7 Solvent- and/or Chemical Agent-Based Separation

Multilayer plastic packaging films cannot be recycled properly, as the different plastic layers (3 up to 20) and/or metal foils cannot be separated with mechanical technologies. Solvent and/or chemical agent technology is a promising approach for the separation of multilayer packaging films. A large number of patents have been disclosed for this technology, which are applicable to both flexible and rigid multilayer plastic packaging. Despite the large number of disclosed patents, scientific publications, research and industrial projects with promising preliminary results, the solvent and/or chemical agent technology is still not commercially used.

7.1 Stripping

Stripping agents are solvents for the dissolution or swelling of the interlayer binder (tie layer), or for the delamination and separation of the individual layers from a multilayer packaging film and/or chemical agents for the separation or delamination of the aluminum foil from plastic layers.

DE4215573 A1 (1993, HOECHST AG) discloses a method for separating a multilayer film into its individual layers by treating the film with an organic liquid, which acts as a solvent or swelling agent for the adhesive or which, in the case of heat-laminated composites, can penetrate between the different layers and split them apart. Preferably, the multilayer film is first pulverized by grinding and then stirred with the organic solvent, or the solvent can be added during the grinding stage. The different film components are then separated on the basis of their different densities. The organic solvent must be a nonsolvent for the film components; preferred solvents are ethyl acetate, toluene, and gasoline. The treated film components are then separated, e.g., in a hydrocyclone or by stream classification. It is also possible first to separate off the organic liquid in a known manner, such as filtration or centrifugation, to redisperse the residue in water and to effect separation by the treatment of heavy liquids (addition of soluble or insoluble substances). The method enables the separation of multilayer films into the individual layers (e.g., PVC and aluminum; polyester and polyethylene; PVC and polyethylene, etc.),

which can then be recovered separately in a sufficiently pure form for recycling in high-grade products.

WO9304116 A1 (1993, SCHERING AG) discloses a method for separating layers bonded together by an adhesive from waste packaging materials by immersing the packaging material, preferably with agitation, in a solvent for the adhesive with optional flotation to save the separated layers. The adhesive is dissolved by a solvent in which the bonded layers are themselves insoluble. The packaging material is preferably first cut into pieces of 10 cm^2 , preferably 2 cm^2 , and then immersed in or sprayed with a solvent. The invention can be used for the separation of packaging materials such as aluminum blister packs of aluminum and PVC, and toothpaste tubes, for material recovery and reuse. The selection of the solvent system depends on the type of the adhesive. Suitable solvents are methyl formate, methyl acetate, toluene, or chloroform. A preferred solvent system is a mixture of acetone with water (1%-20%). The patent is claimed to have the following advantages: providing a simple and flexible separation process; saving raw material; avoiding the problems of incineration and consequent fume disposal; and reducing need for dumping. On the other hand, acetone has a very low flash point $(-20^{\circ}C)$, and it is highly flammable and prone to accidents. The plastics are also fairly flammable. In industrial application, where a large amount will be required, the hazard of an accident is very high (2004, WO2004031274 A1, MUKHOPADHYAY ASHUTOSH).

US5246116 A (1993, REYNOLDS METALS CO) discloses a method of recovering the components from an aluminum foil—containing laminate used in packaging comprising the steps of

- providing an aluminum foil—containing laminate in a predetermined size, said foil-containing laminate comprising foil/plastic laminate or a foil/plastic/paper laminate;
- 2) combining the foil-containing laminate with a polyalkylene glycol aqueous solution to form a mixture;
- 3) agitating the mixture;
- 4) heating the mixture to at least about 80 °C for a predetermined period of time to delaminate the foil-containing laminate;
- 5) cooling the mixture;
- 6) separating the plastic from the mixture by flotation;
- separating foil and recovering the foil from the polyalkylene glycol aqueous solution;

- heating the remaining polyalkylene glycol solution to at least 90 °C to separate and recover the polyalkylene glycol polymer from the remaining polyalkylene glycol solution; and
- 9) reusing the recovered polyalkylene glycol in step (2).

The polyalkylene glycol is believed to function in one mode as a type of solvent to separate or delaminate the aluminum foil from plastic or paper components, especially where adhesive is used for bonding of foil with another component. Where pressure type bonding, as in extrusion, is used to laminate the components together, the polyalkylene glycol softens the nonfoil components to facilitate delamination. In a preferred embodiment, the polyalkylene glycol includes linear polymers of equal amounts of ethylene oxide and propylene oxide started with butanol. The molecular weight is dependent on the chain length. The preferred molecular weights vary from 270 to 1230. The overall range extends from about 200 to 10,000. The polyalkylene glycol is water soluble at temperature below 40 °C. Because of ethoxylation, these compounds exhibit reverse solubility. At temperatures above 40 °C, a solution of the polyalkylene glycol separates into two layers, the top being the polyalkylene glycol polymer and the bottom layer being water. This separation characteristic of the glycol fluid permits recycling of the polyalkylene glycol solution after foil separation. Utilization of the polyalkylene glycol fluids also minimizes any adverse effect on the environment during processing of the foilcontaining laminates. The polyalkylene glycol fluids have low vapor pressures, e.g., less than 0.01 torr (1.33 Pa) at 100 °C. Thus, there are no volatile organic compounds associated during separation and recovery of the aluminum foil from the laminate. Suitable commercial polyalkylene glycols are Carbowax and UCON-HB (Union Carbide Corporation) and Pluronic and Tetronic (BASF).

EP0538730 A (1993, NORDENIA VERPACKUNG) discloses a method and an apparatus for the separation of the various layers from a used multilayer packaging film comprising at least one first layer made of polyethylene and at least one second layer made of the same polyethylene, a similar polyethylene, another polymer, or another material, for example, aluminum (see Fig. 7.1). The used packaging film is shredded into pieces, and the pieces are brought into at least one solvent bath containing an organic solvent under vigorous agitation. Packaging films containing a bonding agent (adhesion promoter) between the individual layers of the film, which comprises relatively high-percentage copolymers or terpolymers of polyethylene with acrylic acid and derivatives thereof,



Figure 7.1 Schematic diagram of the process flow (B) for transforming polyethylene multilayer film (A) into reusable raw materials (1993, **EP0538730** A, NORDENIA VERPACKUNG). 1, Polyethylene; 2, Aluminum; 3, Polyethylene; 4, 5, Bonding agents; 6, Shredding station; 7, 10, 11, 14, 16, and 17, Indicating arrow; 8, Solvent; 9, Solvent bath; 12, Cleaning station; 13, Mixing device; 15, Separation station

and relatively high-percentage ethylene vinyl acetate (EVA) copolymers, are bought into contact with a solvent, which causes the coupling agent to swell, for example, low-boiling esters of acetic acid (e.g., ethyl acetate and isopropyl acetate) or aliphatic ethers (e.g., propylene glycol monomethyl ether).

The process often results in decomposition of the packaging components, long processing times, and insufficient separation. Further, the pigments present in the films are not removed, and residues of adhesion promoters always remain on the separate film layers, which largely consist of nitrocellulose. In subsequent processing, these residues result in charring so that high-quality films cannot be obtained (2002, **WO02100932** A1, DER GRUENE PUNKT DUALES SYST; 2017, **WO2017108014** A1, USTAV CHEMICKYCH PROCESU AV CR V V I).

US2004129372 A1 (2004, HUANG CHAO-KUO; SHAO CHUNG-HSING) discloses a method for separating and recycling an aluminum foil containing composite packaging material using an acid solution containing nitric acid as a stripping agent to soak the foil-laminated material (see Fig. 7.2). The nitric acid in the stripping agent permeates



Figure 7.2 Block diagram of a separating method for recycling aluminum foil–laminated packaging material (2004, **US2004129372** A1, HUANG CHAO-KUO; SHAO CHUNG-HSING).

the plastic layer (made mostly of polyethylene) and into the interfaces between the aluminum foil layer and the plastic layer to dissolve the alumina (Al_2O_3) and separate the layers. After separating the different layers of the Al_2O_3 foil—laminated material, the striping agent remaining on the separated layers is drained out and neutralized; the separated layers are cleaned, dried, and classified for a subsequent recycling process.

The concentration of the nitric acid in the acid solution of the striping agent is 15%-68%. Acetic acid and phosphoric acid can be added to nitric acid solution to increase the efficiency of the striping agent. Optionally, a heating process is carried out within a temperature range of $40-70^{\circ}$ C when soaking the foil-laminated material to accelerate stripping speed. The concentration of the stripping agent and the heating temperature are determined according to thickness of the plastic layer. Practically, when the concentration of the stripping agent is 68% and the heating temperature is 60°C, a soaking time in the stripping agent for the foil-laminated material is about 40 min. When the concentration of the nitric acid is 34% and the heating temperature is 65°C, the soaking time for the foillaminated material in the stripping agent is 60 min. If the stripping is carried out without heating, the operational conditions are when the stripping agent is 30%-34%, the soaking time is 7 h; and when the stripping agent is 20%-30%, the soaking time is 15 h. The method is suitable for treating foil-laminated material in large quantity batches and has lower operation cost.

WO0250175 A2 (2002, MUKHOPADHYAY ASHUTOSH) discloses a method for the recovery of aluminum foil and polyethylene from multilayer fragments from packaging industrial refuse in sheet, strip, tube, or shredded form. The multilayer fragments are treated with an inorganic acid solution being 50%-70% concentrated nitric acid for about 4-7 h, so as to loosen the bonding of the constituents; the constituents are stripped physically and washed. The washing step is carried out with dilute lime water followed by one or more water baths for total removal of adhered acid from the delaminated fragments. The delaminated fragments are physically separated into polyethylene and aluminum. The constituents are further dried, preferably by conventional centrifuge, optionally followed by drying under the sun or in a conventional dryer.

WO2004031274 A1 (2004, MUKHOPADHYAY ASHUTOSH) discloses a method for the recovery of aluminum foil and polyethylene from multilayer fragments of packaging industrial refuse in sheet, tube, or shredded form as separate constituents by treating the comminuted fragments with an inorganic base solution, in particular sodium hydroxide (NaOH), so as to dissolve the aluminum foil to subsequent recoverable

aluminum salts, namely sodium aluminate (NaAlO₂), and polyethylene retained in its physical form. From the recovered sodium aluminate, aluminum hydroxide gel (Al(OH)₃) is obtained. From the aluminum hydroxide gel, dried powder of alumina (Al₂O₃) or other aluminum salts can also be obtained. According to the invention, the method is relatively economical and efficient than that of the applicant's earlier patent application **WO0250175** A2 (2002) also because sodium aluminate (either concentrated solution or dried powder) is the main recovery product of the process.

Example: In a 1000 ml clear conical flask were added 66 g of pure dried sodium hydroxide flakes. Clear water was poured to make 800 ml of 2M sodium hydroxide solution. A few pieces of laminated toiletry tubes were added to the flask. The shoulder and tail end seal of the tubes were shredded out through manual cutting with scissors. Then taking 0.25 cm breadth-wisely, the tubes were longitudinally shredded, and all the contaminants were cleared and washed out. The shredded fragments (0.25 cm) of the laminated tubes were dipped into the conical flask. The flask was closed with stopcock and allowed to stand for 48-84 h with inbetween stirring. When all aluminum was dissolved, the two layers of plastics that were released from lamination floated in the solution. The released plastics were taken out from the resultant very dilute solution of sodium aluminate and dipped in a dilute nitric acid solution for 0.5-2 min with fast stirring and washed with water. The resulting mixture was further processed to yield pure sodium chloride as a by-product having its own specific market.

WO03104315 A1 (2004, MASSURA ANDERSON CROVADOR; CROCHEMORE GUILHERME BALTAR; MARCAL DE SOUZA EDSON ALEXANDR) discloses a method for the separation of polymer, aluminum, and/or paper from multilayered films, from pack- and decorative-type food packaging, by introducing the films in heated baths of organic solvents, protonic carboxylic acid, and water at temperature ranging from 20 to 140°C and time between 5 s and 2 h. Preferred organic solvents include tetrahydrofuran, xylene, toluene, carbon tetrachloride, acetone, and chloroform. A preferred protonic carboxylic acid is acetic acid. The complete recovery of each component film is enabled by the solubilization of the adhesive used among the layers. According to Hildebrand's law, the nearer the solubility parameters of the adhesive and the solvent, the more easily the solubilization will occur; in particular, if the difference of absolute values between the two solubility parameters is lower than 1.7 Hildebrand, the solubilization is assured. Another parameter to be taken into consideration is the cohesive energy density, which

especially depends on the temperature in general; the greater the cohesive energy density, the greater is the difficulty to make the polymer or any type of organic molecule with lower molecular weight soluble, as it happens with adhesives. The higher the temperature, the greater the thermal agitation state of adhesive molecules and, therefore, the lower is its cohesive energy density, thereby enabling solubilization thereof.

Solubilization of polyurethane adhesive joining the polyethylene film with PET film, polypropylene film, aluminum, or paper sheet can be performed in chloroform bath at atmospheric pressure with temperature in the range of 20–61 °C within a time between 30 s and 1 h. Solubilization of poly(vinyl alcohol) (PVOH) adhesive joining the different polymeric films each other or to aluminum or paper sheet is performed in protonic carboxylic acid bath at atmospheric pressure with temperature in the range of 20–115 °C within a time between 30 s and 2 h or further in water bath at atmospheric pressure with temperature in the range of 15–100 °C within a time between 5 s and 1 h. The recovered films can be reused in the manufacture of several articles by usual recycling processes.

The use of organic solvents, like halogenated media, in this method has, however, a negative environmental impact (2018, **WO2018109147** A2, SAPERATEC GMBH).

BRPI0402112 A (2006, MARCAL DE SOUZA EDSON ALEX-ANDR; MASSURA ANDERSON CROVADOR) discloses a method for recycling flexible multilayer comprising oxidation, solubilization, and defunctionalization of the polyurethane (polyether- or polyester-based), polyester, hot melt, PVOH, and dextrin base adhesives, which bind the laminated layers formed of polymer films (metallized or not), aluminum foil, and paper to be separated, using a bath of a chemical solution containing acetic acid (of concentration 70%–90%) and formaldehyde (of concentration 0.1%–10%) heated at a temperature ranging from 85 to 95 °C, for a time period between 5 and 100 min.

WO2014162238 A (2014, JAIN PRANAY) discloses a method for recycling metalized PET film including a washing step for removing aluminum. Metalized PET film or flakes are washed in a hot washing water bath tank or at room temperature with an alkaline solution, such as a solution containing caustic soda or in a solvent such as a hydrocarbon solvent. The desired level of caustic soda is in the range of 0.5%-3% in a water solution at room temperature to 90 °C or any other suitable alkali solution. Keeping the metalized film in 1% caustic soda solution at a water temperature of 80–85 °C, the alumimum was removed within few seconds. The time required to remove aluminum from the metalized PET film for similar caustic soda solution was 2 min at room

temperature water. The aluminum completely dissolves and the water acts as an acid. The aluminum layer from metalized PET film is removed, and clear PET film is obtained after multiple washing steps varying from 2 to 10 times.

CN104744724 A (2015, DAI XIANGHUI) discloses a method for separating the layers of an aluminum—plastic multilayer packaging with the use of a separating agent prepared by mixing 40-200 pbw, preferably 42 pbw, formic acid, 5–10 pbw, preferably 6 pbw, dichloromethane (methylene dichloride) and further 1–4 pbw, preferably 3 pbw, nonionic surfactant. The separating method comprises the following steps: mixing the separating agent with water to obtain the separating agent, and soaking a pulverized cleaned aluminum—plastic composite film in the separating agent for 4–12 h; pulling out the fragments of the composite film, cleaning, centrifuging, and drying. The separating agent that is used in this patent application is highly volatile and also contains components that are harmful to the environment (2018, **WO2018109147** A2, SAPERATEC GMBH).

CN104669467 A (2015, XU CHAO; ZHANG QIUHUA; CHEN GUANG) discloses a stripping agent to separate plastic, such as PVC, and aluminum foil from waste pharmaceuticals packaging materials. The stripping agent comprises 10%–40% tetrahydrofuran, 30%–50% ethyl acetate, 15%–30% ethanol (ethyl alcohol), and 5%–20% n-hexane.

KR20060000247 A (2006, HEA SONG COMMERCIAL FIRM) discloses a method for recovering EVA copolymer and PET from a waste laminate film comprising the following steps: (1) pulverizing the laminate; (2) precipitating the pulverized laminate film in a settling tank containing a 35%, or preferably 50%, hydrogen peroxide solution for a predetermined time; (3) transferring the pulverized film from the precipitation tank into an extruder; (4) discharge the pulverized to a precipitation separation tank and separating the EVA floating at an upper layer and the PET precipitated at a lower layer owing to the difference of specific gravity; and (5) dehydrating the separated EVA and PET.

GB2525858 A (2015, SAPERATEC GMBH) discloses a method and an apparatus for recovering individual material components from multilayer packaging waste comprising a metal layer at least one polymer layer and, optionally, a paperboard layer. In one nonlimiting example of the invention, the polymer layers are made of low-density polyethylene (LDPE) and the metal layer is made of aluminum. The multilayer packaging waste is collected together as bales. The bales are placed into a first vat to remove a substantial portion of the paper layer as a slurry and thus to produce residual waste, subsequently placing the residual waste in a second vat comprising a separation fluid to produce a mixture of aluminum shreds, plastic shreds, and residual components. The separation fluid is a microemulsion comprising a carboxylic acid, a swelling agent for the polymer, and a surfactant. The carboxylic acid is selected from the group of short chain carboxylic acids consisting of acetic acid, formic acid, or propanoic acid, or mixtures thereof. The swelling agent used is a hydrocarbon solvent selected from the group of aromatic hydrocarbons, such as toluene, xylene, ethylbenzene, or solvents of the naphtha types, alicyclic hydrocarbons, such as cyclohexane or decalin, olefins, terpenes, and acyclic aliphatic hydrocarbons, or mixtures thereof. Additional swelling agents include aprotic solvents, such as ketones, esters, or ethers. In a further aspect of the invention, the separation fluid further comprises water and at least one anionic surfactant and is a microemulsion. The microemulsion must be stable in the temperature range at which the second vat is operating $(20-50^{\circ}C)$. This can be achieved by combining anionic surfactants with cosurfactants or with hydrotropes, such as phosphoric acid decyl ester. The anionic surfactants are selected from alkyl sulfates, alkylbenzene sulfonates, and olefin sulfonates, or mixtures thereof. An exemplary cosurfactant is caprylic acid, and an exemplary hydrotrope is phosphoric acid decyl ester.

The pros and cons of Saperatec's microemulsion technology can be summarized as follows:

Pros: The only currently available technology that can separate plastic layers from a multilayer plastic packaging material to obtain raw materials of high purity. The recovered raw materials can be reclaimed as secondary raw materials, thus fully preserving the cycle of materials. The separation process functions well at room temperature. The microemulsion can be reconditioned and reused [1].

Cons: Higher water and energy demand than alternatives as a result of washing and drying requirements. It still requires an understanding of structure composition before beginning the process. This makes it unfeasible for curbside collection programs and limits processing to one structure format at a time [2].

WO2018109147 A2 (2018, SAPERATEC GMBH) discloses a method for recycling a multilayer packaging material comprising a metal layer and at least one polymer layer using a separation fluid that is a mixture of water, a short-chained carboxylic acid, phosphoric acid, and an alkali metal hydroxide solution. The short-chain carboxylic acid and the phosphoric acid react partially with the alkali metal hydroxide to produce alkali metal phosphates and alkali metal carboxylates. The short-chain carboxylic acids used are water miscible C1–C4 monocarboxylic acids,

| Table 7.1 | Composition c | of a Separation | 1 Liquid (20 | 018, WO20181 | 09147 A2, |
|-----------|---------------|-----------------|--------------|---------------------|------------------|
| SAPERAT | EC GMBH) | | | | |

| Components | Content (wt%) |
|--------------------------------|---------------|
| Water | 45.7 |
| Glacial acetic acid | 45.0 |
| Phosphoric acid, 30% solution | 3.0 |
| Sodium hydroxide, 33% solution | 6.3 |

such as formic acid, acetic acid, propionic acid, and butyric acid. In one aspect of the invention, formic or acetic acid is used. The alkali metal hydroxides include hydroxides of lithium, sodium, and potassium. In general, other hydroxides can be used if the other hydroxides do not form insoluble phosphate salts because these insoluble salts would interfere with passivation of aluminum.

In the following examples, flakes of flexible multilayer plastic packaging used for drinks, food, and coffee packaging are stirred in a separation liquid (see Table 7.1) at 70°C. The detachment of the plastic layer from the aluminum is complete within 2-5 h (see Table 7.2).

WO2017108014 A1 (2017, USTAV CHEMICKYCH PROCESU AV CR V V I) discloses a method for the separation of individual components from a multilayer packaging material, wherein the multilayer packaging material is crushed and combined with an organic separation agent in weight ratio material/agent 1/5 to 1/10; the resulting mixture is heated to a temperature in the range of 40–100 °C and left to react at stirring until separation of the individual components occurs, and the individual components are then isolated by a method based on their different specific weights. The organic separation agent is a mixture of crude oil fraction with distillation curve from 50 to 200 °C with an organic solvent selected from toluene, xylene, acetone, N-methyl pyrrolidone, N-ethyl pyrrolidone, and formic acid. The composite packaging material contains the following components: LDPE/polypropylene, LDPE/aluminum/PET, polyethylene/aluminum/polyethylene, or polyethylene/aluminum/polypropylene.

WO2017037260 A1 (2017, CENTRE NAT RECH SCIENT) discloses a method and an apparatus for delaminating multilayer systems including at least one polymeric layer, the layers being separated by interfaces, comprising at least the following steps: mixing the multilayer system with
 Table 7.2
 Separation of Aluminum Foil from Multilayer Plastic Packaging Materials by Treatment With the Separation

 Liquid of Table 7.1 (2018, WO2018109147 A2, SAPERATEC GMBH)

| Packaging | Multilayer Type | Flakes' Surface Area (cm ²) | Amount of Packaging Material (g) | Amount of Separation Liquid (g) | Detachment Time (h) |
|-------------------------------|-----------------|--|--|---------------------------------------|------------------------|
| Beverage stand- up pouches | LDPE/AI/PET | 1 | 60 | 1000 | 4 |
| Snack food packaging | LDPE/AI/PET | 3 | 30 | 30 | 4 |
| Toothpaste tubes | LDPE/AI/LDPE | 2 | 60 | 1000 | 2 |
| Coffee packaging | PP/AI/PET | 1 | _ | 20 | 5 |

Al, Aluminum; LDPE, Low-density polyethylene; PET, Poly(ethylene terephthalate); PP, Polypropylene.

a fluid made up of at least one gas having the capacity of causing at least one of the layers to swell and one or more nonreactive liquids having the capacity of allowing each layer individually or subsets of layers to be disconnected without damaging the components of the layers, the gas/ liquid fluid being brought to the required temperature and pressure, and separately recovering at least one or more layers or a subset of layers which are undamaged. The fluid is preferably a mixture of CO₂, water, and acetone. The volume proportion of the liquid mixture with respect to the gas is at least 15%. The volume proportions of the constituents of the acetone/water mixture are, for example, 80% acetone and 20% water or with a proportion of water relative to acetone ranging from 0% to 100%. The method allows the separation of layers without the need for mechanical action. The method can be used for the recycling of multilayer packaging waste, for example, food packaging, cosmetic, or pharmaceutical packaging composed of at least a polymer layer coated with an aluminum foil. Particular examples include chewing gum packaging comprising an assembly of polymeric layers and an aluminum foil, and fresh cream package consisting of polyethylene/cardboard/polyethylene/ aluminum/polyethylene.

Yousef et al. [3,4] developed a process that uses a switchable hydrophilicity solvent to delaminate the layers of a multilayer flexible packaging and uses ultrasonic treatment to accelerate the separation process. The solvent used is N, N-dimethylcyclohexylamine (DMCHA). The delamination was conducted on six common types of multilayer flexible packaging from food wrapping (crisps, chocolate bars, bakery products, ground coffee, ice cream, and biscuits) and six different types of waste pharmaceutical blister packets. The polarity of the solvent is switched by adding water and CO_2 , allowing the remaining dissolved adhesives and inks to be recovered. The recycling rate using this method is >99%, and the recovered materials are aluminum flakes, PVC films, EVA films, PET films, and polyethylene powder. The solvent can also be recycled by heating it overnight to remove the CO_2 and to evaporate water that has been added.

The main stripping agents used for the delamination of flexible plastic multilayer packaging films are listed in Table 7.3.

A new development uses supercritical liquids for the delamination of multilayer packaging films. An application of this technology can be found in **WO2017037260** A1 (2017, CENTRE NAT RECH SCIENT), which discloses a method for delaminating a multilayer system used in food packaging, cosmetic or pharmaceutical packaging, and photovoltaic module by treating the multilayer system with a gas/liquid mixture fluid, preferably CO_2 /water/acetone, at a temperature that is greater than the

| Multilayer Packaging Material | Use | Bonding System | Stripping Agent | Patent |
|--|---|---|---|--|
| PVC and Al; PVC and PE; PET and PE | | Adhesive; thermal lamination | Ethyl acetate, toluene, and gasoline | DE4215573 A 1 (1993, HOECHST AG) |
| PE/AI, PVC/AI | Al blister packs of Al and PVC and toothpaste tubes | Adhesive | Acetone (90%) and water (10%) | WO9304116 A1 (1993, SCHERING AG) |
| (PE, PP)/Al | | Adhesive; pressure bonding | Polyalkylene glycol (Carbowax and UCON- HB, Union Carbide Corporation; Pluronic and Tetronic, BASF) | US5246116 A (1993, REYNOLDS METALS CO) |
| PE/AI/PE | | Copolymers or terpolymers of polyethylene with acrylic acid and derivatives and ethylene vinyl acetate copolymers | Swelling agent: ethyl acetate and isopropyl acetate) or aliphatic ethers (e.g., propylene glycol monomethyl ether) | EP0538730 A (1993, NORDENIA VERPACKUNG) |

Table 7.3 Stripping Agents for the Delamination of Flexible Plastic Multilayer Packaging Films

| PE/AI | | | Nitric acid; optionally acetic acid and phosphoric acid | US2004129372 A1 (2004, HUA NG CHAO-KUO; SHAO CHUNG-HSING) |
|--|--|-------------------|---|--|
| PE/AI | Medicinal strips or blister type packs, toiletry tubes | | Nitric acid (50%-70%) | WO0250175 (2002, MUKHOPADHYAY ASHUTOSH) |
| PE/AI | Medicinal strips or blister type packs, toiletry tubes | | Sodium hydroxide; nitric acid | WO2004031274 A1 (2004, MUKHOPADHYAY ASHUTOSH) |
| PE-PET/PP-AI- paper; BOPP/OPP-AI- paper | Pack- and decorative-type food packaging | PU, PVOH | Chloroform, xylene, tetrahydrofuran; acetic acid | WO03104315 A1 (2004, MASSURA ANDERSON CROVADOR; CROCHEMORE GUILHERME BALTAR; MARCAL DE SOUZA EDSON ALEXANDR) |
| (PE, PP, PET, PA)/ Al, paper/Al | | PU, PVOH, dextrin | Acetic acid | BRPI0402112 A (2006, SOUZA EDSON ALEXANDRE MARCAL D; MASSURA ANDERSON |

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| Multilayer Packaging Material | Use | Bonding System | Stripping Agent | Patent |
|----------------------------------|--|----------------|---|---|
| PET/EVA | Coating films, printing materials, or labels | | Hydrogen peroxide solution (35%-50%) | KR20060000247 A (2006, HEA SONG COMMERCIAL FIRM) |
| PET/AI | Film | | Caustic soda (0.5%–3% in water solution, 25–90 °C) | WO2014162238 A (2014, JAIN PRANAY) |
| PVC/AI | Packaging of pharmaceuticals (tablets, capsules, suppositories, etc.) | | Tetrahydrofuran (10%-40%), ethyl acetate (30%-50%), ethanol (15%-30%), and n-hexane (5%-20%) | CN104669467 A (2015, XU CHAO; ZHANG QIUHUA; CHEN GUANG) |
| Plastic/Al | | | Formic acid (40–200 pbm), dichloromethane (5–10 pbm) and | CN104744724 A (2015, DAI XIANGHUI) |

Table 7.3 Stripping Agents for the Delamination of Flexible Plastic Multilayer Packaging Films (Continued)

| | | nonionic surfactant (5 -10 pbm) | |
|--|--|--|--|
| PE/adhesive/Al | | First stage in organic solvent (acetone, chloroform, ethyl ether, benzene. and toluene); second stage in 1–2 mol/l hydrochloric acid solution, 2–5 h, at 30–70°C | CN107599234 A (2018, ANHUI TENGYUE ALUMINUM PLASTIC CO LTD) |
| PE/AI/PE; PE/cardboard/PE/AI/ PE | Chewing gum packaging, fresh cream package | Mixture of CO ₂ , water (e.g., 20%) and acetone (e.g., 80%) | WO2017037260 A1 (2017, CENTER NAT RECH SCIENT) |
| PE/AI/PET; PP/AI/PET | Coffee packaging, drinks packaging, pet food packaging | Microemulsion: acetic acid (6.0%–12.0%); xylene isomers (20.0%–21.7%) or naphtha, heavy aromatic, naphthalene depleted (25.0%); sulfonic acids, C14-17-sec-alkane sodium salts (12%–14.4%); caprylic acid (3.3%–4.8%) or phosphoric acid decyl | GB2525858 A (2015, SAPERATEC GMBH) |

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| Multilayer Packaging Material | Use | Bonding System | Stripping Agent | Patent |
|--|---|----------------|---|---|
| | | | ester, sodium salt (1.8%); water (51.4%–53.4%) | |
| LDPE/AI/PET; LDPE/AI/LDPE; PP/AI/PET | Beverage stand-up pouches, snack food packaging, tooth paste tubes, coffee packaging | | Water (45.7%), glacial acetic acid (45.0%); phosphoric acid 30% solution, (3.0%); sodium hydroxide 33% solution (6.3%) | WO2018109147 A2 (2018, SAPERATEC GMBH) |
| PE/AI/PET; PVC, PP/AI/EVA | Pharmaceutical blister packets, food products (crisps, chocolate bars, bakery products, ground coffee, ice cream, and biscuits) | | DMCHA (40-80 °C) | [3,4] |

| Table 7.3 | Stripping Agen | its for the Delaminatio | n of Flexible Plastic | Multilayer Packagir | ng Films (Continued) |
|-----------|----------------|-------------------------|-----------------------|---------------------|----------------------|
|-----------|----------------|-------------------------|-----------------------|---------------------|----------------------|

Al, Aluminum; BOPP/OPP, Biooriented/oriented polypropylene; DMCHA, N, N-Dimethylcyclohexylamine; EVA, Ethylene vinyl acetate; PE, Polyethylene; PET, Poly(ethylene terephthalate); PP, Polypropylene; PVOH, Poly(vinyl alcohol); PU, Polyurethane.

critical temperature¹ of the gas (CO₂) and lower than the degradation temperature of the layers of the multilayer system and at a pressure that is higher than the critical pressure of the gas, and the volume proportion of the mixture of liquids (water and acetone) with respect to the gas is at least 15%.

Some processes use chemical separating agent(s) in combination with water or organic solvent(s) for the separation of layers and/or metal foils.

WO2015159301 A2 (2015, PATEL KETAN MAHADEV; VAVIYA MAHESH MAHADEV; PATEL MAHESH HARJI) discloses a method for recovering LDPE from flexible packaging material comprising at least polyester and LDPE by treating the flexible packaging material in an acidic environment having sulfuric acid, thereby removing at least the polyester component in the packaging material and extracting at least the LDPE component from the acidic environment by washing with water to remove traces of at least the sulfuric acid. The flexible packaging material includes packaging material for food products, agricultural products, medicinal products, pharmaceutical products, and detergents.

Example 1: 30 g of a detergent packaging made up of polyester and LDPE was treated with 500 g of 68% sulfuric acid for 2 min. The color gradually turned to dark brown on mixing detergent packaging with sulfuric acid. No further color change was observed for around 2 min, which indicated the end point of the reaction. The sulfuric acid burnt the polyester component, and the LDPE component was retained. LDPE was extracted from the acidic environment by a physical method and washed with water to remove traces of sulfuric acid. 6 g of polyester was burnt, and 24 g of LDPE was extracted.

CN107599234 A (2018, ANHUI TENGYUE ALUMINUM PLASTIC CO LTD) discloses a method for separating and recycling waste aluminum and plastic from a composite packaging by combining an organic solvent method and a chemical separating method. The method comprises the steps of;

 putting a waste aluminum plastic composite packaging material into a shredder; placing the shredded aluminum plastic material in a stirring barrel; adding an organic solvent (acetone, chloroform, ethyl ether, benzene, and toluene) in the stirring barrel till the aluminum

 $[\]overline{}^{1}$ The critical temperature of a substance is the temperature at and above which vapor of the substance cannot be liquefied, no matter how much pressure is applied.

plastic packaging material is fully immersed and stirring the mixture at a rotating speed of 200-500 r/min for 2-8 h; separately washing the plastic floating on the surface of the organic solvent and the aluminum foil precipitated in the bottom of the stirring barrel with clean water;

- drying, pelletizing, and remolding the plastic; drying the precipitated aluminum foil and transferring it to a reaction container for secondary separation;
- adding a 1-2 mol/l hydrochloric acid solution into the reaction container, stirring the mixture for 2-5 h at 30-70 °C; filtering and washing to obtain a filtrate for later use;
- adding 1-2 mol/l sodium hydroxide solution to the filtrate obtained in step (3); stirring the mixture at 60-90°C for 3-5 h to obtain polyaluminum chloride;
- 5) adding ammonia/water to the filtrate obtained in step (3) until the pH of the solution is 10 and then filtered; adding 0.3–1 mol/l sodium hydroxide solution to the precipitate obtained by filtration until the precipitate is completely dissolved; charging the dissolved solution with carbon dioxide until the pH of the solution is 5–7; after aging for 18–48 h, the solution is filtered, washed, and dried to obtain precipitated aluminum hydroxide; and
- 6) calcining the precipitated aluminum hydroxide at a high temperature of 1200 °C to obtain an alumina solid.

CN106832393 A (2017, HENAN WANBANG HIGHLY-EFFICIENT AGRICULTURAL DEV CO LTD) discloses a method of separating the layers of a polyethylene/aluminum/PET film comprising the following steps: (1) slitting the packaging film, putting the slitted film into a stainless steel tank; (2) adding water and a surfactant into the stainless steel tank, and heating to a preset temperature to soak the slitted film; (3) taking out the soaked slitted film, and separating the polyethylene film; (4) packing the residue mixed material where the polyethylene film is separated and soaking it in a PVC tank at room temperature; (5) hot-dipping the soaked residue mixed material in the stainless steel tank; (6) subjecting the residue mixed material subjected to hot dipping to separate aluminum and PET film; (7) drying the separated aluminum. The film separation method has the following beneficial effects: the problem of air pollution in the traditional separation method is avoided; the separation method provided

by the invention realizes the safe production at the normal temperature in the whole process; no pollution waste is produced; and the method is favorable for environmental protection.

7.2 Cleaning Solutions

Cleaning systems using solvent and/or an aqueous surfactant solution are used for removing printing inks, film additives, impurities, etc., from flexible plastic packaging waste. These cleaning systems are distinguished from wet cleaning or washing using water (see Chapter 8, Section 8.1.1).

EP0521418 A1 (1993, NORDENIA VERPACKUNG GMBH) discloses a method and an apparatus for removing film additives, nonpolar polyethylene waxes, and adhering printing inks from used packaging films made of polyethylene, such as shrinking films, bags, and pouches manufactured from the films. The method comprises the steps of: (1) shredding the polyethylene films and washing the shreds with water to remove dirt followed by drying; (2) placing the shreds in a first solvent bath containing boiling solvent and intensively stirring mechanically for about 30 min to rub the shreds on one another and remove the printing inks adhering to the shreds by friction; (3) removing the shreds from the first solvent bath, which is loaded with printing inks, placing the shreds in a second solvent bath so that the shreds are acted on by fresh solvent, and boiling and intensively stirring again for 30 min; (4) placing the shreds in a third solvent bath and boiling and intensively stirring for about 30-60 min; (5) removing the shreds from the third solvent bath and dripping off the solvent; (6) drying the dripped-off shreds under evaporation of solvent residues adhering thereto; and (7) subsequently, melting and shaping the shreds into granulates as reusable raw material.

Preferably, a solvent is used having a boiling temperature that is significantly below the softening temperature of polyethylene. When using such a solvent, it is avoided during the regeneration that the polyethylene shreds soften to a high degree or that they melt to a lesser or higher degree and stick to one another. At the same time, printing ink particles are prevented from irreversibly embedding in the polyethylene shreds, which might lead to dyeing of the recycling product. Furthermore, advantageously, a solvent is used having a density that is lower than the density of the shreds to be regenerated. In this way, the polyethylene shreds are prevented from floating up. Because of their higher specific weight, the shreds sink and are in this way subjected more intensively to mutual friction for rubbing off the printing inks adhering thereto. Particularly, suitable solvents are low-boiling acetic acid esters such as methyl acetate, ethyl acetate, and isopropyl acetate or also alcohols such as ethanol. In this connection, the esters have advantages over ethanol only with respect to their power of extracting film ingredients.

The shreds treated under heat with an organic solvent, following mechanical separation of the solvent, still contain about 50–60 wt% solvent, for example, in the case of ethyl acetate. The solvent can be found both on the surfaces of the shreds and diffused into the interior of the shreds. The surfaces of the shreds contain also residues of nitrocellulose, the preferred vehicle for flexographic printing inks. Such residual amounts of nitrocellulose, even though low, lead to carbonization during regranulation and, thus, to black spots in the recycled film (1994, **EP0602658** A1, NORDENIA VERPACKUNG GMBH). Further, the solvent is contaminated with water, which makes the process considerably more expensive. In addition, the color pigments contained in the film chips are not easily removed (2002, **WO02100932** A1, DER GRUENE PUNKT DUALES SYST).

EP0602658 A1 (1994, NORDENIA VERPACKUNG) discloses a method for the removal of solvent and/or nitrocellulose residues from precleaned polyolefin, particularly from precleaned polyethylene recycled shreds comprising the steps of: (1) mixing the polyolefin shreds with washing water in a weight ratio of 1/9 to 1/10; (2) removing the solvent, preferably ethyl acetate, by heating the water to a temperature above the boiling temperature of the solvent (77 °C), preferably 85–90 °C; (3) washing the nitrocellulose residues from each surface of the polyolefin shreds; (4) using the washing water for precipitating nitrocellulose from the solvent; and (5) collecting solvent in the form of vapors during washing and passing said vapors into a solvent tank and using the collected solvent as circulation solvent.

The disadvantage of this method is the resulting three-phase mixture of solvent, water, and nitrocellulose, which again must be separated. Also, the rinse water must be cleaned with ultrafine filters, which increases the total cost (2002, **WO02100932** A1, DER GRUENE PUNKT DUALES SYST).

WO2013144400 A1 (2013, UNIV ALICANTE) discloses a method using a number of devices for removing ink printed on a plastic film (see Fig. 7.3). The method comprises the following steps:

- conditioning the input printed material in a plunger obtaining a film free of impurities;
- 2) grinding the film free of impurities in a grinder;



Figure 7.3 Diagram of the method and the devices used for removing ink from the printed film (2013, **WO2013144400** A1, UNIV ALICANTE). 1, Conditioning the film; 2, Grinding the film; 3, Removing ink from the film; 4, Washing the film; 5, Recovering the cleaning solution; 6, Recovering the pigment; 7, Drying the film; 101, Plunger; 102, Blade grinder; 103, Cleaning system; 104, Centrifuge; 105, Ink thermal treatment reactor; and 106, Briquette machine

- 3) removing ink from the film in a cleaning system with a cleaning solution consisting of surfactants in water at basic pH, where a cleaning tank stirred with vanes generates a treated plastic film containing part of that cleaning solution and the dispersed ink residues, and in addition, the cleaning solution together with the ink removed from the film;
- washing the treated plastic film in the preceding cleaning system where at least two washing tanks obtain a clean film free of ink and cleaning solution residues;
- 5) recovering the cleaning solution in a centrifuge;
- 6) recovering the pigment in a thermal treatment reactor; and
- 7) drying the film for obtaining a ground film free of ink and cleaning solution in a drying element.

The input printed material can be polyethylene, polypropylene, polyester, or polyamide. The cleaning solution contains hexadecyltrimethylammonium bromide, dodecyltrimethylammonium bromide, or dodecyl sulfate as surfactants.

7.3 Selective Dissolution

In a selective dissolution process, the solvent and process conditions are selected in such a way that only the targeted plastic is dissolved, so that all the other composite components can be removed from the solution by means of the known solid/liquid separation techniques (filters, centrifuges, decanters), before the polymer is isolated again from the solution and processed further to form a new plastic (2010, **DE102008056311** A1, APK ALUMINIUM UND KUNSTSTOFFE).

Selective dissolution—based processes in organic solvents have been used to separate commingled and multilayer postconsumer plastic packaging products, which usually are mixtures of polyolefins, such as polyethylenes, with other polymers. Solvent-based recycling is selective for polyolefins and generates pure and high-quality, recovered polymers from mixed postconsumer waste.

The main advantages of the dissolution-based method in organic solvents are as follows: the input consisting of a heterogeneous mixture of multilayer and nonmultilayer packaging material does not have to run through a complex sorting process, and the precipitated polymer is expected to be of very high quality.

The main disadvantages of the dissolution-based method are as follows: the energy-intensive drying of the polymer and the fact that all polymer components that do not dissolve remain as a residue of little value [5].

An overview of the solvents and acids suitable to dissolve the most common polymers used for the production of flexible packaging is given in Table 7.4.

US5286424 A (1994, MOBIL OIL CORP) discloses a method for the recycling of biaxially oriented polypropylene (BOPP) film, coated with a chlorine-containing polymer, such as poly(vinylidene chloride) (PVDC), and having a primer, such as polyethyleneimine, there between. First, a caustic solution is formulated containing from about 0.1 to about 50 wt % of a caustic compound, such as potassium hydroxide, calcium hydroxide, and sodium hydroxide, and from about 0.05 to about 1.0 wt% of a wetting agent, such as sodium lauryl sulfate. The formulated caustic solution is heated to a temperature from about 25 to about 140°C. Pieces of BOPP film are soaked in the heated caustic solution until the PVDC is separated from the BOPP film. After separating the BOPP film from the PVDC, the BOPP material is reprocessed into desired product by extrusion, molding, or other product-forming process.

US4031039 A (1977, MITSUBISHI HEAVY IND LTD) discloses a method for treating waste of plastic laminates by fractionating the waste

Table 7.4 Solvents and Acids Suitable to Dissolve Polymers Used in

 Flexible Plastic Packaging [6]

| Polymer/Coating/Adhesive | Solvent/Acid |
|---------------------------------------|--|
| Polyethylene | Boiling p-xylene, boiling toluene, boiling dimethyl sulfoxide |
| Polypropylene | Boiling toluene, boiling dimethyl sulfoxide |
| Ethylene vinyl alcohol (EVOH) | Boiling N,N-dimethylformamide, hot concentrated sulfuric acid (turns black) |
| Ethylene vinyl acetate (EVA) | Toluene |
| Polyacrylates | Boiling xylene, toluene, methylene chloride, acetone, ethyl acetate |
| Poly(vinylidene chloride) (PVDC) | Boiling xylene, boiling N,N- dimethylacetamide, boiling cycloheptanone, di-n-butyl sulfoxide |
| Polyamide (PA) | Hot concentrated formic acid (≥95%), hydrochloric acid (37%), hot concentrated sulfuric acid (96%), boiling N,N- dimethylformamide |
| Poly(ethylene terephthalate) (PET) | Boiling N,N-dimethylformamide (swells), hot concentrated sulfuric acid |
| Polyurethane | Formic acid, methylene chloride (swells), acetone (swells), ethyl acetate (swells) |

consisting essentially of polyolefins, polystyrene, PVC, thermosetting polymers, and natural polymers (e.g., pulp, paper, and cellophane), taking advantage of their dissimilar solubilities in different organic solvents. The method comprises the steps of bringing the mixture into contact with o-xylene, p-xylene, or m-xylene, the isomers being used either singly or in a combination of two or more, at a temperature of $5-50^{\circ}$ C to dissolve and fractionate the polystyrene, and then at a temperature of $90-150^{\circ}$ C to

dissolve and fractionate the polyolefins such as polyethylenes and polypropylenes, and finally dissolving and fractionating the PVC by heating the remainder by use of at least one solvent selected from the group consisting of tetrahydrofuran, cyclohexanone, dioxane, and methyl ethyl ketone, at a temperature of $5-60^{\circ}$ C, whereby the waste mixture is fractionated into polyolefins, polystyrene, PVC, and thermosetting and natural polymers.

Example: 100 g of plastic waste of a flexible laminated film composed of cellophane² and polyethylene fractured in size of less than 50 mm and 1 l of industrial xylene were placed in a separable flask having a content volume of 2 l equipped with a thermometer, a cooler, and a stirrer. Under stirring, the materials were heated to $120-130^{\circ}$ C in an oil bath thereby to dissolve polyethylene. Then, the dissolved material and undissolved material were separated by use of a wire screen, and cellophane remaining on the wire screen was freed from solvent by a vacuum drier. The other solution was cooled to room temperature to phase separate xylene and polyethylene completely. The separated polyethylene was filtered under reduced pressure by a Buchner funnel and then freed from solvent by a vacuum drier. The amounts of cellophane and polyethylene recovered were 40 and 60 g, respectively. Cellophane could not be detected in the recovered polyethylene.

The aforementioned solvents are either aromatic or flammable low boiling (b.pt. $< 115^{\circ}$ C) and do not show very high electrical conductivities and are hazardous due to the risk of electrostatic charging and/or explosion. Thus, these organic solvent—based techniques require strict and expensive safety measurements to protect human health and environment. Another disadvantage is the low selectivity of the disclosed solvents for the target polyolefins that make preextraction necessary. A further disadvantage is that the residual solvent traces, which are foreign substances for virgin polyolefin qualities, have a negative impact on the applicability of the recovered polymer (2018, **EP3305839** A1, FRAUNHOFER GES FORSCHUNG).

Although there are efforts to preextract nonpolyolefins or to use more selective solvents or solvent mixtures, there are still traces of codissolved nonpolyolefins, which will be concentrated (together with the target polymer) during the drying process in which the filtered polymers are separated from the solvent. At locally higher concentrations, the

 $^{^2}$ Cellophane is a thin, flexible, translucent film made of regenerated cellulose. Cellophane is a registered trademark in Europe and elsewhere and a generic term in the United States.

nonpolyolefins are incompatible with the target polymer and result in undesired impurities, such as stickies, crusts, or gel particles, in the recovered polymer, in particular during melt drying and extrusion with high temperature and friction (2018, **EP3305839** A1, FRAUNHOFER GES FORSCHUNG).

Such a melt filtration of target polymer gel after a first solvent separation is known from **WO2011082802** A1 (2011, FRAUNHOFER GES FORSCHUNG). In an embodiment, the method comprises treating a flexible multilayer packaging waste with a swelling agent to swell the target polymer to a polymer gel as the first phase having a polymer content of at least 20 wt% and forming a liquid phase, which is immiscible with the polymer gel and in which the substance to be separated, such as other polymers, is dissolved. The substance is separated from the polymer gel by sedimentation or filtration, using preferably a screen or a split filter with a mesh size of $1-1000 \,\mu$ m. The method requires a low amount of solvent based on the polymer flow rate, is simple to operate and it does not require cleaning of the dissolved polymer at molecular level and also it reduces costs and energy consumption associated with the complex multistage process for the recovery of the solvent and the further treatment of the polymer and the solvent.

WO9103515 A1 (1991, RENSSELAER POLYTECH INST) discloses a method for separating polymers from a physically commingled solid mixture containing at least three polymers by selective dissolution comprising: (1) dissolving at least one first polymer of the mixture in a selected solvent at a first temperature to form a first solution and a first remaining solid component that contains at least two polymers of the mixture, which are insoluble in the selected solvent at the first temperature but soluble in the selected solvent at higher temperatures; (2) separating the first solution from the first remaining solid component (e.g., by filtration); (3) separating the at least one first polymer from the selected solvent of the first solution; (4) dissolving at least one second polymer from the first remaining solid component in the selected solvent at a second temperature to form a second solution and a second remaining solid component that contains at least one third polymer of the mixture that is insoluble in the selected solvent at the second temperature but soluble in the selected solvent at a third higher temperature; (5) separating the second solution from the second remaining solid component; separating the at least one second polymer from the selected solvent of the second solution; dissolving at least one third polymer from the second remaining solid component in the selected solvent at the third higher temperature to form a third solution; and (6) separating the at least one third polymer from the selected solvent of the third solution. Each of the first, second, and third solutions initially contain a solid concentration of polymer of from 5 to about 20 wt% and dissolve at least two of the polymers in the solvent at a single temperature simultaneously, one of the simultaneously dissolved polymers being present at concentrations of less than about 10 wt% of the other one of the simultaneously dissolved polymers, the simultaneously dissolved polymers forming a single-phase solution.

The tested solvents were xylene, tetrahydrofuran, and toluene (see Table 7.5). The method was also tested for multilayer packaging structures. The selective dissolution method will work for bilayer packaging as both polymers will be in contact with the solvent. It will not work, or at least not as well, in multilayer packaging when an inner layer or dispersed phase would normally dissolve at a lower temperature than the outer material. In this case, the entire packaging would dissolve at the higher temperature and a cosolution would result.

WO0077082 A1 (2000, LINDNER WOLFGANG) discloses a method for separating postconsumer plastic material using a starting material that consists of a polyolefin fraction or another plastic material mixture. The

| Polymer | Xylene | Tetrahydrofuran | Toluene |
|---------|--------|-----------------|---------|
| LDPE | 75 | 65 | 50 |
| HDPE | 105 | 160 | 105 |
| PP | 118 | 160 | 105 |
| PS | RT | RT | RT |
| PET | NS | 190 | NS |
| PVC | 138 | RT | NS |

Table 7.5 Dissolution Temperatures of the Six Major Polymers Used inPackaging and Solvents (1991, WO9103515 A1, RENSSELAER POLY-TECH INST)

NS, Not soluble; RT, Room temperature; LDPE, Low-density polyethylene; HDPE, High-density polyethylene; PET, Poly(ethylene terephthalate); PS, Polystyrene; PVC, Poly(vinyl chloride); THF, Tetrahydrofuran. starting material is brought into contact with a solvent, and the temperature of the solution, and preferably also the proportion of solvent to volume of plastic material, is adjusted in such a manner that at least one of the polymer types and preferably several of the polymer types from the plastic material batch dissolve and the solution as a whole has sufficiently low viscosity for the final solid—liquid separation. Finally, at least the single dissolved polymer type is sheared and precipitated from the solution to separate the polymer type from all other components in the solution, including the additional types of polymers contained in the solution. To separate each polymer type, the solution passes through one or multiple precipitation steps. Each precipitation step could include several cooling steps to cool the solution to a transportation temperature at which no polymer will be precipitated and finally, to cool the solution in the next or, as the case may be, last, cooling step, to a precipitation temperature at which each specific polymer type is sheared and precipitated.

A preferred embodiment of the invention is shown in Fig. 7.4. A mixture of polypropylene, LDPE, linear low-density polyethylene (LLDPE), and high-density polyethylene (HDPE) is used as starting material, as shown in step 10. This starting material is put into contact with a solvent, such as petroleum spirits or n-hexane, and is completely dissolved at an elevated temperature, for example, approximately 140 °C, as shown in step 12. Instead of petroleum spirits or n- hexane, decalin or xylene could also be used as a solvent. An advantageous value for the adjustment of the polymer concentration in the solvent is about 20%. Finally, the solution is cleaned of undissolved compounds in one or several steps, using filtration, centrifugion, or other mechanical separation techniques, as shown in step 14. In this particular case, when used plastic packaging material is employed, the insoluble compounds are usually inorganic contaminants, undissolved cellulose parts, PVC, PET or polystyrene packaging materials, paper fibers, nonpolyolefin packaging, inorganic filling, and the like. Following this mechanical cleaning step, the solution consists 99% or more of the solvent and the dissolved polyolefin plastic materials polypropylene, HDPE, LDPE, and LLDPE. Each polymer type is precipitated one after the other from the solution using crystallization under simultaneous shearing action to separate each polymer type and to keep waxes, polymer chain fragments, and as many coloring agents and filling materials as possible in the solution.

When shearing and precipitating, it must be considered that the choice of solvent to be used and the shearing rate will strongly influence the exact precipitation temperature of each polymer type. It should be noted that the precipitation temperatures for the different polymer types must be



Figure 7.4 Schematic diagram showing a sequence of operations of a preferred embodiment of the invention (2000, **WO0077082** A1, LIND-NER WOLFGANG).

sufficiently different to ensure definite separation of the different polymer. In the case of the polyolefin fraction consisting of LDPE, HDPE, and polypropylene, a separation method using crystallization and simultaneous shearing provides a better separation of the plastic fractions into each different component than the selective dissolving method from the abovementioned patent **WO9103515** A1, as can easily be inferred from Table 7.6.

It is clear from the above table that the temperature ranges for dissolving HDPE and polypropylene overlap in the selective dissolving method from **WO9103515** A1 (1991, RENSSELAER POLYTECH INST) so that selective dissolving is virtually impossible. However, the precipitation temperatures for the different polymer types HDPE and **Table 7.6** Dissolution and Precipitation Temperatures of Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), and Polypropylene Used in Packaging (2000, **WO0077082** A1, LINDNER WOLFGANG)

| | Dissolving Temperature in Method according to WO9103515 A1 (1991, RENSSELAER POLYTECH INST) | | | Precipitatio WO0077082 A | n Temperature a 1 (2000, LINDNE | according to R WOLFGANG) |
|----------------------|---|---------|---------|-----------------------------|------------------------------------|-----------------------------|
| | LDPE | HDPE | PP | LDPE | HDPE | PP |
| Petroleum spirits | 70-75 | 96–103 | 100–113 | 67–70 | 95—100 | 78–86 |
| Decalin | 80—90 | 115-130 | 130-140 | 50-60 | 90-100 | 70-80 |
| N-hexane | >100 | >100 | >100 | 70-80 | 100-110 | 80-110 |

polypropylene in the method from the invention **WO0077082** A1 (2000, LINDNER WOLFGANG) differ by approximately 9-10 °C, while the precipitation temperatures for polymer types polypropylene and LDPE using the same solvents would show a difference of approximately 8-9 °C.

EP0543302 A1 (1993, KERSTING JOHANNES) discloses a method for separating aluminum foil from a plastic film, in particular polyethylene film, to enable the recycling of the aluminum. The composite film is placed in a 20% solution of a lower fatty acid $C_nH_{2n+1}(COOH)$, where $n\leq 4$ (e.g., acetic acid, propionic acid, formic acid, butyric acid) and heated at 100 °C for 10–20 min. The method is preferably carried out in a closed vessel to operate the liquid at and/or above its boiling point. After cooling, the detached plastic film is separated from the aluminum foil. Cooling preferably takes 3–4 h and is carried out in a tightly sealed vessel in such a way that a reduced pressure, up to 80% of the natural air pressure, is formed on cooling.

Used films made of polyethylene are shredded and subjected in a solvent bath containing an organic solvent, under intensive motion, for example, through mechanical stirring, to a frictional surface cleaning, and simultaneously to an extraction without dissolving the plastic material. By the extraction, ingredients added to the foils and PE waxes are separated from the shreds and the printing inks are removed especially through the frictional surface cleaning.

Used polyethylene films are shredded and subjected to frictional surface cleaning and simultaneously, without dissolving the plastic, to extraction in a solvent bath containing an organic solvent with intensive movement, for example, by mechanical agitation. The extraction dissolves out added ingredients of the films and PE waxes from the shreds as well as, specifically by the frictional surface cleaning, removs printing inks.

Example: 10 g of a multicolor printed polyethylene–polyamide composite film for cheese packaging was shredded into about $3 \times 3 \text{ cm}^2$ large slices of film, placed in a conventional Soxhlet extraction apparatus and extracted with a normal paraffin fraction (paraffin wax) with an initial boiling point of about 180 °C. In the extraction sleeve remained 5.5 g of polyamide content including the majority of the printing. The resulting green-colored polyethylene solution was mixed with 0.5 g of bleaching earth and 0.5 g of active coal, stirred for 30 min at 120 °C and then filtered at about 100 °C. After cooling of the colorless filtrate to room temperature, the precipitated polyethylene was filtered and largely freed from the solvent by vacuum drying at 50 °C. The remaining solvent odor in the polyethylene powder was removed by treatment with 50 g of acetone at

room temperature and subsequent removal of the acetone by vacuum drying at 20 $^{\circ}\rm C$ resulting in an odorless product of pure white color.

According to **WO2018109147** A2 (2018, SAPERATEC GMBH), the industrial feasibility of the above method is questionable, as the whole waste material in the form of aluminum foil and plastic layers together with the solution has to be heated and cooled for every charging cycle. This can be difficult to implement fast enough with large vessels and requires vast amounts of energy.

EP0644230 A1 (1995, VAW VER ALUMINIUM WERKE AG) discloses a method for the extraction of polyolefins, especially polyethylenes, from a composite packaging using organic solvents. The solvents used are cycloalkanes (e.g., cyclohexane), C₉ to C₁₆ n-alkanes and C₁₀-C₂₅ iso-alkanes, or their mixture. After the insoluble components have been separated off, the polyolefin solution and an aqueous surfactant solution are dispersed in one another. The obtained dispersion comprising precipitated polyolefin, an aqueous phase and an organic phase is then separated into its constituents in a manner known per se. At a temperature between 30 and 60° C, a polyolefin concentration of 5–30 wt%, and a surfactant concentration of 0.025 wt%, polyolefin particles of a size of 2–8 mm are obtained. The precipitation of the polyolefin is nearly quantitative, and the particles have a very smooth surface. A further advantage of the method is that the number of washing steps, and also the costs and time expenditure, can be reduced.

EP0849312 A1 (1998, PARAFFINWERK WEBAU GMBH) discloses a method for the production of impurity-free, colorless, and odorless polyolefin-containing plastic packaging polyolefin from waste. comprising: (1) extraction of the plastic packaging waste with a hydrocarbon fraction in the petrol or diesel fuel range with a boiling point above 90 °C, by heating to a temperature between 90 °C and the boiling range of the hydrocarbon; (2) separation of the hot primary polyolefin solution from the extraction residue and treatment of the solution by intensive contact with active earth and/or active carbon and then removing the earth and/or carbon with the adsorbed impurities; and 3) cooling to below 70 °C and isolating the crystallized polyolefin. The invention is claimed to be economically feasible on an industrial scale due to its simple procedure and inexpensive feedstocks.

WO02100932 A1 (2002, DER GRUENE PUNKT DUALES SYST) discloses a method for the recovery of LDPE from used packaging films comprising the following steps: (1) washing the film material in a first organic solvent, wherein a suspension is formed and printing inks adhering to the surface of the film material are washed off; (2) dissolving

the film in a second organic solvent and extracting low molecular weight components from the film; (3) dissolving selectively in at least one third organic solvent; (4) precipitating of at least one disruptive polymer from the solution by applying shearing forces to said solution; and (5) recovering the LDPE from the remaining polymer solution. The starting material can be ground film arising from dry or wet treatment. If the ground film arises from dry treatment, the step wherein the film material is washed in a first organic solvent, resulting in a suspension, and printing ink adhering to the surface is washed, is performed at an earlier stage. The organic solvents used for suspension washing, extraction, and selective solution can be the same or different; preferably, the same solvent is used for extraction and selective solution, i.e., commercial hexane.

KR100361735 B1 (2002, KOREA IND TECH INST) discloses a method for separating polyethylene, polypropylene, PET, and aluminum from a multilayer packaging film waste comprising the steps of: (1) introducing the multilayer packaging film waste to a reactor and treating it with an organic solvent; (2) separating the different polymers of the multilayer film waste on the basis of their different solubilities in the organic solvent at a temperature range of 60–135 °C; (3) adding an alkali aqueous solution or an acid aqueous solution (e.g., HCl, H₂SO₄ or H₂NO₃) to the organic solution and dissolving aluminum by heating as needed to obtain a solution; and (4) separating and recovering the polymers and aluminum from the discharged material and the residue in the reactor. The organic solvent is selected from hydrocarbons, halogenated hydrocarbons, esters, and ketones. In an embodiment, a multilayer packaging film made of LDPE, polypropylene, PET, and aluminum is heated at the temperature range of 75-95 °C for 30 min in xylene to dissolve LDPE. After the dissolved LDPE passed through a mesh box, the remaining material is heated at the temperature range of 115-135 °C for 30 min to dissolve the polypropylene. The undissolved residue consisting of PET and aluminum is treated with an aqueous solution of NaOH for 5 min at room temperature (20 °C) to remove the aluminum from the residue; see also EP1683829 A1 (2006, KOREA IND TECH INST).

EP3305839 A1 (2018, FRAUNHOFER GES FORSCHUNG) discloses a method for recycling polyolefin containing waste by using a solvent with a specific Hansen parameter and contacting this mixture with a liquid filtration aid before separating the polyolefin from the mixture. The Hansen parameter (δ H) is an acknowledged parameter that characterizes the solubility of a compound [7]. The recycling method comprises the following steps:

- 1) mixing the polyolefin containing waste with a solvent having a Hansen parameter δH from 0.0 to 3.0 MPa^{1/2};
- 2) contacting this mixture with a liquid filtration aid having a Hansen parameter $\delta H > 4.0 \text{ MPa}^{1/2}$; and
- 3) separating the polyolefin from the mixture.

The polyolefin containing waste is selected from the group consisting of Green Dot collection waste, industrial waste, household-waste, bulky waste, and especially postuse flexible multilayer film packaging waste. The solvent is selected from the group consisting of hydrocarbons, preferably aliphatic hydrocarbon, more preferably cycloaliphatic, linear, or branched hydrocarbon, in particular cycloaliphatic, linear, or branched hydrocarbons with 5-18 carbon atoms and mixtures of those. The liquid filtration aid contains at least one fluid with a Hansen parameter δH from 4.0 to 38.0 MPa^{1/2}, preferably from 10.0 to 35.0 MPa^{1/2}, and more preferably from 20.0 to 33.0 MPa^{1/2} that preferably forms a miscibility gap with the solvent and more preferably shows complete immiscibility with the solvent, in particular at least one fluid selected from the group consisting of mono-/polyhydroxy hydrocarbons with 2-12 carbon atoms, preferably with 3-5 carbon atoms, 3-pentanol, 1,2-propanediol, 1,3-1.3-butanediol. 1,4-butanediol, propanediol. 1,2-butanediol, 1.2pentanediol, 1,3-pentanediol, 1,4-pentanediol, 1,5-pentanediol, 1,2,3propanetriol, 1,2,4-butanetriol, 1,2,3-butanetriol, 2-(hydroxymethyl)-1,3propanediol, 1,3,5-pentanetriol, 2,3,4-pentanetriol, 2-(hydroxymethyl)-2-methyl-propanediol, 2-propene-1-ol, propene-2-ol, 3-butene-1-ol, 2buten-1-ol, 3-buten-2-ol, 1-butene-2-ol, (E)-2-buten-1-ol, (Z)-2-buten-1-2-methyl-2-propen-1-ol, 2-methyl-prop-1-en-1-ol, ol. cvclopropylcarbinol, cyclobutanol, 1-penten-3-ol, 3-methyl-3-buten-1-ol, (Z)-2-penten-1-ol, 3-methyl-2-buten-1-ol, 2-methyl-3-buten-2-ol, (E)-2penten-1-ol, 2-methyl-2-buten-1-ol, 4-penten-1-ol, 3-penten-2-ol, 2penten-1-ol, 4-penten-2-ol, (Z)-2-penten-1-ol, (Z)-3-penten-1-ol, 3methyl-3-buten-2-ol, 3-penten-1-ol, (E)-2-penten-1-ol, (E)- 3-penten-1ol, 2-methyl-3-buten-1-ol, 2-penten-1-ol, pent-2-en-1-ol, 2-methyl-(E)-2-butenol, trans-3-penten-2-ol, 1-penten-3-ol, (Z)-pent-3-en-2-ol, (E)pent-3-en-2-ol, prop-1-en-1,2-dimethyl-1-ol, 1-ethylcyclopropanol, 1methylcyclopropane-methanol, cyclopentanol, cyclobutanemethanol, cyclopropylmethylcarbinol, 1,2-cyclopentanediol, and mixtures of those.

The aforementioned patent forms the basis for the development by Fraunhofer Institute for Process Engineering and Packaging IVV in collaboration with CreaCycle GmbH of a technology called CreaSolv Process, which allows the recovery of high-quality plastic recyclates from plastic waste [8]. The technology can be applied to waste plastics from the production of laminates and composites. Unilever implements the CreaSolv Process into its supply chain for the recycling of plastic sachet waste [9].

WO2016209094 A (2016, 23 RS CORAS SP Z O O) discloses a method outlined in Fig. 7.5 for the separation of components from composite packaging materials including polymer film, aluminum, and/or cellulose comprising the following steps: (1) cutting the waste packaging materials into 10×10 cm or smaller pieces; (2) extracting the polymer fraction using xylene or other organic solvents such as benzene, toluene,



Figure 7.5 Flowchart of the method for the separation of components from composite packaging materials (2016, **WO2016209094** A, 23 RS CORAS SP Z O O).

cumene, ethylbenzene, naphthalene, chlorobenzene, dichlorobenzene, and bromotoluene; (3) separating the insoluble ingredients by fragmenting them in an agitator; (4) forming a slurry from the aluminum and cellulose particles, wherein said slurry has a higher density than the cellulose density and lower than the aluminum density; (5) dosing said slurry into a separator, while evaporating the polymer solutions to recover the solvent; and (6) separating the initial polymer component from the processed packaging waste. According to the invention, the used solvents may be recycled, and thanks to correct design of the entire process, maximum heat recuperation and minimization of operation costs is ensured, thus making the method profitable.

DSM and APK cooperate on recycling multilayer food packaging films using APK's Newcycling[®] process, a solvent-based technique to separate and recover the different polymer types in high-quality regranulates with properties close to virgin polymers (see Fig. 7.6). With conventional recycling systems that is not possible. Newcycling[®] allows the pelletized recyclates to be used in demanding applications, such as flexible packaging, again. The focus is on polyethylene, polypropylene, and polyamide, but also PET, polystyrene, PLA, and aluminum, could be technically recovered. APK is building a plant in Merseburg (DE) for recycling multilayer polyethylene/polyamide 6 (PE/PA6) packaging waste from postindustrial origin, using the Newcycling[®] process, which is planned to start up in 2019 [11].

The APK's technology is based on the following patents:

DE102016015198 A1 (2018, APK AG) discloses a solvent (L) and a method of dissolving a plastic (K) present in and/or on a solid (F) within a waste suspension (S) (see Fig. 7.7). The method involves heating or superheating the suspension (S) within a gastight system to a dissolving temperature (T1) within a temperature range of ± 5 °C around the boiling temperature (T2) of the solvent (L). The solvent is selected from a group consisting of alkanes, isooctane, or cycloalkanes, such as methylcyclohexane. Cyclohexanes are particularly suitable for dissolving polyethylene.

DE102016015199 A1 (2018, APK AG), which is a modification of the above patent, discloses a solvent (L) and a method of dissolving at least two plastics (K1, K2) present in and/or on a solid (F) within a waste suspension (S) (see Fig. 7.8). The solvent (L) has a temperature-dependent dissolving effect on the two plastics. The suspension (S) is heated in several stages to different dissolving temperatures (T1, T2), wherein in a first stage at a first dissolving temperature (T1), the first plastic (K1) is dissolved, and in a second stage at a second dissolving temperature (T2),



Figure 7.6 Newcycling® process overview, e.g., for polyethylene/polyamide (PE/PA) [10].



Figure 7.7 Schematic diagram of the method of a waste separation plant (2018, **DE102016015198** A1, APK AG). F, Solid; K, Plastic; L, Solvent; P, Polymer solution (=K + L); T, Inert gas; S, Suspension (=F + K + L); T1, Dissolving temperature; T2, Boiling temperature of solvent; 1, Waste separation plant; 2, Dissolving station; 3, Inerting device; 4, Separation station; 5, Inlet; 7, Outlet; 8, Outflow; 9, Sluice; 10, Solvent separation; 11, Outflow; and 12, Return

the second plastic (K2) is dissolved. In the preferred composition, the plastic K1 is polyethylene, and the plastic K2 is polypropylene. The dissolving temperature, T1, is 80-100 °C. The dissolving temperature, T2, is 120-180 °C. The difference between the dissolving temperature T1 and the dissolving temperature T2 is 20 °C.

DE102016015197 A1 (2018, APK AG) discloses a centrifuge for separating at least one solid (F) from a waste material suspension (S), the suspension comprising the solid (F), and a polymer solution (P) with at least one solvent (L) and at least one plastic (K) dissolved therein (see Fig. 7.9). The centrifuge has a housing (3) with a rotating insert (4) mounted therein and is characterized by a design of the housing (3), which encompasses the rotating insert (4) such that the suspension (S) can be gas tightly centrifuged inside the housing (3). The housing is provided with an inlet (10) for introducing the suspension and outlets (11, 12) for



Figure 7.8 Schematic diagram of the method of dissolving at least two plastics from solid within waste suspension (2018,а а DE102016015199 A1, APK AG). 1, Waste separation plant; 2, First dissolving station; 3, Separation station; 4, Inlet; 5, Outlet; 6, Second dissolving station; 7, Solid processing; F, Solid; K1, First plastic; K2, Second plastic; L, Solvent; S, Suspension; T1, First dissolving temperature; T2, Second dissolving temperature; ST, Boiling temperature; ΔT , Temperature difference

discharging the polymer solution (P) and the centrifuged solid (F). The plastic can go into solution within a very short time, while the solids due to their inertia by means of centrifuging of the polymer solution are removed in a controlled manner. The consistency of the polymer solution can be adjusted so that it has the lowest possible viscosity. In this way, unlike its separation by pure heating, the dissolved polymer can be separated without appreciable resistance by the remaining centrifuging material. The gastight construction of the centrifuge enables safe handling even of flammable solvents.

WO2016077904 A1 (2016, OLIVEIRA JUAREZ SOUZA DE) discloses a process for the recycling of aluminized and plastic packaging, cartooned or not, by means of an apparatus for extracting and separating the constituents of polyethylene or polypropylene film with aluminum by dissolving the polymer in a compatible primary solvent, at a temperature



Figure 7.9 Waste separation apparatus with a gastight centrifuge for separating solid from a waste suspension (2018, **DE102016015197** A1, APK AG). A, Cross section; F, Solid; K, Centrifuged plastic; L, Solvent; P, Polymer solution; S, Suspension; T, Inert gas; x, Axis of rotation; 1, Waste separation apparatus; 2, Centrifuge; 3, Housing; 4, Rotating insert; 5, Hollow cylindrical surface; 6, Centrifuge compartment; 7, Shaft; 8, Location; 9, Sealing member; 10, Inlet; 11, First outlet; 12, Second outlet; 13, Container; 14, Front opening; 15, First container; 16, Second container; 17, Inserting device; 18, Connecting line; 19, Rear wall; and 20, Through opening

below the polymer softening temperature and under pressure followed by insolubilization via reduction of temperature, separation of the solvent from the polymer, and finally filtration and reuse of the solvent in the step of dissolution. The process comprises at least 11 steps. The dissolving solvent is selected from hexane, kerosene, or mineral oil. In the case of a packaging made only with nonpaper aluminized polymer films containing polypropylene and polyethylene, and if the process is conducted at 100 °C, then, only the polyethylene is dissolved, while the polypropylene remains insoluble. Further, the hot solution is filtered and the undissolved solid components, polypropylene and aluminum are washed with petroleum ether and subsequently with ethanol, in an aluminum crusher. The aluminum is crushed leaving the polypropylene in a larger size, thus allowing easy separation by sieve filtration.

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