Results from Prior NSF Support

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Title: Exploratory Study on Low Temperature Synthesis of Nanostructured Particles by a Novel Aero-Sol-Gel Process.

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Overview.

The mission of this 1-year research initiation project was to demonstrate the feasibility of a new aero-sol-gel (*ASG*) process for the synthesis of nanoparticles by simultaneous condensation and reaction of reactant vapor streams in an aerosol reactor. The process involves formation of reactant vapors at atmospheric pressure and co-condensation of reactant vapor streams in a mixing/reaction zone at *room temperature*. The project focused on the development of an experimental base using simple hydrolysis/condensation reactions. Most work under this grant focused on the production of micro- and mesoporous silica from tetraethylorthosilcate (TEOS) and acidified water [1-3]. These fractal, nano-powders bear structural resemblance to expensive aerogel nano-powders. Specific surface areas of *ASG* silicas approach 700 m²/g by BET analysis of N₂ adsorption data! Manipulation of processing conditions allows for control over structure in an inexpensive, continuous process operating at room temperature and ambient pressure.

The ASG reactor produces primary particles less than 1.5 nm in diameter (smaller than the resolution limit of small-angle x-ray scattering, as discussed below) aggregated into classical diffusion-limited-aggregates of approximately 30 nm with a mass-fractal dimension close to 2.5 ("Witten-Sanders" aggregates [4-7]). A continuous process for the production of such aggregates has long been sought, for example, in the hope of developing catalyst supports with the maximum possible surface area *or* for high contact-area fillers for elastomers. Current continuous processes used in industry (e.g. flame reactors, precipitation and gelation) are not capable of such morphologies since the primary particles are an order of magnitude larger. Figure 1, below, shows a schematic of the ASG reactor.



Figure 1. Schematic of the Aero-Sol-Gel Process. This is a flameless (room temperature) process for production of powders with extremely high specific surface areas with tunable nano-structure and reduced production costs over pyrolytic routes [1-3].

In the ASG reactor, hydrolysis/condensation reactants are converted to a vapor phase by mild heating and carried to the reactor using dry nitrogen at a controlled rate, typically 45 cm³/sec. The reactants flow through cylindrical conduits where steady laminar flow develops. In the mixing zone aerosol droplets form and immediately react to form nano-structured powders which are collected down stream, presently in an inverted funnel connected to a controlled vacuum. Due to rapid transport in aerosol droplets, the reaction byproducts are quickly removed from the powders simultaneous with their formation, driving the reaction and leading to dry nano- to molecular-structured powders at room-temperature. The process is currently capable of producing compoundable amounts, for elastomer reinforcement, of silica powder with uniform nano-structure in a day, about 50 grams. The ASG reactor produces close to mono-disperse pore distributions, Figure 2, in the mesoporous range. Such a distribution is predicted from mass-fractal aggregates of the type shown in Figure 3, top ASG curve [8, 9].



Figure 2. Typical pore-volume-distribution from BJH analysis of nitrogen adsorption data from ASG silica [3].

Mesoporous structure, in *ASG* powders, can be tuned from low-density, mass-fractal aggregates to surface fractal and close to non-porous structures by varying the reactant types and processing parameters, Figure 3. Figure 3 is a SAXS plot of intensity versus reduced scattering



Figure 3. Small-angle x-ray scattering data showing variability in structure from the ASG process. Upper pattern is a mass-fractal, aero-gel like structure, with meso- and micropores, middle pattern displays micro-pores but no mesopores. Lower displays mesopores but no micropores.

angle, $q = 4\pi/\lambda \sin(\theta/2)$, where weak power-law decays, -2.5 and -1.3 in Figure 3, correspond with the dimensional scaling regime of ramified, mass-fractal aggregates, between the primary particle size and the aggregate size. The aggregate dimension is the negative of the power-law slope in this power-law regime. Steep decays, -4 in Figure 3, correspond to surfaces of 3-d objects and the specific surface area can be calculated from such data using Porod's Law. Figure 3 shows three dramatically different structures that can be reproducibly made in the *ASG* reactor.

ASG powders can be controlled in surface chemistry but most silicate powders, produced to date, are hydrophilic containing significant silanol surface functionality. Figure 4 shows IR patterns from as produced powders, annealed at two temperatures and powders which have been subjected to a vacuum in KBr pellets. Organic groups, C-H stretch shown near 1450 cm⁻¹, can be removed by heating or by subjecting the samples to vacuum at room temperature. Elemental analysis shows less than 1% carbon in these samples. A significant band associated with silanol groups is seen near 950 cm⁻¹.



Figure 4. IR Spectra from ASG powders in the TEOS/water/HCl system. Lower two curves from 5% silica in KBr pellets subjected to vacuum for 10 minutes. Top three curves are pure pressed ASG silica not subjected to vacuum. Both series were subjected to purging in a dry inert gas for 30 minutes prior to IR scan. (Bands are assigned following reference [4] p. 584-585.)

One of the main focuses of this project was to demonstrate the reproducibility and degree of control over nano-structured *ASG* powders. In a controlled series of samples the laminar flow arrangement and reactant concentration were varied in the TEOS/water/HCl system [3]. In some ways this work mimicked the work of Pratsinis in studying laminar flow arrangements in laminar flow pyrolytic reactors [3, 10-13]. Figure 5 shows the effect of laminar flow arrangement (A, B, C) on mesopore structure in SAXS patterns (low-q corresponds to mesoporous structure) also varying the TEOS concentration. High-temperature for the TEOS feed bubbler leads to high concentration in the reaction zone. In this series, a reproducible transition from mesoporous, mass-fractal to surface-fractal structure occurs with laminar flow arrangement or with reactant concentration (TEOS temperature), seen in SAXS at low-q. A corresponding step change in specific surface area of about 100 m²/g is seen in these powder series under conditions where the mass- to surface-fractal transition is observed in SAXS. Steep decays in scattered intensity, in Figure 5, correspond with surface-fractal structures, shallow decays with mass-fractal mesoporous structures. The surface-fractal morphologies display lower specific surface area.

The mass-fractal dimensions observed in ASG powders are well described by particle growth simulations based on diffusion-limited, monomer-cluster aggregation at early stages of

growth (power-law decays of -2.5 in SAXS), with a transition to reaction-limited, monomercluster growth when surface-fractal scaling is observed [3, 4-7]. These transitions in growth mechanisms have been directly associated with transport effects in the process [3]. We have manipulated the arrangement of the laminar flow streams in Figure 1 to control these structural effects [3], A, B, and C of Figure 5, as discussed in the Proposed Work section below.



Figure 5. a) Variability in structure with TEOS temperature and laminar flow arrangement. Reactors A, B and C for water bubbler temperature 75 °C carrier N_2 at 45 cm³/sec for each reactant in Figure 1. b) Cartoon of mass- and surface-fractal aggregates. For ASG powders, primary spheres (circles above) are themselves microporous, mass-fractal aggregates with $d_f = 2.4$ (not shown). Large circle in (b) is the limit of N_2 penetration in the surface-fractal aggregate.

We have recently begun studies on the use of ASG titania and mixed titania/organic systems as organically compatibilized UV absorbers for incorporation in organic polymers, paints and other products. Figure 6 shows the UV absorption spectrum from an ASG nano-structured titania powder which displays significant absorption in the UV range. This is further discussed in the Proposed Work section.



Figure 6. UV absorption spectrum from an ASG titania powder from titanium isopropoxide/HCl/Water ASG process.

We have also been active, under this grant, in comparison of these nano-powders with traditional industrial powders from pyrolytic and precipitation routes [10] using unique scattering facilities that were transferred to this grant from Sandia National Laboratories (\$306,000 original cost). We have, in the past, developed scattering theories capable of quantitatively describing nano-structured, mass fractal morphologies [14-18] over wide size-ranges using combined light

and x-ray scattering data. In addition to this work we have begun collaborative efforts with Goodyear and PPG aimed at development of *ASG* powders as tunable fillers for organic elastomers and with P&G in development of organically-dispersible, UV absorbers using nanopowder titania, which are discussed in this proposal.

Development of Human Resources.

This 1-year project has resulted in one PhD, Jingyu Hyeon-Lee who will complete her work in this area in August of 1998 (MS U. Illinois 1996). Hyeon-Lee will return to her native Korea for a post-doctoral position at Seoul National University in the fall. Additionally, one undergraduate student has worked on this project and assisted Hyeon-Lee, Douglas Kohls. Doug graduated with a BS in Materials Science and Engineering in May of 1998 and will begin graduate studies working on this project in the fall. He is performing an internship this summer at Procter & Gamble's Central Research Laboratory (Miami Valley Laboratories) on the development of titania based UV absorbers using the *ASG* technology. At P&G he is under the direction of Michael Satkowski who has also acted as an industrial mentor to Hyeon-Lee during her PhD work. This project has attracted industrial interest from GE Silicones, PPG Industries, Cabot as well as Goodyear with whom we have close contacts.

Publications/Presentations/Service.

3 papers [1-3] have resulted from the ASG reactor and 1 paper [10] under this grant on comparison of nano-structure in pyrolytic and ASG powders. The 1-year project still has 3 months remaining where we plan to continue development of an experimental basis for control of the ASG process. A paper on nano-structure titania synthesis is in preparation.

We have widely disseminated the results of this work in talks at national meetings of the AIChE, American Physical Society, American Crystallographic Society, 7'th Annual ISCMS at Northwestern, American Ceramics Society, Aerosol Society (poster) and Materials Research Society. I have been invited to present this work at the Joint ESF-NSF Symposium on Aerosols for Nanostructured Materials and Devices meeting in Edinburgh, Scotland under separate NSF funding. We have also been active in service within the nano-particle field, partly through this grant's support, in organizing a 3-day symposium for MRS on Industrial Nano-Powders (S98P) and chairing a session at the AIChE's Fall Meeting in Miami. I am editor of the Symposium Proceedings book which resulted from the MRS symposium [19]. I am also an officer in the American Crystallographic Society where I focus on nano-powder characterization using small-angle light and x-ray scattering. I have given invited lectures at Goodyear and the University of Akron on the ASG process and it's application to elastomer reinforcement, as well as having presented the work to Cabot's Cabosil Division, Degussa and GE Silicones. I have given a departmental seminar in the Chemical Engineering Department at UC on this topic also.

Other Related Work.

Prior to our efforts in the ASG reactor we have worked extensively in hydrolysis/condensation reactions to produce polymer modified ceramic insulation materials [20-22], in ceramic reinforced elastomers [23-29] and in silica aero- and xerogels [30-36]. Much of this work focused on polydimethylsiloxane elastomers modified with various silica alkoxide systems bv hydrolysis/condensation reactions. UC efforts in this area have been funded by Sandia National Laboratories, Dow Chemical, Dow Corning and Armstrong Corporation. These efforts partially supported the graduate student who worked on the ASG project, Hyeon-Lee, in the initial stages of her PhD, as well as one MS student who now works at Procter & Gamble's Miami Valley We have been active in the study of zeolite reinforced elastomers [37-40], Laboratories. Resorcinol/Formaldehyde (RF) aerogels [41], discussed below, as well as in characterization of nano-structured materials from zirconia systems in collaboration with workers at ORNL [42, 43] and in polymer dispersed colloidal crystals with workers at Oklahoma State University [44]. Additionally, we have extensive experience with nano-porous polymer foams from polyolefins and other synthetic polymers [45, 46]. I have develop scattering theory to describe mass-fractal structures such as those exhibited by ASG powders as mentioned above [14-18].

Career Development Plan

Objective of Proposal

The aim of this proposal is the development of new processes for the controlled production of nano-structured powders and application of these Aero-Sol-Gel (*ASG*) powders in two targeted applications: 1) Development of chemically and structurally tuned silica for reinforcement of organic elastomers. 2) Development of organically modified titania for UV absorption as a potential polymer additive. The project will rely on close contacts at Procter & Gamble, PPG Industries and Goodyear in this effort. Graduate and undergraduate students will work in a mentoring relationship with industrial partners. This cooperative education plan will take advantage of the College of Engineering's undergraduate coop program which is the oldest in the US. A new course on the synthesis, characterization and use of nano-structured powders is planned to parallel our research efforts and a related web-page "book" will be developed.

Present State of Knowledge in the Field

Previously, we reported a new reactor for the production of silica and titania oxide powders with nano-scale structure and high specific surface areas (100 to 700 m^2/g) [1-3]. This aero-sol-gel reactor (*ASG*) is similar in design to laminar flow pyrolytic reactors such as those reported previously by Pratsinis and coworkers [3, 10-13]. The *ASG* reactor differs from these flame reactors first in that there is *no flame* present. Instead, oxide powders are produced by an *ambient temperature and pressure* hydrolysis/condensation chemical reaction that occurs simultaneously with thermal condensation of precursor vapor streams to an aerosol. The precursor vapor streams are fed into a mixing zone from a heated laminar flow assembly which mimics the laminar flow assemblies of Pratsinis mentioned above. Since no flame is present, the assembly is made of low-cost, plastic tubing rather than the high temperature materials needed in flame reactors. Formation of metal oxides at ambient temperatures avoids sintering of primary particles and the associated reduction in specific surface area [4]. Byproduct removal from these powders occurs in a rapid, continuous manner simultaneous with condensation of the precursor streams into a fine aerosol and hydrolysis/condensation reactions, alleviating pore collapse on drying, common to room temperature solution processes [1-4]. Rapid byproduct removal also serves to speed the reaction.

The concept of chemical reactions in aerosols aimed at ceramic oxide production has precedence in the work of Egon Matijevic at Clarkson University [47-49]. Matijevic produced an aerosol stream of alkoxide precursors and humidified the aerosol in a reaction chamber. One aim of Matijevic's efforts was to produce close to monodisperse *sub-micron-scale* particles (0.1 to 1.0 μ m) by process control over the aerosol droplet size [50]. Matijevic's aerosol reactor differs from the *ASG* reactor in that an alkoxide aerosol is formed *prior to* humidification, whereas, in the *ASG* reactor, reactant vapor streams co-condense simultaneously with initiation of the reaction. Much of Matijevic's work involved production of amorphous titania particles which could be transformed into anatase or rutile by annealing in a separate process. Matijevic has also studied mixed oxides [49]. One advantage of Matijevic's aerosol reactor is strict process control over aerosol formation. The control over aerosol droplet size is mimicked in virtually monodisperse powder particle-size.

In the ASG reactor, aerosol formation occurs simultaneous with mixing of reactants and initiation of oxide production. It is believed that this sequence is advantageous for production of aerogel-like nano-structure in ASG powders as discussed below. Several other groups have used the Matijevic aerosol reactor approach with a pre-formed aerosol using different techniques for aerosol formation such as jet nozzles [51-56]. In most cases the specific surface area of oxide particles produced from these pre-formed aerosol streams are less than 100 m²/g. The ASG powders reported here, generally display specific surface areas in the 400 to 700 m²/g range indicating that they may have a distinct structure from processes where a pre-formed aerosol is used. Additionally, the ASG reactor appears to have a lower reaction temperature, close to room temperature, in comparison to the Matijevic-type reactors because the ASG reaction zone is open to ambient air.

In the control series of powders, reported in reference [3], an acid catalyzed (HCl) hydrolysis/condensation reaction of tetraethoxysilicon (TEOS) and water is performed

simultaneous with formation of small aerosol droplets from condensing vapor streams. Two chemical reactions occur, 1) hydrolysis of $Si(OEt)_4$ to $Si(OH)_4$ and 2) condensation of $Si(OH)_4$ to silica nano-powders. In such reactions, hydrolysis of the alkoxide, 1), is accelerated by the Condensation of the resulting $Si(OH)_4$ and partial condensates, presence of acid [4]. $Si(OH)_x(OC_2H_5)_{(4-x)}$, 2), is a slower reaction than hydrolysis under acidic conditions. Nonetheless, in solution reactions, if sufficient acid catalyst is present to fully hydrolyze TEOS to Si(OH), the condensation rate to silica is faster than the transport rate of hydrolyzed TEOS in the solution and the reaction is transport limited, i.e. acid catalyzed hydrolysis/condensation leads to low-dimension, ramified, mass-fractal aggregates [4-7] reflecting transport-limited growth. If insufficient HCl is present, it is likely that partial hydrolysis of TEOS occurs. Partially hydrolyzed TEOS is less likely to condense to silica in growing aggregates since fewer condensable sites are available, -OH sites. It is expected that in partially condensed TEOS the formation of aggregates might exhibit a transition from low- to high-dimension growth, i.e. denser growth, as the degree of TEOS hydrolysis is reduced and the formation mechanism (condensation reaction) changes from transport limited to reaction limited. This is further discussed in reference [3]. This approach can explain the ASG mass- to surface-fractal transition mentioned above and shown in Figure 5.

Comparison of ASG Powders with Other Continuous Process Powders.

ASG powders show unique mesoporous to microporous structures for a continuous process synthesis, reminiscent of supercritically extracted aerogel powders made by a batch process. This can be show by a comparison of small-angle x-ray scattering data from a series of silicas produced by different synthetic routes, Figure 7. In a small-angle x-ray scattering pattern the scattered intensity (arbitrarily scaled in Figure 7) is plotted as a function of the scattering vector, "q", which is a reduced scattering angle (θ), $q = 4\pi/\lambda \sin(\theta/2)$, where λ is the wavelength (here 1.54Å). "q" has units of inverse size and reflects the inverse of a Bragg-size, $d = 2\pi/q$, i.e. large "q" is associated with small size. The data of Figure 7 is typical of pinhole SAXS cameras and covers a size range from about 0.2 nm, at high-q, to about 50 nm, at low-q. This corresponds to the microporous (high-q) to mesoporous (low-q) ranges described in the gas adsorption literature [57]. The cut-off size for micropores is about 2 nm in diameter which corresponds to about q =0.15Å⁻¹ in Figure 7. In pyrolytic silicas, which are non-porous, a steep decay is seen at intermediate-q with a power-law decay of -4 indicating the surface of primary particles following Porod's Law for surface scattering [17], light circles in Figure 7. At lower-q a mass-fractal aggregate regime is observed with a weaker power-law slope, here about -1.8 which corresponds with diffusion-limited-cluster-cluster aggregation (DLCA) [4-7]. For pyrolytic silica, the dilute conditions (aerosol/vapor reactor) and rapid reaction lead to transport control of growth.

Precipitated silica displays a similar Porod regime but a different mass-fractal regime of about -2.1 slope ($d_e = 2.1$) associated with *reaction-limited-cluster-cluster* aggregation (RLCA) [4-7]. In precipitated silica, cluster aggregation is again a major route to aggregate growth but the chemistry is slower leading to reaction-limited growth. The bottom curve in Figure 7 is from an acid-catalyzed silica aerogel powder produced using TEOS and supercritical extraction of CO₂ after solvent exchange [4, 16]. Primary particles are not observed in the q-range available (no powerlaw -4 regime), and the meso- to microporous structure is mass-fractal with a dimension of about 2.5 associated with diffusion-limited-monomer-cluster growth (DLMC) [4-7]. Some ASG powders display scattering curves very similar to that of the supercritically extracted aerogel powders (Reactor A, Figure 7). In other cases a change in growth mechanism is observed as reflected by a transition in slope in the mesoporous range [3] shown in Figure 7, upper of two ASG curves. Both the ASG powders and the supercritically extracted aerogel display high specific surface areas by nitrogen adsorption using BET analysis, circa 500 to 700 m²/g. The pyrolytic and precipitated silicas have surface areas in the 100 m²/g range that can be directly associated with the Porod regime and primary particle knee (following Guinier's Law) observed in Figure 2. At highest-q, for precipitated silica, which is produce in a solution process by acidification of sodium silicate, a deviation from the Porod regime can be seen in Figure 2, which may be related to a microporous structure within the primary particles.



Figure 7. Comparison of scattering from the control series *ASG* silica powders (two black curves), pyrolytic (from S. E. Pratsinis), precipitated (commercial sample), and a supercritically extracted aerogel powder (from Carol Ashley at Sandia National Laboratories). Both pyrolytic and precipitated silicas display a Porod decay, -4 slope at high-q.

Mild ASG Conditions are Amenable with Organic Modification of Powders.

This proposal includes two targeted applications for ASG nanoparticles: 1) Interfacial compatibilization of silica with organic elastomers and 2) Titania UV absorbers with low catalytic reactivity and compatibilized with oils and organic polymers for commercial applications. In both of these applications there is significant advantage to the mild reaction conditions of the ASG process for incorporation of organic components at the surface of ceramic nano-powders.

Hydrolysis/condensation reactions are possible with a number of organic reactants. This route has been taken advantage of in the production of in situ filled polymers, for instance, where hydroxyl terminated polymers such as polydimethylsiloxane are reacted with TEOS or TMOS [20-29, 58-59]. This field was pioneered by Jim Mark at the University of Cincinnati and Garth Wilkes at VPI [58-59] and has received considerable industrial and government attention. Another route to organic incorporation in ceramic nano-materials is through the use of partially substituted silicon and titanium alkoxides (M(OR)_x(R)_y) in hydrolysis/condensation reactions [36, 58-59]. In addition to siloxane elastomers and partially substituted alkoxides, so called *RF-aerogels*, which bear a striking resemblance to silica aerogels, have been produced from resorcinol-formaldehyde (RF) hydrolysis/condensation reactions. Surface areas of 500 to 900 m²/g have been reported for RF-aerogels [41, 60-64], although the low skeletal density of these organic materials skews a direct comparison of these S_y values with those of silica aerogels.

Formation of mixed organic/inorganic nano-structured powders has been inhibited by miscibility issues which potentially could be overcome in the *ASG* reactor. Through manipulation of laminar flow streams and reactant concentrations it may be possible to produce inorganic-based, organic-coated powders as well as mixed oxides. RF, Melamine/formaldehyde and several other hydrolysis/condensation reacting organic systems could be compatible with alkoxide inorganic

synthesis in the *ASG* reactor. A wide range of precursors are possible since the ASG reactor involves forced compatibilization, due to co-condensation of reactant vapors in aerosol micro-droplets and room-temperature reaction conditions.

A brief background on the two technological areas of focus in this proposal are given below.

Research Plan

The research plan of this Career proposal will involve 6 focal areas.

- 1) Optimization and process control of silica formation from TEOS/TMOS, SiCl₄ and Sodium silicate.
- 2) Titania production from titanium butoxide, titanium propoxide, TiCl₄.
- 3) Mixed oxide production from titania and silica systems with the aim of forming silica-coated titania for non-reactive UV absorbing titania as well as titania-coated silica for reactive silica nano-powders for elastomer reinforcement.
- 4) Resorcinol/formaldehyde nano-powder synthesis [41, 60-64], mainly as a research tool for cofeed reactor design.
- 5) Silica/RF ASG powders for elastomer reinforcement with tunable structure.
- 6) Titania/RF ASG powders for UV absorbers, consumer product and polymer incorporation.

Items 1 and 2 are continuations of our efforts, under CTS-97-30535, aimed at the establishment of a solid set of experimental data to understand transport and concentration control of the aero-sol-gel process [1-3, 10]. Continuation of this effort will involve mapping out of parameter space versus nano-structure (Table 1 below). This will assist in building a data base that would lead to an understanding of particle growth in the *ASG* process. A main focus is to broaden the scope of reactants to common industrial precursors such as sodium silicate and SiCl₄ as well as TiCl₄. This expansion of the reactant base is at the suggestion of our industrial collaborators, and is aimed at potential adoption of the *ASG* process in industry. We already have some exposure to these precursors from interaction with Sotiris Pratsinis in the Chemical Engineering Department at UC who uses these precursors in parallel pyrolytic reactors. These industrial precursors are generally more reactive than the alkoxides used previously in the *ASG* reactor. From our experience with two alkoxides, TEOS and TMOS we know that more reactive precursors are generate larger primary particles (figure 3 and reference [1] for example). Several new reactors will be built to accommodate different precursors for controlled studies aimed at the development of an experimental base and process control.

Information concerning fractal dimension from SAXS and TEM will be useful in providing quantitative support for mechanistic models of aggregate and primary particle growth, inferred from the mapping out of parameter space. We also plan to improve particle collection through the addition of a better designed particle collection device. Currently an inverted funnel with a paper filter attached to a controlled vacuum is used. Some effort is planned in the design of a particle collector which will include a heated post reaction chamber ($\approx 100^{\circ}$ C) for assurance of completion of reaction and removal of excess water, and a cyclone or baghouse particle collector.

Reactant	Silica	Na ₂ SiO ₃	(Et O) ₄ Si	(Me O) ₄ Si	(Et O) 4-nR nSi
Туре	Titania	(i-Pr O) ₄ Ti	(Bu O) ₄ Ti		
	RF Systems	RF	Melamine/F	Silica/RF	Titania/RF
Flow Rate	H ₂ O	HCl, NaOH, NH 3	Alkoxide	Overall Reactant/ Extent of Reaction	
Temperature/ Vapor Pressure	"	"	"		
Zonal Temperature	Mixing/ Reacting Zone	Collecting/ Aggregation Zone			
Laminar Flow Arrangement					

Table 1. Important parameters for the Aero-Sol-Gel Process.

Table 1 summarizes the process parameters that can be varied in the ASG reactor. As discussed above, under the proposed funding, we plan to expand the precursor types targeting the production of organically compatible silicas by use of mixed organic and inorganic feed streams, as well as through use of alkane substituted alkoxides of silica and titania. The concentration of reactants can be varied by the temperature, reactant vapor pressure, of the feed bubblers. Titania precursors require a higher bubbler temperature since the boiling point of both titanium butoxide and propoxide are about 50° higher than TEOS and TMOS. TEOS is currently heated to about 85°C using a water bath so several new oil baths will be required for titania production under controlled conditions. We have already produced titania in a boiling water bath from titania propoxide, Figure 6. An oil bath will also be required for heating resorcinol which is a solid at room temperature with a melting point of about 110°C and a boiling point of 280°C. Formaldehyde is a gas at room temperature but can be used in an aqueous solution, formalin. Under this funding temperature control, heating and cooling, is planned for the mixing/reaction zone and an additional chamber for heating the post reaction powders will be added. The latter chamber is to ensure complete reaction and removal of excess water from the powders. In the work under the 1-year initiation grant we studied the structural effects of laminar flow arrangement, Figure 8 below. It was found that the reactor geometry yielded some degree of control over the specific surface area, interfacial chemistry and morphology of the ASG powders [3]. This understanding will be critical in design of mixed RF/silica and RF/titania powders in order to control the coating sequence of the organic and inorganic components.



Figure 8. Schematic of thermally controlled, laminar flow assembly for *ASG* reactor for TEOS/water/HCl system. Reactant streams enter at the bottom of the concentric tubes from temperature controlled bubblers using dry nitrogen as a carrier gas. Laminar flow streams exit at the top into the mixing zone where the reaction takes place [3].

Powders, from the parameter space of Table 1, will be characterized using SEM, TEM, nitrogen absorption, elemental analysis, small-angle x-ray scattering, helium picnometry, and IR spectroscopy. For titania powders, XRD will be performed to determine the extent and type if any of crystallization which may occur. Generally, hydrolysis/condensation reactions lead to amorphous titania which can be converted to anatase at about 320°C and rutile at about 650°C [90]. Amorphous titania is advantageous for use as a UV absorber since it has a much lower catalytic activity than the anatase crystalline form. Rutile can only be obtained at high temperatures and also has a somewhat reduced catalytic activity.

These characterization techniques will generate an initial data base for each of the processing conditions aimed at supporting some of the key hypothesizes presented above. Table 2 presents the type of structural information which will be obtained from the different techniques available in our labs.

Items 3 through 6 of the focal areas deal with two targeted applications of *ASG* powders. This work will involve collaboration with PPG and Goodyear with whom we have already developed a close relationship. Additionally, we have close contacts with Procter & Gamble in development of titania based UV absorbers. From a process perspective, the interfacial issues in these different applications are similar, that is both involve production of organically coated metal oxide powders. Organic coating is a process for which the room temperature *ASG* reactor has particular advantage over alternative, continuous industrial-processes such as pyrolytic or precipitation routes. Additionally, the tunable and fine nano-structure of *ASG* powders provides ideal materials for both of these applications.

As discussed above, organic elastomer reinforcement using silica has been an active area of research and, more recently, application. Silica has long been known to have superior reinforcing ability for elastomers due to its tunable nano-structure and strong, ionically-bonded aggregates. Recent efforts in the elastomer industry have focused on surfactant treatment of pyrolytic and precipitated silica to enhance organic compatibility. In the *ASG* reactor this could be done simultaneously with particle formation through mixed streams of normally incompatible silica and organic precursors. Further, formation of mixed oxides with titania coatings on silica particles could lead to reactive fillers which might attack vinyl groups for instance in commercial elastomers to covalently bond filler and elastomer.

Parameter/ <u>Technique</u>	SALS	SAXS	XRD	Optical Microscopy	SEM	TEM	N ₂ Abs.	Mass Spec.	Bulk Density
Mass Fractal Dimension, d _r		*				*?			
Primary Particle Size, 1-10 nm		*				*			
Mass-Fractal Aggregate Size, 5-100 nm		*			*	*			
Agglomerate Size, μm	*	*		*	*				
Specific Surface Area		*				*?	*		
Crystallinity			*	*					*
Particle Size Distribution	*	*		*	*	*			
Composition		*	*			*		*	*

Table 2. Powder characterization parameters for nano-scale powders. (indicates a match between technique and parameter.*

Impact and Contributions to the Knowledge and Technology Base

The ASG Reactor is a unique process which shows the potential to produce large quantities of tunable nano-structured powders at low (room) temperature. The reactor brings together otherwise incompatible materials for the processing of materials in solvent free reactions at ambient conditions. The unique features of aerosol reactors are focused on two target applications of high potential in this proposal. The ASG process also has potential to dramatically effect a number of other fields which go beyond the scope of this CAREER proposal. Nano-structured ASG powders exceed the specifications of currently available powders with a lower facilities cost and, perhaps, a lower operating cost in spite of the higher cost for some of the reactants detailed in table 1. In the proposed work, we seek to further develop the technology using existing industrial precursors such as sodium silicate, $SiCl_4$ and $TiCl_4$. From initial studies, under CTS-97-30535, the nano-structure is tunable within a wide range. The process is continuous and amenable to adaptation by the chemical processing industry. Particles of this type have been long sought by the chemical industry for a variety of uses ranging from catalyst supports with the maximum possible surface area, to filtration media. We have only scratched the surface of applications of these novel materials. Under research initiation funding, we have demonstrated the existence of molecularsized primary particles, similar to some acid-catalyzed, super-critically extracted aerogels, in these easily-synthesized, ASG materials. A vast potential exists for tunable molecular-scale structure and tunable interfacial chemistries which would lead to applications such as quantum confined optical and electronic structures. There have already been studies, for instance, which suggest that nano-scale silica domains may show unique and tunable optical fluorescent behavior [92]. If such nano-scaled domains could be mass-produced by a viable chemical process, such as the aero-solgel process, applications in a wide range of fields, from micro-electronics to chemical sensors could be envisioned. One likely application in the micro-electronics field would be in the production of slurries for chemical-mechanical polishing (CMP) of large silicon wafers which is a difficult and expensive industrial operation. The proposed process may represent a rare, "quantum leap" in technology which could serve to redirect process design in the nano-structured powder production industry.

Education Plan

The education component of this proposal has two thrusts: 1) Direct industrial involvement in the educational process both at undergraduate and graduate levels. 2) A new graduate course, "Synthesis and Characterization of Nano-Powders" with an associated web page. The University of Cincinnati, operates under a *quarter-system* which facilitates the introduction of new courses

and gives the professor exposure to a wider range of courses than the semester system, albeit at the cost of shorter terms.

The Engineering College at UC has the oldest mandatory coop-based undergraduate program in the US. The undergraduate program can boast close to 100% employment as well as higher than national average starting salaries partly as a consequence of this program. Undergraduates usually can pay for their entire education through funds from their coop exposure. The first educational thrust is therefore a natural emphasis at UC and is in keeping with the past research funding of the PI which includes an industrial based project as a graduate student (Polysar), development of CRADA work as a post-doc and staff member at Sandia National Laboratories (Goodyear, Dow Corning, Dow, Raychem) and continued industrial funding as a faculty member (P&G, Equistar, Cabot, Armstrong). The PI is well versed in balancing fundamental and applied aspects of science as evidenced by his own PhD dissertation which included a US patent, several applied papers and 6 papers dealing with the physics of polymer blends, funded by a corporation with limited basic research efforts. The converse is evidenced by recent support of a P&G operating division in studies of scaling features of non-woven fabrics [8]. It is the PI's belief that good science goes hand in hand with good technology.

1) Industrial Involvement in the Education Process.

It is a basic philosophy in our research group that each graduate student have at least one mentor in industry who serves to guide the student in research and career objectives. Students exposed to such mentoring have demonstrated a higher level of maturity and focus to their efforts. The student who worked under CTS-97-30535, Jingyu Hyeon-Lee had mentoring relationships with A. Macip-Bolis at Armstrong corporation in the early stages of her PhD, and later had strong interactions and mentoring from Mike Satkowski at Procter & Gamble's Central Research Laboratory, Miami Valley Laboratories, in Cincinnati. A new PhD student is working on this project this summer, Doug Kohls. Kohls is involved in a summer internship in Satkowski's lab this summer and it seems likely that Satkowski will also serve as an industrial mentor for his graduate work. Kohls began work on this project as an undergraduate last year, completing a senior research project on a related topic involving hydrolysis/condensation reactions for cell growth substrates.

Student relationships with industrial mentors have been extremely valuable in terms of research directions aimed at reasonable topics and goals, student expectations from a PhD both in terms of self-fulfillment and employment and in introducing the student to parallel researchers in the field independent of his advisor. Other students in our research group have similar mentors at Equistar Chemicals, SCM Chemicals, and P&G and in the past Armstrong and Sandia National Labs. Surprisingly, it has not been difficult to make such mentoring arrangements for graduate students. For our contacts it would seem that such a mentoring process is a natural and rewarding association which adds another dimension to their efforts. In some but not all cases these mentoring arrangements are tied to industrial funding.

The PI has begun topical inclusion of industrial researchers and site visits in his graduate and undergraduate classes at UC. This includes a week long series of classes on block copolymers from workers at P&G in a class on Polymer Morphology, a one week series on film blowing in a course on Polymer Processing by workers at Equistar as well as site visits in the Polymer Processing class. Class critiques often cite such guest lectures as highly positive aspects. These guest industrial lectures, and site visits have to be carefully included in the homework, and examination scheme and arranged to naturally fit into the course flow. This proposal will include continuation of existing efforts and extension of this involvement in several undergraduate and graduate classes. Specifically, inclusion of industrial lectures on diffraction from nano-structural powders by D.-W. Hua of SCM Inorganics in an undergraduate course on XRD, a site visit to the analytic labs at Equistar and a guest lecture on IR by workers at P&G in a course on Polymer Analysis. Under this proposal, dissemination of these efforts through publication in education journals and presentation at national meetings are planned.

Undergraduate research is an integral part of our research effort. We have already benefited from undergraduate involvement in this project, through Doug Kohls. Undergraduates in engineering are required to complete an undergraduate thesis based on either a design project or

a research project. Under the research program of this proposal it is planned to include one undergraduate student who will contribute under an existing senior projects course and through a summer work study funded by this grant.

2) New Course in "Synthesis and Characterization of Nano-Powders".

The two focused applications of this proposal, elastomer reinforcement and nano-titania base UV absorbers are directly tied to a course in Polymer Processing, I developed, that includes a hands-on lab using processing equipment donated to me by Dow Chemical and Equistar. Under this grant I plan to incorporate further topics in the polymer additives area especially dealing with nano-structured fillers and UV absorbents as well as to incorporate nano-powder characterization in an undergraduate XRD class and a polymer analysis class.

UC operates under a "*quarter system*" which is highly amenable to the introduction of new courses. A new course dealing with the "Synthesis, Characterization and Use of Nano-Powders" will be developed under this grant. The course will overview industrial synthetic routes ranging from pyrolysis, precipitation, gelation and colloidal synthesis. Newer approaches, such as the *ASG* process, will be discussed. Techniques for the characterization of nano-structure and comparison of different materials will be presented. Finally, some common industrial uses for these materials will be examined. Currently there is no good textbook dealing with this subject and one goal of this course will be to develop a web page which could be used by faculty at other universities in similar courses, by industrial researchers as a reference source and by others with a general interest in this field. Such a resource could be invaluable to the nano-powder community. It is possible that the web page could be developed into a formal text if sufficient demand exists.