change in hardness, points	±10	±10	±10	±10	±10
	Change in tensile strength, max, %	-30	-30	-30	-30	-30
	Change in ultimate elongation, max, %	-30	-30	-30	-30	-30
	Change in volume, %	-10 to	-10 to	-10 to	-10 to	-10 to
		+15	+15	+15	+15	+15
EO34	Fluid resistance, ASTM D 471, IRM 903 Oil, 70 h at 100°C:					
	Change in tensile strength, max, %	-70	-60	-45	-60	-60
	Change in ultimate elongation, max, %	-55	-50	-30	-60	-50
	Change in volume, %	+120	+100	+80	+100	+100
F17	Low-temperature brittleness, ASTM D 2137, Method A, 9.3.2, nonbrittle after 3 min. at -40°C	pass	pass	pass		pass
F19	l ow-temperature brittleness					
110	ASTM D 2137 Method A 9.3.2					
	nonbrittle after 3 min. at -55°C				pass	
C21	Toor registered ASTM D 624 Dia C					
GZT	Linder 7.0 MPa tensile load min kN/m	22	22	22		
	7 0 to 10 MPa topollo load, min, kN/m	22	22	22		
	10 MPa tensile load & over min kN/m	20	20	20	26	26
		20	20	20	20	20
K11	Adhesion, ASTM D 429, min:					
	Method A, min, MPa	1.4	1.4	1.4	1.4	2.8
P2	Staining resistance, ASTM D 925.					
	Method B, control panel	pass	pass	pass	†	+
7	(Special requiremente) Any appendit require	omonto ch		agaifiad in	dotoil inc	luding
2	test methods and aging parameters.	entents SI		pecilieu III		luuling

# ASTM D 2000 - BC MATERIALS

* Grade No. 1 covers basic properties only, no suffix requirements.

*†* = The requirement is applicable, and materials are available having these characteristics, but values have not yet been established.

# INTERNATIONAL SYSTEM OF UNITS

The International System of Units (called SI units) consists of seven base units, two supplementary units and many derived units.

		SI	
Quantity	Unit	Symbol	Formula
Base Units:			
Length	meter	m	
Mass	kilogram	kg	
Time	second	S	
Electric current	ampere	A	
Thermodynamic temperature	kelvin	K	
Amount of substance	mole	mol	
Luminous intensity	candela	cd	
<b>.</b>			
Supplementary Units:			
Plane angle	radian	rad	
Solid angle	steradian	sr	
Examples of Derived Unite:			
Examples of Derived Onits.	squara motor		$m^2$
Area	mogagram por cubic motor		Ma/m ³
Electric consoitance	farad	 F	A.e/\/
	siemens	I S	ΔΛ/
Electrical conductance	volt	V	ΑV V \\//Δ
Electric potential difference	ioule	V	Nem
Energy, work	pouton	N	ka m/s²
Force	hertz		(cyclo)/c
Dowor	watt	112	
Power Quantity of algotrigity	coulomb	vv C	J/S A.s
Stroop or proceuro	nascal	Pa	N/m ²
Vienosity dynamia	pascal_second	гa	Da-e
Viscosity, Uyrianiic	square meter per second		r a•s m²/s
Volumo	cubic meter		m ³
volume			III.

Multiplication Factors	Prefix	Symbol
$1\ 000\ 000\ 000\ 000\ =\ 10^{12}$	tera	Т
$1\ 000\ 000\ 000\ =\ 10^9$	giga	G
$1\ 000\ 000 = 10^6$	mega	Μ
$1\ 000 = 10^3$	kilo	k
$100 = 10^2$	hecto*	h
$10 = 10^{1}$	deka*	da
$0.1 = 10^{-1}$	deci*	d
$0.01 = 10^{-2}$	centi*	С
$0.001 = 10^{-3}$	milli	m
$0.000\ 001 = 10^{-6}$	micro	m
$0.000\ 000\ 001\ =\ 10^{-9}$	nano	n
$0.000\ 000\ 000\ 001\ =\ 10^{-12}$	pico	р
$0.000\ 000\ 000\ 000\ 001\ =\ 10^{-15}$	femto	f
$0.000\ 000\ 000\ 000\ 000\ 001\ =\ 10^{-18}$	atto	а

SI PREFIXES

* To be avoided where possible

The following non-SI units are acceptable because of long time usage:

Quantity	Unit	Symbol
time	minute	min
**	hour	h
**	day	d
temperature	Celsius	°C
volume	litre	1

### Use of SI Unit Symbols:

1. Singular and plural forms of SI unit symbols are the same. A period is not used with the symbol except at the end of a sentence.

1 kg (NOT 1 kg.) and 15 kg (NOT 15 kgs.)

2. A space is left between the number and the symbol except when listing Celsius temperature.

15 m (NOT 15m), but 3°C (NOT 37 °C)

3. Symbols are written in lower case letters except when the symbol is derived from a proper name. See rule 4.

meter (m)	hertz (Hz)	joule (J)
kilogram (kg)	watt (W)	Newton (N)
ampere (A)	Pascal (Pa)	

4. As can be seen in rule 3, the full name of the unit is written in lower case letters even though the unit is derived from a proper name. But as in most SI rules, there is an exception, which is Celsius temperature.

22 degrees Celsius

5. Compound units formed by multiplication can be written in a variety of ways. The centered dot is preferred.

moment of force = N·m or N.m or Nm

6. Compound units formed by division can also be written in 3 ways. The virgule or solidus / is preferred.

Mg/m³ or 
$$\underline{Mg}$$
 or Mg·m⁻³  
m³

7. Compound prefixes are not used.

Mm (NOT kkm) GPa (NOT MkPa)

8. Common fractions are not used.

.0625 kg (NOT 1/16 kg)

9. Prefixes are not used in the denominator of a compound unit except that kilograms are used rather than grams because the kilogram is a base unit.

MN/m² (NOT N/mm²) m³kg (NOT dm³/g)

10. In calculations, for simplicity, the prefixes should be changed to scientific notation. The exception being k in kg, because kg is a base unit.

 $\frac{1.07 \text{ MN}}{3.14 \text{ km} \cdot \text{kg}} = \frac{1.07 \text{ x } 10^3 \text{ N}}{3.14 \text{ x } 10^3 \text{ m} \cdot \text{kg}}$ 

Note: For many years, density in the metric system has been listed in grams per cubic centimeter. To keep the decimal point in the same place, it is suggested that density in SI units be listed as Mg/m³ rather than kg/m³.

The relationships are: 1 Mg/m³ = 1g/cm³ = 1000 kg/m³ Density is now the preferred term to replace specific gravity although the numbers are the same for both in the international system (SI units). For all practical purposes the following calculations can be utilized, if the fact that density has units is considered.

Density (specific gravity) is the ratio between the weight of unit volume of a substance and the weight of the same volume of water at a given temperature, usually at  $15.5^{\circ}$ C ( $60^{\circ}$ F). Density multiplied by 1000 gives approximately the weight of 1 cubic foot in ounces avoirdupois, or the weight of 1 liter (cubic decimeter) in grams.

Unit Volume (specific volume) is the reciprocal of density (1 divided by density) and represents the volume in liters of 1 kg, or the volume in cubic feet of 1000 ounces (998.9 exactly).

To determine the density of a compound:

- 1. Express the weight of each ingredient in kilograms.
- Divide the weight of each ingredient by its density (or multiply the weight by the unit volume), add the results together and divide the sum into the total weight of the compound. Time may be saved by using the density tables on the following pages.

	Mass		Density		Volume
Ingredients	kg	+	Mg/m ³	=	liters
Natural Rubber	100.0		0.92		108.696
VANPLAST® R	2.0		0.845		2.367
Stearic Acid	4.0		0.85		4.706
Zinc Oxide	5.0		5.57		0.898
AGERITE [®] RESIN D [®]	1.0		1.06		0.943
Carbon Black	45.0		1.80		25.000
Sulfur	3.0		2.07		1.449
ALTAX®	1.0		1.51		0.662
Totals	161.0				144.749

Density (Calc.) =	<u>    161.0    </u>	=	1.1123 Mg/m ³
	144.749		
Density (of cured co	(bnuogm	=	1.116 Ma/m ³

*Note:* The method of calculation shown gives the density of the uncured stock. The density of the cured stock is somewhat higher due to a volume decrease which accompanies the combination of rubber with sulfur. For small sulfur ratios, this volume decrease can be taken into account by using the fictitious value 6 for the density of sulfur. This value has been computed from data given in Bureau of Standards Research Paper RP760, "Specific Volume, Compressibility, and Volume Thermal Expansivity of Rubber-Sulfur Compounds" by Arnold H. Scott.

# **Volume Cost Calculations**

Per Cubic Foot:

- 1. Calculate the material cost per pound in the usual way.
- Determine the density by laboratory experiment using a small piece of the cured stock.
- 3. Multiply the cost per pound by the density, and this product by the constant factor 62.43. The final result is the material cost of the compound per cubic foot.

Example: cost per lb. x density x 62.43 = cu. ft. cost

\$0.31 x 1.64 x 62.43 = \$31.74 per cu. ft.

Per Pound Volume:

For those who figure volume costs on the density (specific gravity) basis (i.e. "pound volume," or volume unit equal to that of 1 pound of water) instead of on the cubic foot basis, the calculation of volume cost is as follows: multiply the cost per pound by the density of the compound; the result is the cost of 1 pound volume".

Example: cost per lb. x density = lb. vol. cost 0.31 x 1.46 = 0.45 per lb. vol.

### Per Cubic Decimeter:

For calculating in metric units multiply the cost per kilo by the density. The result is cost per cubic decimeter.

Example: cost per kg x density = cost per dm³ 0.24 x 1.46 = 0.35 per dm³

### **Designing Compounds by Volume**

This procedure calls for expressing the quantities of compounding materials to be used as volumes per 100 volumes of elastomer. However, since most compounds are written with 100 parts by weight of elastomer instead of 100 volumes, it is convenient to have volume loading with their corresponding weights already calculated to the desired base. For natural rubber or SBR, an average density of 0.93 is satisfactory for this calculation.

Ordinarily to get 10 volumes of carbon black per 100 volume of elastomer, we take 18 parts by weight ( $10 \times 1.8$ ), but to refer this weight to 100 parts by weight of elastomer, we must take  $18 \div 93$  which is 19.35 parts by weight of carbon.

Volume Addition to 100 lbs. of Elastomer							
	Density	Required	Added				
Carbon Black	1.80	10 volumes	19.35				
Zinc Oxide	5.57	2 volumes	11.98				
DIXIE CLAY®	2.62	5 volumes	14.09				

-					
Accelerators	Density Ma/m ³	Unit Volume	Accelerators	Density Ma/m ³	Unit Volume
Accelerators	wig/iii	i/Kg	Accelerators	wig/iii	i/kg
ALTAX®	1.51	0.662	TUADS, ETHYL	1.31	0.763
AMAX®	1.37	0.730	TUADS, ISOBUTYL	1.14	0.877
BISMATE®	2.04	0.490	TUADS, METHYL	1.40	0.714
BUTYL EIGHT®	1.00	1.000	UNADS®	1.37	0.730
CADMATE [®] , ETHYL	1.48	0.676	VANAX [®] A	1.35	0.741
CAPTAX®	1.51	0.662	VANAX CPA	1.35	0.741
CUMATE [®] , METHYL	1.75	0.571	VANAX DOTG	1.20	0.833
CURE-RITE [®] 18	1.34	0.746	VANAX MBM	1.44	0.694
Diak [®] No. 1	1.28	0.781	VANAX DPG	1.19	0.840
Diak No. 3	1.09	0.917	VANAX MBM	1.44	0.694
Diak No. 4	1.23	0.813	VANAX NS	1.28	0.781
Diak No. 7	1.16	0.862	VANAX PML	1.25	0.800
DURAX®	1.30	0.679	VANAX PY	0.96	1.042
LEDATE [®] , AMYL	1.10	0.909	VANAX 552	1.20	0.833
LEDATE, METHYL	2.43	0.412	VANAX 808-HP	0.97	1.031
MORFAX®	1.51	0.662	VANAX 833	0.86	1.163
ROTAX®	1.52	0.658	VANAX 882-B	0.80	1.250
SELENAC®, METHYL	1.58	0.633	ZETAX®	1.70	0.588
SULFADS®	1.50	0.667	ZIMATE, AMYL	1.02	0.980
TELLURAC [®] , ETHYL	1.55	0.645	ZIMATE, BENZYL	1.40	0.714
THIATE [®] EF-2	1.23	0.813	ZIMATE, BUTYL	1.21	0.826
THIATE H	1.12	0.893	ZIMATE, ETHYL	1.48	0.676
THIATE U	1.03	0.971	ZIMATE, ISOBUTYL	1.24	0.806
TUADS [®] , BENZYL	1.31	0.763	ZIMATE, METHYL	1.71	0.585
TUADS, BUTYL	1.06	0.943	ZITHATE [®] , PROPYL	1.56	0.641

Density and Unit Volume of R.T. Vanderbilt Compounding Materials

Antioxidants	Density Mg/m³	Unit Volume I/kg	Antioxidants	Density Mg/m³	Unit Volume I/kg
AGERITE [®] DPPD [®]	1.28	0.781	SONGNOX 1290	1.01	0.990
AGERITE MA	1.06	0.943	SONGNOX 3114	1.03	0.971
AGERITE MA PASTILLES	1.06	0.943	VANOX [®] AM	1.15	0.870
AGERITE RESIN D®	1.06	0.943	VANOX CDPA	1.14	0.877
AGERITE RESIN D PAST.	1.06	0.943	VANOX HT	1.45	0.690
AGERITE STALITE®	0.99	1.010	VANOX MBPC	1.08	0.926
AGERITE STALITE S	1.02	0.980	VANOX MTI	1.33	0.752
AGERITE SUPERFLEX [®]	1.10	0.909	VANOX NDBC	1.26	0.794
" SOLID G	1.33	0.752	VANOX ZMTI	1.69	0.592
AGERITE SUPERLITE®	0.96	1.047	VANOX ZS	1.30	0.769
" "SOLID	1.26	0.794	VANOX 12	1.01	0.990
NICLATE [®] , ISOBUTYL	1.27	0.787	VANOX 13	0.93	1.075
NICLATE, METHYL	1.77	0.565	VANOX 1001	0.93	1.075
SONGNOX [®] 1010	1.15	0.870	VANOX 1320	0.90	1.111
SONGNOX 1024	1.12	0.893	VANOX 7723	1.06	0.943
SONGNOX 1076	1.02	0.980			

Antiozonants and Waxes	Density Mg/m³	Unit Volume I/kg	Antiozonants and Waxes	Density Mg/m³	Unit Volume I/kg
ANTOZITE [®] 67P	0.99	1.010	VANWAX [®] H	0.90	1.111
VANOX 3C	1.10	0.909	VANWAX H Special	0.90	1.111
VANOX 6H	1.18	0.847	VANWAX OZ	0.90	1.111

		Unit			Unit
Activator	Density Mg/m³	Volume I/kg	Retarder	Density Mg/m ³	Volume I/kg
OCTOATE Z [®]	1.12	0.893	VANTARD® PVI	1.30	0.769

Crosslinking Agents	Density Mg/m³	Unit Volume I/kg	Crosslinking Agents	Density Mg/m³	Unit Volume I/kg
VAROX® 130-XL	1.26	0.794	VAROX DBPH	0.87	1.14
VAROX 230-XL	1.55	0.645	VAROX DBPH-50	1.25	0.800
VAROX 231	0.91	1.099	VAROX DCP	1.001	0.999
VAROX 231-XL	1.41	0.709	VAROX DCP-40C	1.61	0.621
VAROX 802-40C	1.50	0.667	VAROX DCP-40KE	1.56	0.641
VAROX 802-40KE	1.61	0.621	VAROX TBPB	1.042	0.960
VAROX ANS	1.22	0.820	VAROX VC-R	0.93	1.075

Mineral Fillers	Density Mg/m³	Unit Volume I/kg	Mineral Fillers	Density Mg/m³	Unit Volume I/kg
BILT-PLATES [®] 156	2.62	0.382	Silica (High S.A.)*	2.05	0.488
DIXIE CLAY®	2.60	0.385	VAN GEL [®] B	2.60	0.385
LANGFORD [™] CLAY	2.62	0.382	VANSIL® W 20	2.90	0.345
McNAMEE [®] CLAY	2.62	0.382	VANSIL W 50	2.90	0.345
PAR [®] CLAY	2.62	0.382	VANSIL HR-1500	2.90	0.345
PYRAX [®] A	2.80	0.357	VANTALC [®] 6H	2.75	0.364
PYRAX B	2.80	0.357	VANTALC F2003	2.75	0.364
PYRAX WA	2.80	0.357	VANTALC R	2.80	0.357
Silica (low S.A.)*	2.10	0.476			

* Low and high surface area precipitated silica

Polymers	Density Mg/m³	Unit Volume I/kg	Polymers	Density Mg/m³	Unit Volume I/kg
Bromobutyl (BIIR)	0.93	1.075	Neoprene (CR)	1.23	0.813
Chlorobutyl (CIIR)	0.92	1.087	Nipol [®] IR (IR)*	0.91	1.099
Chlorinated PE (CPE)	1.16	0.862	Polyacrylate (ACM)	1.10	0.909
Epichlorohydrin (ECO)	1.27	0.787	Polybutadiene (BR)	0.90	1.111
EXXON Butyl (IIR)	0.92	1.087	Polyurethane (AU/EU)	1.19	0.840
HNBR	0.95	1.053	SBR	0.94	1.064
Hypalon [®] 40 (CSM)	1.17	0.855	Silicone Rubber (MQ)	1.11	0.901
Natural Rubber (IR)	0.92	1.087	Vamac [®] (AEM)	1.03	0.971
NBR (Low ACN)	0.98	1.020	Vistalon [™] (EPDM)	0.89	1.123
NBR (High ACN)	1.00	1.000	Viton [®] (FKM)	1.86	0.538

* Synthetic polyisoprene

Processing Aids and Plasticizers	Density Mg/m³	Unit Volume I/kg	Processing Aids and Plasticizers	Density Mg/m³	Unit Volume I/kg
LEEGEN®	1.08	0.926	VANFRE M	0.87	1.149
VANFRE® AP-2	0.98	1.020	VANFRE UN	0.98	1.020
VANFRE AP-2 Special	0.98	1.020	VANFRE VAM	0.97	1.031
VANFRE DFL	1.08	0.926	VANPLAST [®] PL	0.84	1.190
VANFRE HYP	0.97	1.031	VANPLAST R	0.85	1.176
VANFRE IL-2	1.17	0.855			

Carbon Blacks	Density Mg/m³	Unit Volume I/kg	Carbon Blacks	Density Mg/m³	Unit Volume I/kg
N110 SAF	1.80	0.556	N762 SRF	1.80	0.556
N234 ISAF	1.80	0.556	N990 THERMAL	1.80	0.556
N330 HAF	1.80	0.556	Conductive	1.80	0.556
N550 FEF	1.80	0.556	Acetylene	1.75	0.571
N650 GPF	1.80	0.556			

Vulcanizing Agents	Density Mg/m³	Unit Volume I/kg	Vulcanizing Agents	Density Mg/m³	Unit Volume I/kg
Diak No. 1	1.28	0.781	VANAX 829	2.09	0.478
Diak No. 3	1.09	0.917	VANAX 882-A	1.90	0.526
Diak No. 4	1.23	0.813	VANDEX®	4.80	0.208
TELLOY®	6.26	0.160			

lume of Other Compounding Materials				
	Density Mg/m³	Unit Volume I/kg		
	2.42	0.413		
	1.58	0.633		
	0.97	1.031		
	4.45	0.224		
	4.20	0.238		
	5.15	0.194		
	2.70	0.370		
	2.10	0.476		
	0.99	1.010		
	0.92	1.087		
	1.64	0.610		
	1.18	0.847		
	0.4-1.20	2.5-0.833		
	1.05	0 000		

# **Density and Unit Vo**

Materials

Aluminum Hydroxide	2.42	0.413
Ammonium Bicarbonate	1.58	0.633
Balata	0.97	1.031
Barytes, Ground	4.45	0.224
Blanc Fixe	4.20	0.238
Brown Iron Oxide	5.15	0.194
Calcium Carbonate	2.70	0.370
Calcium Silicate, precipitated	2.10	0.476
Carnauba Wax	0.99	1.010
Ceresin Wax	0.92	1.087
Chlorinated Rubber	1.64	0.610
Coal Tar	1.18	0.847
Cork. Ground	0.4-1.20	2.5-0.833
Cotton Flock. Dark	1.25	0.800
Coumarone Indene Resins	1.07-1.15	0.935-0.870
Diatomaceous Earth	2.15	0.465
Dibutyl Phthalate	1.02	0.981
Dibutyl Sebacate	0.94	1.063
Dioctvl Phthalatete	0.97	1.031
Dolomite	2.34	0.428
Fluorosilicone	1.40	0.714
Fuller's Earth	2.15	0.465
Gelatin	1.27	0.787
Gilsonite	1.10	0.910
Glue, Bone	1.27	0.787
Graphite, Flake	2.25	0.444
Guayule	0.96	1.042
Gutta Percha	0.98	1.020
Hard Rubber Dust	1.17-1.20	0.855-0.833
Hexamethylenetetramine	1.02	0.980
Iron Oxide (Red Oxide)	5.14	0.195
Kerosene	0.82	1.220
Lauric Acid	0.90	1.111
Lead Oleate	1.34	0.746
Lead (Powder)	11.34	0.088
Lead Sulfate	6.20	0.161
Lignin	1.30	0.770
Lime, Hydrated	2.20	0.454
Litharge	9.35	0.107
Lithopone (30% ZnS)	4.15	0.241

	Density	Unit Volume								
Materials	Mg/m ³	l/kg								
Magnesia (Magnesium Oxide)	3.20	0.313								
Magnesium Carbonate	2.22	0.450								
Mica, Powdered	2.95	0.339								
Mineral Rubber	1.04	0.962								
Montan Wax	0.89	1.124								
Oil, Aromatic (790)	0.998	1.002								
Oil, Castor	0.96	1.041								
Oil, Cottonseed	0.92	1.087								
Oil, Palm	0.88	1.136								
Oil, Paraffinic (2280)	0.89	1.122								
Oil, Mineral	0.84	1.190								
Oil, Naphthenic	0.92	1.087								
Oleic Acid (Red Oil)	0.89	1.124								
Petrolatum	0.84	1.190								
Pine Pitch	1.11	0.901								
Pine lar	1.08	0.926								
Polynorbornene	0.96	1.042								
Polysuifide	1.25-1.34	0.800-0.746								
Pumice, Powaerea	2.35	0.426								
Rosin (Colophony)	1.08	0.926								
Salicylic Acid	1.44	0.095								
Silian fumed	1.10	0.909								
Silica, luiteu Silican Carbida	2.20	0.400								
Silicon Calbide Seanstone (Tale)	3.17 2.72	0.313								
Sodium Acotato	2.72	0.307								
Sodium Acetate Sodium Bicarbonate	2.20	0.050								
Stearic Acid	0.85	1 176								
Sulfur	2.07	1 449								
Thiocarbanilide	1.30	0 769								
Titanium Dioxide	3.88	0.258								
Tricresyl Phosphate	1 13	0.885								
Triethanolamine	1 12	0.893								
Ultramarine Blue	2.35	0.426								
Urea	1.34	0.747								
Whiting, Ground Limestone	2.70	0.370								
Whiting, Precipitated	2.62	0.382								
Wood Flour	1.25	0.800								
Zinc Carbonate (pptd.)	3.30	0.303								
Zinc Laurate	1.10	0.909								
Zinc Oxide	5.61	0.178								
Zinc Stearate	1.05	0.952								
Zinc Sulfide	3.92	0.255								
Diameter	Thickness of disk, inches									
--------------------	---------------------------	--------------	----------------	--------------	----------------	--------------	--------------	--	--	--
of disk, inches	1/16 0.0625	1/8 0.125	3/16 0.1875	1/4 0.250	5/16 0.3125	3/8 0.375	1/2 0.500			
1/4	0.050	0.100	0.151	0.201	0.251	0.302	0.402			
3/8	0.113	0.226	0.339	0.452	0.565	0.678	0.905			
1/2	0.201	0.402	0.603	0.804	1.05	1.21	1.61			
5/8	0.314	0.628	0.943	1.26	1.57	1.88	2.51			
3/4	0.452	0.905	1.36	1.81	2.26	2.71	3.62			
7/8	0.625	1.25	1.87	2.50	3.12	3.75	5.00			
1	0.804	1.61	2.41	3.22	4.02	4.83	6.43			
1 1/8	1.02	2.03	3.05	4.07	5.09	6.11	8.14			
1 1/4	1.26	2.51	3.77	5.03	6.28	7.54	10.0			
1 3/8	1.52	3.04	4.56	6.08	7.60	9.13	12.2			
1 1/2	1.81	3.62	5.43	7.24	9.05	10.9	14.5			
1 5/8	2.12	4.25	6.37	8.50	10.6	12.7	17.0			
1 3/4	2.46	4.93	7.39	9.85	12.3	14.8	19.7			
1 7/8	2.83	5.65	8.48	11.3	14.1	17.0	22.6			
2	3.22	6.43	9.65	12.9	16.1	19.3	25.7			

#### Weights of Rubber Disks in Grams for Density of 1.00 Mg/m³

For dimensions in cm, multiply the weights shown by 16.387

Diameter	Thickness of disk, inches									
of disk,	1/4	3/8	1/2	5/8	3/4	7/8	1			
inches	0.250	0.375	0.500	0.625	0.750	0.875	1.00			
2.00	0.0283	0.0425	0.0567	0.0709	0.0851	0.0993	0.1135			
2.25	0.0359	0.0538	0.0718	0.0897	0.1077	0.1256	0.1436			
2.50	0.0443	0.0663	0.0886	0.1105	0.1329	0.1547	0.1772			
2.75	0.0536	0.0804	0.1072	0.1340	0.1608	0.1876	0.2144			
3.00	0.0638	0.0957	0.1276	0.1595	0.1914	0.2234	0.2553			
3.25	0.0750	0.1125	0.1500	0.1875	0.2250	0.2625	0.2996			
3.50	0.0868	0.1302	0.1737	0.2170	0.2605	0.3041	0.3475			
3.75	0.1000	0.1496	0.1993	0.2496	0.2992	0.3846	0.3987			
4.00	0.1135	0.1702	0.2270	0.2837	0.3405	0.3972	0.4540			
4.25	0.1280	0.1920	0.2560	0.3200	0.3840	0.4481	0.5121			
4.50	0.1435	0.2135	0.2871	0.3588	0.4306	0.5025	0.5743			
4.75	0.1600	0.2400	0.3200	0.4000	0.4800	0.5600	0.6400			
5.00	0.1776	0.2663	0.3551	0.4439	0.5372	0.6215	0.7103			
5.25	0.1954	0.2931	0.3908	0.4885	0.5862	0.6835	0.7816			
5.50	0.2144	0.3216	0.4289	0.5360	0.6433	0.7505	0.8578			
5.75	0.2344	0.3516	0.4688	0.5860	0.7032	0.8204	0.9376			
6.00	0.255	0.382	0.510	0.637	0.765	0.893	1.021			
6.50	0.299	0.449	0.599	0.749	0.899	1.048	1.198			
7.00	0.347	0.521	0.695	0.868	1.042	1.215	1.390			
7.50	0.372	0.559	0.745	0.931	1.117	1.304	1.491			
8.00	0.453	0.680	0.907	1.133	1.361	1.588	1.815			
8.50	0.512	0.768	1.024	1.280	1.536	1.793	2.049			
9.00	0.547	0.861	1.148	1.435	1.722	2.010	2.297			
9.50	0.640	0.960	1.280	1.600	1.920	2.240	2.560			
10.00	0.712	1.068	1.425	1.781	2.137	2.493	2.850			

Weights of Rubber Disks in Pounds for Density of 1.00 Mg/m³

For dimensions in cm and weights in kg, multiply the weights shown by 7.433.

To estimate the weight of an O-ring, find the weight of a disk based on the OD of the O-ring and subtract the weight of a disk equal to the ID of the O-ring. To adjust for the circular cross-section, multiply the difference by 0.7854.

For	Liquids <u>H</u> e	eavier	Than Water	For L	For Liquids <u>Lighter</u> Than Water						
	Density =	<u>145</u>			Density =	<u>145</u>					
		(145 - °	Be)			(130 + °E	Be)				
°Be	Mg/m ³	°Be	Mg/m ³	°Be	Mg/m ³	°Be	Mg/m ³				
1	1.0069	36	1.3303	10	1.0000	56	0.7527				
2	1.0140	37	1.3426	12	0.9859	57	0.7487				
3	1.0211	38	1.3551	15	0.9655	58	0.7447				
4	1.0284	39	1.3679	18	0.9459	59	0.7407				
5	1.0357	40	1.3810	20	0.9333	60	0.7368				
6	1.0432	41	1.3942	21	0.9272	61	0.7330				
7	1.0507	42	1.4078	22	0.9211	62	0.7292				
8	1.0584	43	1.4216	23	0.9150	63	0.7254				
9	1.0662	44	1.4356	24	0.9091	64	0.7216				
10	1.0741	45	1.4500	25	0.9032	65	0.7179				
11	1.0821	46	1.4646	26	0.8974	66	0.7143				
12	1.0902	47	1.4796	27	0.8917	67	0.7107				
13	1.0985	48	1.4948	28	0.8861	68	0.7071				
14	1.1069	49	1.5104	29	0.8805	69	0.7035				
15	1.1154	50	1.5263	30	0.8750	70	0.7000				
16	1.1240	51	1.5426	31	0.8696	71	0.6965				
17	1.1328	52	1.5591	32	0.8642	72	0.6931				
18	1.1417	53	1.5761	33	0.8589	73	0.6897				
19	1.1508	54	1.5934	34	0.8537	74	0.6863				
20	1.1600	55	1.6111	35	0.8485	75	0.6829				
21	1.1694	56	1.6292	36	0.8434	76	0.6796				
22	1.1789	57	1.6477	37	0.8383	77	0.6763				
23	1.1885	58	1.6667	38	0.8333	78	0.6731				
24	1.1983	59	1.6860	39	0.8284	79	0.6699				
25	1.2083	60	1.7059	40	0.8235	80	0.6667				
26	1.2185	61	1.7262	41	0.8187	81	0.6635				
27	1.2288	62	1.7470	42	0.8140	82	0.6604				
28	1.2393	63	1.7683	43	0.8092	83	0.6573				
29	1.2500	64	1.7901	44	0.8046	84	0.6542				
30	1.2609	65	1.8125	45	0.8000	85	0.6512				

0.7955

0.7910

0.7865

0.7821

0.7778

0.6481

0.6452

0.6422

0.6393

0.6364

#### **Conversion Tables**

Conversion of Baumé to Density at 15.6°C (American Standards)

1.2719

1.2832

1.2946

1.3063

1.3182

Note: 1.0000 Mg/m³ = 1.0000 g/cm³ = 8.3454 lbs/U.S. gallon

1.8354

1.8590

1.8831

1.9079

1.9333

	Change Per										
psi	MPa	kgf/cm ²		Increme	nt	psi	MPa	kgf/cm ²			
100 200 300 400 500	0.69 1.38 2.07 2.76 3.45	7.03 14.06 21.09 28.12 35.15	psi	MPa	kgf/cm ²	4100 4200 4300 4400 4500	28.27 28.96 29.65 30.34 31.03	288.3 295.3 302.3 309.4 316.4			
600 700 800 900 1000	4.14 4.83 5.52 6.21 6.90	42.18 49.22 56.25 63.28 70.13	10 20 30 40 50	0.07 0.14 0.21 0.28 0.35	0.70 1.41 2.11 2.81 3.52	4600 4700 4800 4900 5000	31.72 32.41 33.10 33.78 34.48	323.4 330.4 337.5 334.5 351.5			
1100 1200 1300 1400 1500	7.58 8.27 8.96 9.65 10.34	77.34 84.37 91.40 98.43 105.5	60 70 80 90	0.41 0.48 0.55 0.62	4.22 4.92 5.63 6.33	5100 5200 5300 5400 5500	35.16 35.85 36.54 37.23 37.92	358.6 365.6 372.6 379.7 386.7			
1600 1700 1800 1900 2000	11.03 11.72 12.41 13.10 13.79	112.5 119.5 126.5 133.6 140.6	MPa	psi	kgf/cm ²	5600 5700 5800 5900 6000	38.61 39.30 39.99 40.68 41.37	393.7 400.7 407.8 414.8 421.8			
2100 2200 2300 2400 2500	14.48 15.17 15.86 16.55 17.24	147.7 154.7 161.7 168.7 175.8	0.1 0.2 0.3 0.4 0.5	14.5 29.0 43.5 58.0 72.5	1.02 2.04 3.06 4.08 5.10	6100 6200 6300 6400 6500	42.06 42.75 43.44 44.13 44.82	428.9 435.9 442.9 450.0 457.0			
2600 2700 2800 2900 3000	17.93 18.62 19.31 20.00 20.68	182.8 189.8 196.9 203.9 210.9	0.6 0.7 0.8 0.9	87.0 101.5 116.0 131.5	6.12 7.14 8.16 9.18	6600 6700 6800 6900 7000	45.51 46.19 46.88 47.57 48.26	464.0 471.1 478.1 485.1 492.1			
3100 3200 3300 3400 3500	21.37 22.06 22.75 23.44 24.13	218.0 225.0 232.0 239.0 246.1				7100 7200 7300 7400 7500	48.95 49.64 50.33 51.02 51.71	499.2 506.2 513.2 520.3 527.3			
3600 3700 3800 3900 4000	24.82 25.51 26.20 26.89 27.58	253.1 260.1 267.2 274.2 281.2				7600 7700 7800 7900 8000	52.40 53.09 53.78 54.47 55.16	534.3 541.4 548.4 555.4 562.5			

## Tensile Strength Conversion Table

#### **Temperature Conversion Table**

°C	°F	Per Degre	ee Change		°C	(	°F
-56.7	-70	-94.0			104.4	220	428.0
-51.1	-60	-76.0			110.0	230	446.0
-45.6	-50	-58.0			115.6	240	464.0
-40.0	-40	-40.0			121.1	250	482.0
-34.4	-30	-22.0			126.7	260	500.0
-28.9	-20	-4.0			132.2	270	518.0
-23.3	-10	14.0			137.8	280	536.0
-17.8	0	32.0			143.3	290	554.0
-12.2	10	50.0	°C	٥r	148.9	300	572.0
-6.7	20	68.0	1	1.8	- 154.4	310	590.0
-1 1	30	86.0	2	3.6	160.0	320	608.0
44	40	104.0	3	5.4	165.6	330	626.0
10.0	50	122.0	4	72	171 1	340	644.0
15.6	60	140.0	5	9.0	176.6	350	662.0
21.1	70	158.0	6	10.8	182.2	360	680.0
26.7	80	176.0	7	12.6	187.8	370	698.0
32.2	90	194.0	8	14.4	193.3	380	716.0
37.8	100	212.0	9	16.2	198.9	390	734.0
43.4	110	230.0			204.4	400	752.0
48.9	120	248 0	°F	°C	210.0	410	770.0
54.4	130	266.0	1	0.6	215.6	420	788.0
60.0	140	284.0	2	11	221.1	430	806.0
65.6	150	302.0	3	17	226.7	440	824.0
71.1	160	320.0	4	2.2	232.2	450	842.0
76.7	170	338.0	5	2.8	237.8	460	860.0
82.2	180	356.0	6	3.3	243.3	470	878.0
87.8	190	374.0	7	3.9	248.9	480	896.0
93.3	200	392.0	8	4.4	254.4	490	914.0
98.9	210	410.0	9	5.0	260.0	500	932.0

Locate temperature to be converted in unlabeled, middle column. Read Celsius equivalents to left and Fahrenheit equivalents to right.

#### **Conversion Table of Liquid Masses and Measures**

Ounces (avoir.) per U.S. gallon to grams per liter on left columns. Grams per liter to ounces (avoir.) per U.S. gallon on right columns.

Ounces					Ounces
(avoir.)	Grams	Chang	je per	Grams	(avoir.)
per Gallon	per Liter	Increi	ment	per Liter	per Gallon
0.5	3.745			0.5	0.067
1	7.489			1	0.134
1.5	11.234			1.5	0.200
2	14.978			2	0.267
2.5	18.723			2.5	0.334
3	22.467			3	0.401
3.5	26.212			3.5	0.467
4	29.957			4	0.534
4.5	33.701			4.5	0.601
5	37.446	oz/gal	a/l	5	0.668
5.5	41.190	0.1	0.749	- 5.5	0.734
6	44.935	0.2	1.498	6	0.801
6.5	48.679	0.3	2.247	6.5	0.868
7	52.424	0.4	2.996	7	0.935
7.5	56.169	0.5	3.745	7.5	1.001
8	59,913			8	1.068
8.5	63.658			8.5	1.135
9	67.402			9	1.202
9.5	71.147			9.5	1.269
10	74.891			10	1.335
		g/l	oz/gal		
10.5	78.636	0.1	0.013	20	2.671
11	82.381	0.2	0.027	30	4.006
11.5	86.125	0.3	0.040	40	5.341
12	89.870	0.4	0.053	50	6.676
12.5	93.614	0.5	0.067	60	8.012
13	97.359	0.6	0.080	70	9.347
13.5	101.103	0.7	0.094	80	10.682
14	104.848	0.8	0.107	90	12.017
14.5	108.593	0.9	0.120	100	13.353
15	112.337			200	26.705
15.5	116.082			300	40.058
16	119.826			400	53.411
16.5	123.571			500	66.763
17	127.315			600	80.116
17.5	131.060			700	93.469

U.S. to SI (Metric)									
Units of Length									
Inch	=	2.5400 centimeters							
Foot	=	0.3048 meter							
Yard	=	0.9144 meter							
Mile (U.S. Statute)	=	1.6093 kilometers							
	Units of Area								
Sq. in. (in²)	=	6.4516 sq. cm (cm ² )							
Sq. foot (ft ² )	=	0.0929 sq. meter (m ² )							
Sq. yard (yd ² )	=	0.8361 sq. meter (m ² )							
Sq. mile (U.S.Statute)	=	2.5900 sq. kilometers (km ² )							
	Units of Volume and Capacity								
Cu. inch (in ³ )	=	6.3871 cm ³							
Cu. foot (ft ³ )	=	28.3169 liters							
Cu. yard (yd3)	=	0.7646 cu. meter (m ³ )							
Pint (liquid)	=	0.4732 liter							
Quart (dry)	=	0.9464 liter							
Quart (liquid)	=	1.1012 liters							
Gallon (liquid)	=	3.7854 liters							
	Units of Mass								
Grain	=	0.0648 gram							
Ounce (avior.)	=	28.3495 grams							
Ounce (troy)	=	31.1035 grams							
Pound (avoir.)	=	0.4536 kilogram							
Pound (troy)	=	0.3732 kilogram							
Short Ton (2000 lb.)	=	907.2000 kilograms							
Long Ton (2240 lb.)	=	1016.0000 kilograms							
	Units for Rubber								
Adhesion (pli)	=	0.1751 kNm							
Stress (psi)	=	0.006895 MPa							
Torque (in-lb)	=	0.1130 N•m							

## Interconversion Table of Masses and Measures

SI (Metric) to U.S.								
	Units of Length							
Meter	=	39.3700 inches						
Meter	=	3.2808 feet						
Meter	=	1.0936 yards						
Kilometer	=	0.6214 (U.S. Statute)						
	Units of Area							
Sq. centimeter (cm ² )	=	0.1550 sq. inch (cm ² )						
Sq. meter (m ² )	=	10.7639 feet (ft ² )						
Sq. meter (m ² )	=	1.1960 sq. yards (yd ² )						
Hectare	=	2.4710 acres						
Sq. kilometer (km ² )	=	0.3861 sq. miles (U.S.Statute)						
Uni	its of Volume and Cap	acity						
Liter	=	1.0567 quarts (liquid)						
Liter	=	0.2642 gallon (liquid)						
Liter	=	61.0234 cu. inches						
Cubic meter (m ³ )	=	35.3147 cu. feet						
Cubic meter (m ³ )	=	1.3079 cu. yards						
Cubic meter (m ³ )	=	28.3776 bushels (dry)						
	Units of Mass							
Grain	=	15.4324 grams						
Kilogram	=	35.2740 oz. (avoir.)						
Kilogram	=	2.2046 lbs. (avoir.)						
Metric ton (1000 kg)	=	2204.6200 lbs. (avoir.)						
	Units for Rubber							
Adhesion (kN/m)	=	5.7101 pli						
Stress (MPa)	=	145.039 psi						
Torque (N·m)	=	8.8507 in Ib						

Metric	to	SI	to	U.S.			
Unit of Force per Unit of Length							
1 kgf/cm	=	9.80665 N/cm	=	5.600 lbf/in			
1 kgf/m	=	9.80665 N/m	=	0.672 lbf/ft			
1 kgf/m	=	9.80665 N/m	=	2.016 lbf/yd			
1 kgf/m	=	9.80665 N/m	=	0.0031 tonf/foot			
1 kgf/m	=	9.80665 N/m	=	0.0010 tonf/yd			
1 kgf/km	=	980665 N/km	=	3.547 lbf/mile			
Unit of Force per Unit of Area							
1 kgf/cm ²	=	98.0665 kPa	=	14.223 lbf/in ²			
1 kgf/mm ²	=	9.80665 MPa	=	0.711 tonf/in ²			
1 kgf/m ²	=	9.80665 Pa	=	0.2049 lbf/ft ²			
1 Metric tonf/m ²	=	9.80665 kPa	=	0.1024 tonf/ft ²			
1 Metric tonf/m ²	=	9.80664 kPa	=	0.919 tonf/yd ²			
Units of Mass per Unit of	f Volume	9					
1 kg/m ³	=	1 kg/m ³	=	1.686 lb/yd3			
1 kg/m ³	=	1 kg/m ³	=	0.0624 lb/ft ³			
1 Metric ton/m ³	=	1 Mg/m ³	=	0.843 ton/yd ³			
1 kg/liter	=	1 Mg/m ³	=	8.3454 lb/US gallon			
Bulk density	=	1 Mg/m ³	=	62.427 lbs/ft3			

U.S.	to	Metric	to	SI		
Unit of Force per Unit	of Length					
1 lbf/inch	=	0.1786 kgf/cm	=	175.1 N/m		
1 lbf/foot	=	1.488 kgf/m	=	14.59 N/m		
1 lbf/yard	=	0.496 kgf/m	=	4.86 N/m		
1 tonf/foot	=	2976.0 kgf/m	=	29.18 MN/m		
1 tonf/yard	=	992.0 kgf/m	=	9.73 MN/m		
1 lbf/mile	=	0.2819 kgf/km	=	2.76 N/m		
Unit of Force per Unit of Area						
1 lbf/in ²	=	0.0703 kgf/cm ²	=	6.894757 kPa		
1 tonf/in ²	=	1.406 kgf/cm ²	=	13.79 MPa		
1 lbf/ft ²	=	4.883 kgf/m ²	=	47.88 Pa		
1 tonf/ft ²	=	9.761 tonsf/m ²	=	5.72 kPa		
1 tonf/yd ²	=	1.085 metric tonsf/m ²	=	0.64 kPa		
Units of Mass per Uni	t of Volume					
1 lb/yd ³	=	0.5933 kg/m ³	=	0.5933 kg/m ³		
1 lb/ft ³	=	16.018 kg/m ³	=	16.018 kg/m ³		
1 ton/yd ³	=	1.186 metric ton/m ³	=	1.186 kg/m ³		
1 lb/US gallor	า =	0.1198 kg/liter	=	0.1198 Mg/m ³		

#### Interconversion Table - Double Units

	Pressure	<u>ə</u>	Tempe	rature		Pressure		Tempe	erature
psi	kgf/cm ²	kPa	°C	°F	psi	kgf/cm ²	kPa	°C	°F
0	0.000	0.0	100.0	212.0	85	5.97	586.1	164.2	327.6
5	0.352	34.5	108.4	227.1	90	6.32	620.5	166.2	331.2
10	0.703	68.9	115.2	239.4	95	6.679	655.0	168.1	334.6
15	1.055	103.4	121.0	249.8	100	7.031	689.5	169.9	337.8
20	1.406	137.9	126.0	258.8	105	7.382	723.9	1/1./	341.1
22	1.547	151.7	127.8	261.2	110	7.734	758.4	173.4	344.1
24	1.687	165.5	129.6	265.3	115	8.085	792.9	175.1	347.2
26	1.828	179.3	131.3	268.3	120	8.437	827.4	176.7	350.1
28	1.969	193.1	132.9	271.2	125	8.788	861.8	178.3	352.9
30	2.109	206.8	134.5	274.1	130	9.140	896.3	179.8	355.6
32	2.250	220.6	136.0	276.8	135	9.491	930.8	181.3	358.3
34	2.390	234.4	137.4	279.3	140	9.843	965.3	182.7	360.9
36	2.531	248.2	138.8	281.8	145	10.195	999.7	184.1	363.4
38	2.672	262.0	140.2	284.4	150	10.546	1034.2	185.5	365.9
40	2.812	275.8	141.5	286.7	155	10.898	1068.7	186.8	368.2
42	2.953	289.6	142.8	289.0	160	11.249	1103.2	188.1	370.6
44	3.094	303.4	144.0	291.2	165	11.600	1137.6	189.4	373.9
46	3.234	317.2	145.3	293.5	170	11.952	1172.1	190.7	375.3
48	3.375	330.9	146.4	295.5	175	12.304	1206.6	191.9	377.4
50	3.515	344.7	147.5	297.7	180	12.655	1241.1	193.1	379.6
52	3.656	358.5	148.7	299.7	185	13.007	1275.5	194.3	381.7
54	3.797	372.3	148.9	301.6	190	13.358	1310.0	195.4	383.7
56	3.937	386.1	150.9	303.6	195	13.710	1344.5	196.6	385.9
58	4.078	399.9	151.9	305.4	200	14.061	1379.0	197.7	387.9
60	4.218	413.7	153.0	307.4	205	14.410	1413.4	198.8	389.8
62	4.359	427.5	154.0	309.2	210	14.760	1448.0	199.8	391.6
64	4.500	441.5	154.9	310.8	215	15.120	1482.0	200.5	392.9
66	4.640	455.1	155.9	312.6	220	15.470	1517.0	201.7	395.4
68	4.781	468.8	156.8	314.2	225	15.820	1551.0	202.9	397.2
70	4.921	482.6	157.8	316.0					
72	5.062	496.4	158.7	317.7					
74	5.203	510.2	159.6	319.3		1 Atmosph	ere = 101	.325 kPa	l
76	5.343	524.0	160.5	320.9			= 14	.969 psi	
78	5.484	537.8	161.3	322.3			= 1	.0335 ka	f/cm ²
80	5.625	551.6	162.1	323.8				5	

#### Pressure-Temperature Equivalents of Saturated Steam* Gage Pressure at Sea Level

* Computed from the Steam Tables of Marks and Davis; Longmans, Green & Co., Publishers.

			Required Pressure at Altitudes of:								
Temperature		0 me	ters	152 m	152 meters		305 meters		610 meters		
		0 fe	eet	500	500 feet		1,000 feet		2,000 feet		
°C	°F	kPa	psi	kPa	psi	kPa	psi	kPa	psi		
100.0	212	0.0	0.0	1.4	0.2	3.4	0.5	6.9	1.0		
104.4	220	17.2	2.5	18.6	2.7	20.7	3.0	23.4	3.4		
110.0	230	42.1	6.1	43.4	6.3	45.5	6.6	49.0	7.1		
115.6	240	71.0	10.3	72.4	10.5	74.5	10.8	77.9	11.3		
121.1	250	104.0	15.1	106.0	15.4	108.0	15.6	111.0	16.1		
126.7	260	143.0	20.7	145.0	21.0	146.0	21.2	150.0	21.7		
129.4	265	166.0	24.0	168.0	24.3	169.0	24.5	172.0	25.0		
132.2	270	188.0	27.2	190.0	27.5	191.0	27.7	194.0	28.2		
135.0	275	212.0	30.8	214.0	31.1	216.0	31.3	219.0	31.8		
137.8	280	238.0	34.5	240.0	34.8	242.0	35.0	245.0	35.5		
140.6	285	267.0	38.8	270.0	39.1	271.0	39.3	274.0	39.8		
143.3	290	296.0	42.9	298.0	43.2	299.0	43.4	303.0	43.9		
146.1	295	328.0	47.6	330.0	47.9	332.0	48.1	335.0	48.6		
148.9	300	361.0	52.3	363.0	52.6	364.0	52.8	367.0	53.3		

Gage Pressure - Temperature Relations at Various Altitudes

		915 meters 3,000 feet		1220 meters 4,000 feet		1525 meters 5,000 feet		1830 meters 6,000 feet	
°C	°F	kPa	psi	kPa	psi	kPa	psi	kPa	psi
100.0	212	10.3	1.5	13.8	2.0	16.5	2.4	20.0	2.9
104.4	220	26.9	3.9	30.3	4.4	33.8	4.9	36.5	5.3
110.0	230	52.4	7.6	55.2	8.0	58.6	8.5	62.1	9.0
115.6	240	80.7	11.7	84.1	12.2	87.6	12.7	90.3	13.1
121.1	250	114.0	16.6	118.0	17.1	121.0	17.5	24.0	18.0
126.7	260	153.0	22.2	157.0	22.7	159.1	23.1	63.0	23.6
129.4	265	176.0	25.5	179.0	26.0	182.0	26.4	185.0	26.9
132.2	270	198.0	28.7	201.0	29.2	204.0	29.6	208.0	30.1
135.0	275	223.0	32.3	226.0	32.8	229.0	33.2	232.0	33.7
137.8	280	248.0	36.0	252.0	36.5	254.0	36.9	258.0	37.4
140.6	285	278.0	40.3	281.0	40.8	284.0	41.2	288.0	41.7
143.3	290	306.0	44.4	310.0	44.9	312.0	45.3	316.0	45.8
146.1	295	338.0	49.1	342.0	49.6	345.0	50.0	348.0	50.5
148.9	300	371.0	53.8	374.0	54.3	377.0	54.7	381.0	55.2

#### Time-Temperature Relations in Vulcanization

When the temperature of vulcanization is increased, vulcanization time at the higher temperature is decreased. Conversely, when the vulcanization temperature is decreased, the time to produce an equivalent state of cure becomes longer.

For most compounds, this time-temperature relation during vulcanization follows a generally accepted rule applicable to chemical reactions which indicates that for each 10°C rise in temperature, the rate increases by a fixed factor, or temperature coefficient, of approximately 2. On the Fahrenheit scale, the temperature coefficient of vulcanization is approximately 1.5 per 10 degrees.

When vulcanizing temperature is increased 10°C, divide by 2 to find the equivalent cure at the higher temperature.

To find the equivalent cure using the Fahrenheit scale, use the factor 1.5 and proceed as above.

#### Cure Conversion Chart

The chart on the following page is designed to make quick cure conversions for molded parts up to >14 inch thick over a wide temperature range. It is applicable to most soft, natural and synthetic rubber compounds containing the commonly used loading and reinforcing materials. Exceptions have been noted, however, among which are certain curing systems containing thiazole modified with ultra accelerators, notably BISMATE and LEDATE. These accelerators exhibit a level of activity at temperatures of 175-200°C (350-400°F) range that would be unpredictable from curing data obtained at lower temperatures.

To Estimate Vulcanization Time at a Revised Temperature:

- 1. Locate a point on the chart representing known time and temperature of vulcanization.
- Project a line vertically from the temperature axis at the desired new curing temperature to intersect the diagonal line running through established point.
- 3. Run the line across from the newly established point of intersection to time axis. This is the equivalent cure at revised temperature.



Figure 1: Time - Temperature Cure Relationship

### Mensuration Formulas

```
Circumference of a circle = diameter x 3.1416
                           = radius x 6.2832
Radius of a circle = circumference x 0.159155
Diameter of a circle = circumference \times 0.31831
Side of an inscribed equilateral triangle = diameter of circle x 0.86
Side of an inscribed cube = radius of sphere x 1.1547
Side of an inscribed square = diameter of circle x 0.7071
                             = circumference of circle x 0.225
Area of a circle = radius<sup>2</sup> x 3.1416
              " = diameter<sup>2</sup> x 0.7854
 ...
         ...
              " = circumference<sup>2</sup> x 0.07958
Area of a square = a side<sup>2</sup>
Area of a triangle = base x 1/2 altitude
Area of a rectangle = base x altitude
Area of a parallelogram = base x altitude
Area of a trapezoid = altitude x 1/2 sum of parallel sides
Area of a parabola = 2/3 base x altitude of exterior triangle
Area of a trapezium = area of the two constituent triangles
Area of a regular polygon = 1/2 the perpendicular from the center to one of the
 sides x sum of the sides
Area of a sector = 1/2 radius x arc
Area of an ellipse = 1/2 short diameter x 1/2 long diameter x 3.1416
Area of a solid section of tube = 3.1416 x wall thickness x bore + wall thickness
Surface of sphere
                      = circumference x diameter
                      = diameter<sup>2</sup> x 3.1416
Surface of a cube = area of one side x = 6
Surface of a cylinder = area of both ends + (length x circumference)
Surface of a zone or convex surface or segment of a sphere = 6.2832 x radius
 of sphere from which it is cut x altitude of the zone
Surface of a frustum of a cone = 1/2 (sum of circumferences at both ends) x
 slant height + area of both ends
Volume of a sphere = surface x 1/6 diameter
                      = diameter3 x 0.5236
                      = one side<sup>3</sup>
Volume of a cube
Volume of a cylinder or prism = area of end x length
Volume of a cone or pyramid = area of base x 1/3 altitude
Volume of a frustum of a cone or pyramid = 1/3 altitude x area of both ends +
 square root of area of both ends multiplied together
Volume of a wedge = area of base x 1/2 altitude
Volume of a spherical segment of one base = 1/2 altitude x 3.1416 x radius of
 base^{2} + 1/6 altitude^{3} \times 3.1416
```

#### **Useful Factors and Constants**

```
1 Horse Power = 33000 foot pounds per min.
              " = 550 foot pounds per sec.
         ...
              " = 0.746 kilowatt
1 Boiler Horse Power = the work of converting 30 lbs. of water per hour from
 an initial temp. of 100°F. to steam at 70lbs. gage pressure; or the evaporation
 of 34 1/2 lbs. of water per hour at 212°F, into steam at 212°F.
1 Watt = 0.00134 horse power
      " = 44.3 foot pounds per min.
1 Kilowatt = 1000 watts
            = 1.341 horse power
            = 44300 foot pounds per min.
1 Gram weight = 981 dynes (force) approximately
Degrees Centigrade = 5/9 (Degrees F, -32.0)
Degrees Fahrenheit = 9/5 (Degrees C, +32.0)
Absolute Zero = -273.13°C
               = -459.6°F
1 British Thermal Unit (B.T.U.) = 252 gram calories
                             " = 777.5 foot pounds
1 Gram Calorie
                                = 4.185 joules
                   ..
                                = 3.968 x 10<sup>3</sup> B.T.U.
                   ..
                             "
                                = 3.087 foot pounds
Heat of fusion of ice = 79.24 calories per gram
Heat of vaporization of water = 535.9 calories per gram
Volume (V) of a gas at temp. (t°C) and press. (p) becomes: V_{a} = V_{a} (273 + t<sub>a</sub>)
 (p_{1}) / (273 + t_{2})(p_{1})
1 Gram-molecular volume of a gas at 760 mm pressure and 0°C = 22.4 liters
1 Atmosphere = 14.7 lbs. per sq. in. = 1.0333 kilograms per cm<sup>2</sup>.
1 Kilogram per cm<sup>2</sup> = 0.9677 atmosphere = 14.22 lbs. per sg. in.
1 Inch (pressure) of mercury = 13.6 inches of water
Coefficient of expansion of gases = 0.003665 per degree C
1 Gram per cm<sup>3</sup> = 8.33 lbs. per gallon
Density of dry air at 0°C and 760 mm = 1.293 milligrams per cm<sup>3</sup>
Density of sea water = 1.025 grams per cm<sup>3</sup>
Mean density of the earth = 5.52 grams per cm<sup>3</sup>
Diameter of the earth = 12,754 kilometers = 7,926 miles
1 Degree of latitude at the equator = 111.3 km
                                     = 69.2 miles
Acceleration of gravity (sea level, lat. 45^{\circ}) = 980.60 cm per sec. per sec.
                                      ...
                                             = 32.172 feet per sec. per sec.
1 Radian = 180^{\circ}/\pi = 57.29578^{\circ} = 57^{\circ}17'45''
1 Angstrom (Å) = 0.1 nanometer = 0.1 millimicron = 4 X 10<sup>-9</sup> inch
1 Micron (\mu) = one micrometer = 0.001 millimeter = 0.00003937 inch
Velocity of sound = 331.36 meters (1089 feet)/sec. in dry air at 0°C (32°F)
Velocity of light in a vacuum = 299,792.5 km/sec. = 186,282 miles/sec.
```

## **STANDARD SIEVES**

Desid	nation	Sieve Op	enina	_
Standard	Alternative	micrometers	inches	
4.76 mm	No. 4	4,760	0.187	-
4.00 mm	No. 5	4,000	0.157	
3.35 mm	No. 6	3,350	0.132	
2.80 mm	No. 7	2,800	0.111	
2.36 mm	No. 8	2,360	0.0937	
2.00 mm	No. 10	2,000	0.0787	
1.70 mm	No. 12	1,700	0.0661	
1.40 mm	No. 14	1,400	0.0555	
1.18 mm	No. 16	1,180	0.0469	
1.00 mm	No. 18	1,000	0.0394	
850 μm	No. 20	850	0.0331	
710 μm	No. 25	710	0.0278	
600 μm	No. 30	600	0.0234	
500 μm	No. 35	500	0.0197	
425 µm	No. 40	425	0.0165	
355 μm	No. 45	355	0.0139	
300 µm	No. 50	300	0.0117	
250 µm	No. 60	250	0.0098	
212 µm	No. 70	212	0.0083	
180 µm	No. 80	180	0.0070	
150 µm	No. 100	150	0.0059	
125 µm	No. 120	125	0.0049	
106 µm	No. 140	106	0.0041	
90 µm	No. 170	90	0.0035	
75 μm	No. 200	75	0.0029	
63 µm	No. 230	63	0.0025	
53 µm	No. 270	53	0.0021	
45 µm	No. 325	45	0.0017	
38 µm	No. 400	38	0.0015	
32 µm	No. 450	32	0.00126	
25 µm	No. 500	25	0.00098	
20 µm	No. 635	20	0.00079	

### (ASTM E 1101 Standard Specification for Wire Cloth and Sieves for Testing Purposes)

MOHS Hardness Scal
--------------------

Mohs Hardness		Representative Minerals	Absolute Hardness
Soft	1	Talc, Soapstone, Waxes, Aggregated Salt Crystals	1
	2	Gypsum, Rock Salt, Crystalline Salts, Soft Coal, Kaolin Clay	3
	3	Calcite, Marble, Soft Limestone, Barite, Chalk, Brimstone	9
Intermediate	4	Fluorite, Soft Phosphate, Magnesite, Limestone	21
	5	Apatite, Hard Phosphate, Hard Limestone, Chromite, Bauxite, Wollastonite	48
	6	Orthoclase Feldspar, Ilmenite, Hornblende	72
Hard	7	Quartz, Granite	100
	8	Тораz	200
	9	Corundum, Sapphire, Emery	400
	10	Diamond	1600

# Abbreviations and Symbols

Abbr.	Full Name (Trade Name)
±	Plus or minus
<	Less than
>	Greater than
α	Greek letter alpha: thermal diffusivity
β	Greek letter beta: coefficient of volume expansion
γ	Greek letter gamma: deformation, electrical conductivity
δ	Greek letter delta: heat diffusivity
$\Delta$	Greek letter delta (capital): change
ε	Greek letter epsilon: strain, expansion coefficient
η	Greek letter eta: viscosity, flow index
λ	Greek letter lambda: thermal conductivity
μ	Greek letter mu: micro or 10-6, coefficient of friction
π	Greek letter pi: ratio of circumference of circle to d = 3.1416
ρ	Greek letter rho: electrical resistivity, density
σ	Greek letter sigma: stress, standard deviation
$\overline{\omega}$	Greek letter omega: frequency
А	Acid, area, Ampere
AA	Atomic absorption
ABS	Acrylonitrile butadiene styrene (plastic)
ACM	Polyacrylic rubber
ACS	American Chemical Society
ACSM	Alkylated chlorosulfonated polyethylene
ADPA	Diphenylamine-acetone reaction product (AGERITE SUPERFLEX)
AEIC	American Edison Illuminating Companies
AEM	Ethylene acrylic rubber
al	
APPD	N-AlkyI-N'-phenyI-p-phenylenediamine (ANTOZITE 6/P)
ar	Aromatic
ASTM	American Society for Testing and Materials
AU	Polyester urethane
BAPER	Bromometnyl alkylated phenol formaldenyde resin
BDO	1,4-butanedioi
BIIK	Bromobutyl rubber
BIM2M	Brominated polymer of isobutylene and p-methylstyrene
BP	Bolling Point
DK C	Polybulaciene rubber (BODENE)
	Circo or opprovimetoly
	Corporate average fuel economy
CRE	Outputate average fuel economy
	Cadmium diathyldithiocarhamate (ETHVL CADMATE)
CED	Code of Eederal Regulations

CIIR	Chlorobutyl rubber
CM	Chlorinated polyethylene
CO	Epichlorohydrin rubber (homopolymer)
CPEC	Centrally Planned Economy Countries
CPPD	N-Cyclohexyl-N'-phenyl-p-phenylenediamine
CR	Polychloroprene (Neoprene)
CRF	Channel replacement furnace. ASTM N326 carbon black
CRU	Constitutional repeating unit
CSM	Chlorosulfonated polyethylene (Hypalon®)
CTAB	Cetvl trimethyl ammonium bromide
СТМ	Cavity transfer mixer
CTP	N-(cvclohexvlthio) phthalimide (PVI)
CUDMC	Copper dimethyldithiocarbamate (METHYL CUMATE)
cut	Controlled unward tapping (of natural rubber)
CV	Continuous vulcanization
d	Decomposes diameter
	Di(hutoxyethoxyethyl) adipate
DRP	Dibuty/ nhthalate
DRPH	2.5-dimethyl-2.5-di/t-butylperoxy)bexane (VAROX DBPH)
DRTU	1 3-dibuty/thiourea (THIATE II)
DCP	
	Dicyclopentadiene monomer
den	Density
	1 3-diethylthiourea (THIATE H)
dil	Dilute
	Deutsches Institut für Normung (West German test standards)
dNm	Decinewtonmetres
DOA	Dioctyl adinate
DOP	Dioctyl ohthalate
DOTG	Di-o-tolylguanidine (VANAX DOTG)
DPG	Diphenyl quanidine (VANAX DPG)
	Diphenyl-n-phenylenediamine (AGERITE DPPD)
DPTT	Dipentamethylenethiuram tetrasulfide (SULFADS)
DPTU	Diphenyl thiourea
DRC	Dry rubber content
DSC	Differential scanning calorimetry
	Differential thermal analysis
	<i>A A</i> '-dithiodicanrolactam
ртрм	4 <i>A</i> '-dithiodimorpholine
F	
	Ethylene-acrylic acid conolymer
FCO	Enichlorohydrin rubber (conolymer)
	Disodium ethylenediamine tetrascetate dihydrate
EEA	Ethylene-ethyl acrylate conclumer
	Ethylidene norbornene monomor

ENR ENRG EOM EPC EPDM EPM ESCR ETU	Epoxidized natural rubber Epoxidized guayule natural rubber Copolymers of ethylene and an octene Easy processing channel; ASTM S300 series carbon black Ethylene propylene rubber (Vistalon) Ethylene propylene rubber, copolymer (Vistalon) Environmental stress crack resistance Ethylene thiourea
EU	Polyether urethane
EV	Efficient vulcanization (cure system)
EVA	Copolymers of ethylene and vinyl acetate
EVM	Copolymers of ethylene and vinyl acetate (ASTM)
EVTMS	Ethylene vinyltrimethoxysilane copolymer
F	Temperature in degrees Fahrenheit, force
FA	Fatty acid
FBCV	Fluid bed continuous vulcanization
FDA	Food and Drug Administration
FEA	Finite element analysis
	Fast extrusion furnace; ASTM N500 series carbon black
	Fluoroelastomers
	Femuonnated rubbers of the polymethylene type
	DIN/ISO designation for fluorestamore
	Elucrosilicono rubbor
	Polyphosphazene rubber
GA GA	Glue acid
	Glue-Alum
GC	Gas chromatograph
GECO	Enichlorohydrin-ethylene oxide allylalycidylether terpolymer
GMF	n-Quinone dioxime
GPF	General purpose furnace: ASTM N600 series carbon black
GR	Guavule rubber
GR-S	Early name for styrene-butadiene rubber
HAF	High abrasion furnace; ASTM N300 series carbon black
HAV	Hot air vulcanization
HD	1,4 Hexadiene monomer
HDPE	High density polyethylene
HER	Hydroxyethyl ether of resorcinol
hi-ar	Highly aromatic
HIPS	High impact polystyrene
HM	High modulus
HMT	Hexamethylenetetramine
HNBR	Hydrogenated nitrile rubber
HNS	Hydroxylamine neutral sulfate; viscosity stabilizer for NR
HP	Heavy process oil
HPLC	High pressure liquid chromatograph

HQEE	Hydroquinone ethoxyether
HS	High structure
HSR	High styrene resin
HVBR	High-vinyl polybutadiene rubber
I	Electrical current
ICEA	Insulated Power Cable Engineers Association
ID	Inside diameter (hose, O-rings)
IIR	Butvl rubber
IISRP	International Institute of Synthetic Rubber Producers
in-lb	Inch-pounds
INRA	International Natural Rubber Agreement
insol	Insoluble
IPPD	N-isopropyl-N'PR-phenyl-p-phenylenediamine
IR	Synthetic polyisoprene (Nipol IR) infra red
IRB	Industry reference black: special preparation of ASTM N330
	carbon black
ISAF	Intermediate super abrasion furnace: ASTM N200 series carbon
	black
ISO	International Standards Organization
IUPAC	International Union of Pure and Applied Chemistry
K	Degrees Kelvin, dielectric constant, thermal conductivity
kV	kilovolt
l	Length
I A-TZ	l ow ammonia-thiuram/zinc oxide (for latex stabilization)
	Liquid chromatograph
LCM	Liquid curing media (molten salt bath)
LD50	Lethal dose for 50% mortality
LLDPE	Linear low density polyethylene
LM	Low modulus
LS	Low structure
lt	Liaht
m	Moderately
MBOCA	Methylene bis(ortho-chloro aniline)
MBM	Meta-phenylene-bis-maleimide (VANAX MBM)
MBS	4-Morpholinyl-2-benzothiazole disulfide (MORFAX)
MBT	Mercaptobenzothiazole (CAPTAX)
MBTS	Benzothiazyl disulfide (ALTAX)
MDA	Methylene dianiline
MDI	Methylene di-4-phenylisocyanate (VANCHEM HM-50)
ML	Mooney large rotor, ODR viscosity
MP	Melting point
MPa	Megapascals
MPFR	Methylol phenol formaldehyde resin
MPR	Melt processable rubber
MPTD	N,N'-dimethyl-N,N'-diphenyl thiuram disulfide
MQ	Silicone rubber

MRRDB	Malaysian Rubber Research and Development Board
MS	Mooney small rotor
MSDS	Material safety data sheet
MT	Thermal carbon black; ASTM N900 series carbon black
MTI	2-mercaptotoluimidazole (VANOX MTI)
mw	Molecular weight
mwd	Molecular weight distribution
Ν	Normality (molar equivalent), Newton (measure of force)
naph	Naphthenic
NBC	Nickel di-n-butyldithiocarbamate (VANOX NDBC)
NBR	Nitrile rubber
NBS	National Bureau of Standards
nd	Non-discoloring
NIOSH	National Institute for Occupational Safety and Health
NIR	Acrylonitrile-isoprene
nmr	Nuclear magnetic resonance
NR	Natural rubber
NRG	Guayule natural rubber
NSA	Nitrogen surface area
nst	Non-staining
OBTS	N-oxydiethylenebenzothiazole-2-sulfenamide (AMAX)
ODPA	Di-octyl diphenylamine (AGERITE STALITE S)
OD	Outside diameter (hose, O-rings)
ODR	Oscillating disk rheometer
OE	Oil extended
OSHA	Occupational Safety and Health Administration
OTOS	N-oxydiethylene thiocarbamyl-N-oxydiethylene sulfenamide
	(CURE-RITE 18)
Р	Power Factor, practically
par	Paraffinic
PBR	Vinylpyridine-butadiene
phr	Parts per hundred of rubber
PIB	Polyisobutylene rubber
PMQ	Methyl-phenyl silicone rubber
PNR	Polynorborene
POE	Polyolefin Elastomer; Ethylene Octene Rubber (Exact)
PPD	Para-phenylenediamine
pphm	Parts per hundred million
ppm	Parts per million
PRI	Plasticity retention index
PSBR	Vinylpyridine-styrene-butadiene
psi	Pounds per square inch
PVC	Polyvinyl chloride
PVI	Prevulcanization inhibitor (VANTARD PVI)
PVMQ	Methyl-phenyl-vinyl silicone rubber
QC	Quality control

R	Resistance
RA	Rosin acid
RCRA	Resource Conservation and Recovery Act
rhc	Rubber hydrocarbon
RMA	Rubber Manufacturers Association
RSS	Ribbed smoked sheets; a grade of Natural rubber
RTV	Room temperature vulcanization
S-AL	Salt alum
SA	Salt Acid
SAE	Society of Automotive Engineers
SAF	Super Abrasive Furnace; ASTM N100 series carbon black
SAN	Styrene-acrylonitrile copolymer
SARA	Superfund Amendments and Reauthorization Act
SBR	Styrene-Butadiene Rubber
SBS	Styrene-Butadiene-Styrene block copolymer
SeDMC	Selenium dimethyldithiocarbamate (METHYL SELENAC)
SG	Specific gravity, see density
SIR	Standard Indonesian rubber, a variety of TSR
SIR	Styrene-isoprene rubbers
SIS	Styrene-Isoprene-Styrene block copolymer
sl	Slightly
sol	Soluble
SMR	Standard Malaysian rubber; a variety of TSR
SPC	Statistical process control
SPF	Super process furnace; ASTM N358 carbon black
SPH	Styrenated phenol
SRF	Semi-reinforcing furnace; ASTM N700 series carbon black
SPRM	Single-ply roofing membrane
st	Staining
syn	Synthetic
t	lime, thickness
1	Polysulfide rubber
t5	Mooney scorch
TAC	
TAIC	Triallylisocyanurate
tan ð	Loss factor
IBBS	N-tert-butyl-2-benzotniazolesultenamide (VANAX NS)
ť C	
IBID	t But dia a strange state (ADOX TODD)
TBPB	t-Butyl perbenzoate (VAROX TBPB)
INSID	Technically classified (neture) where
	Televine distriction (natural) (UDDer
	Teluene diigeovenete
	Total a the second and the second an
IEID	Tetraethylmiuram disulfide (ETHYL TUADS)

Tg	Glass transition temperature
TGA	Thermo gravimetric analysis
TiBTD	Tetra-iso-butylthiuram disulfide (ISOBUTYL TUADS)
tlv	Threshold limit value
tma	Thermal mechanical analysis
TMQ	Polymerized 1,2-dihydro-2,2,4-trimethylquinoline
	(AGERITE RESIN D)
TMT	Tetramethyl thiourea
TMTD	Tetramethylthiuram disulfide (METHYL TUADS)
TMTM	Tetramethylthiuram monosulfide (UNADS)
TPE	Thermoplastic elastomer
TPNR	Thermoplastic natural rubber
Ts	Softening temperature
t _s 2	Scorch time
TSCA	Toxic Substances Control Act
TSR	Technically Specified (Natural) rubber
UL	Underwriters Laboratory
uv	Ultra violet
v	Very
vis	Viscosity
VLDPE	Very low density polyethylene
XBR	Carboxylic-butadiene rubber
XIIR	Crosslinked butyl rubber
XLPE	Crosslinked polyethylene
XNBR	Carboxylated nitrile rubber
XSBR	Carboxylic-styrene-butadiene rubber
ZBEC	Zinc dibenzyl dithiocarbamate (BENZYL ZIMATE)
ZBPD	Zinc O,O-di-n-butyl phosphorodithioate
ZDBC	Zinc di-n-butyl dithiocarbamate (BUTYL ZIMATE)
ZDEC	Zinc diethyldithiocarbamate (ETHYL ZIMATE)
ZDBC	Zinc di-n-butyl dithiocarbamate (BUTYL ZIMATE)
ZDiBC	Zinc di-iso-butyldithiocarbamate (ISOBUTYL ZIMATE)
ZMBT	Zinc salt of Mercaptobenzothiazole (ZETAX)
ZMPC	Zinc N-methylphenyl dithiocarbamate
ZMTI	Zinc salt of 2-mercaptotoluimidazole (VANOX ZMTI)

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