(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 November 2006 (30.11.2006)

PCT

(10) International Publication Number
WO 2006/127746 A2

(51) International Patent Classification:
B29B 9/00 (2006.01) *B32B 5/16* (2006.01)

(21) International Application Number:
PCT/US2006/019983

(22) International Filing Date: 23 May 2006 (23.05.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/683,650	23 May 2005 (23.05.2005)	US
60/694,389	27 June 2005 (27.06.2005)	US
60/778,707	3 March 2006 (03.03.2006)	US
11/438,468	22 May 2006 (22.05.2006)	US
11/438,477	22 May 2006 (22.05.2006)	US

(71) Applicant *(for all designated States except US)*: **NANOGRAM CORPORATION** [US/US]; 165 Topaz Street, Milipitas, CA 95035 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CHIRUVOLU, Shivkumar** [US/US]; 1065 Marilla Avenue, San Jose, CA 95129 (US). **DU, Hui** [CN/US]; Apt. 2-203, 1063 Morse Avenue, Sunnyvale, CA 94089 (US). **MCGOVERN, William, E.** [US/US]; 1346 Maritno Road, Lafayette, CA 94549 (US). **HORNE, Craig, R.** [US/US]; 545 Dawn Drive, Sunnyvale, CA 94087 (US). **MOSSO, Ronald, J.** [US/US]; 46553 Chaparral Drive, Fremont, CA 94539 (US). **KAMBE, Nobuyuki** [JP/US]; 908 Menlo Avenue, Menlo Park, CA 94025 (US).

(74) Agents: **DARDI, Peter, S.** et al.; DARDI & ASSOCIATES, PLLC, US Bank Plaza, Suite 2000, 220 South 6th Street, Minneapolis, MN 55402 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

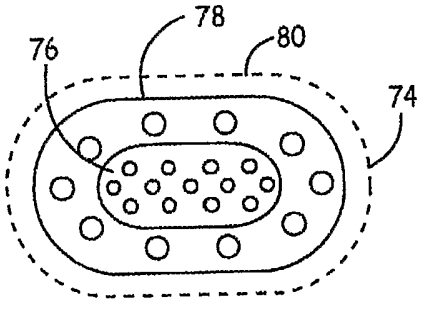
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: NANOSTRUCTURED COMPOSITE PARTICLES AND CORRESPONDING PROCESSES



(57) Abstract: Collections of composite particles comprise inorganic particles and another composition, such as a polymer and/or a coating composition. In some embodiments, the composite particles have small average particle sizes, such as no more than about 10 microns or no more than about 2.5 microns. The composite particles can have selected particle architectures. The inorganic particles can have compositions selected for particular properties. The composite particles can be effective for printing applications, for the formation of optical coatings, and other desirable applications.

WO 2006/127746 A2

NANOSTRUCTURED COMPOSITE PARTICLES AND CORRESPONDING PROCESSES

CROSS REFERENCE TO RELATED APPLICATIONS

This patent application claims priority to copending U.S. Provisional Patent Application serial number 60/683,650 filed on May 23, 2005 to Chiruvolu et al., entitled "Toners, Other Polymer-Inorganic Particle Composite Particles and Corresponding Processes," and to copending U.S. Provisional Patent Application serial number 60/694,389 filed on June 27, 2005 to Chiruvolu et al., entitled "Toners, Other Polymer-Inorganic Particle Composite Particles and Corresponding Processes," to copending U.S. Provisional Patent Application serial number 60/778,707 filed on March 3, 2006 to Chiruvolu et al., entitled "In-Flight Modification of Inorganic Particles Within a Reaction Product Flow," to copending U.S. Patent Application serial number 11/___,___ to Chiruvolu et al. filed on May 22, 2006, entitled "NanoStructured Composite Particles and Corresponding Processes," and to copending U.S. Patent Application serial number 11/___,___ to Chiruvolu et al. filed on May 22, 2006, entitled "In-Flight Modification of Inorganic Particles Within a Reactive Flow," all of which are incorporated herein by reference.

FIELD OF THE INVENTION

The invention relates to particulate composites formed from inorganic particles and polymers, such as organic polymers or inorganic polymers, having small average particle diameters, which in some embodiments can be no more than a micron. The invention further relates to processes for forming polymer-inorganic particle composite particles with desired properties. These materials and process can be used to form toner particles for electrophotography with desired size ranges.

BACKGROUND OF THE INVENTION

Composites of inorganic particles and polymer can be materials that have properties relating to the individual materials or intermediate between the particular properties of the separate materials. Thus, desirable features can be incorporated in a single material through the formation of the composite. With suitable composites, material characteristics can be obtained that may be difficult or impossible to achieve with standard materials. In addition to the growing demands for materials with new properties, there is a trend toward the

formation of smaller devices or other smaller structures. These size reductions impose further demands on material formation and/or processing.

Toner compositions can be used for electrophotography. Electrophotography is used generally for image production applications in printers, copiers, facsimile machines and the like. Dry toners generally involve a composite of several materials with a polymer base that flows upon heating during development of the toner onto the paper or other substrate surface. The material constraints on these composite toner particles introduce corresponding constraints to the toner particle formation process as well as the range of resulting toner properties.

SUMMARY OF THE INVENTION

In a first aspect, the invention relates to a collection of composite particles having an average particle diameter no more than about 2.5 microns. In some embodiments, at least about 95 percent of the composite particles comprise a thermoplastic polymer and a plurality of inorganic particles. The collection of composite particles can form a dry powder. The particle diameter generally refers to a free flowing particle diameter or, in other words, diameters of particles that are not hard fused to each other such that the particles can be dispersed. The particles in general can have any shape, such as roughly spherical or rod shaped. The particles can have architectures and compositions as described further herein. The composites can further comprise one or more other compositions, such as pigments, phosphors, dyes, surface modifiers, charge modulators or the like.

The inorganic particles can have a submicron average particle diameter. Inorganic particles are distinguishable from inorganic polymers in that inorganic particles have a three-dimensional, ordered, disordered or partially ordered structure in which the three-dimensional build up of the structure is a dominant characteristic. In contrast, an inorganic polymer has a significant two-dimensional or secondary structure even with significant amounts of crosslinking.

In a further aspect, the invention pertains to a collection of composite particles having an average particle size of not more than about 2.5 microns. In some embodiments, a majority of the composite particles have an inorganic particle core surrounded by the polymer binder, and the surface of the composite particles have a higher degree of crosslinking relative to the interior of the particles.

In another aspect, the invention pertains to a collection of composite particles comprising inorganic particles and a coating comprising an organic or silicon-based

compound. The composite particles generally have an average particle size of no more than about 10 microns, and the inorganic particles generally have an average particle size of no more than about 100 nanometers. In some embodiments, the inorganic particles are phosphors, metal nitrides, metal carbides, metal sulfides, metalloid nitrides, metalloid carbides, metalloid sulfides, doped particles, combinations thereof or mixtures thereof.

In other aspects, the invention pertains to a collection of composite particles comprising inorganic particles and a polymer. A majority of the composite particles have a core comprising the polymer, and the inorganic particles are embedded along the surface of the composite particles. The collection of composite particles can be in a dry powder. The composite particles have an average particle size of no more than about 10 microns.

Also, the invention pertains to a collection of composite particles having a layered structure with distinct compositions from each other. The composite particles comprise inorganic particles and a thermoplastic polymer binder. The composite particles have an average particle size of no more than about 10 microns, and each layer of the composite particles comprises a polymer.

In an additional aspect, the invention pertains to a collection of composite particles comprising inorganic particles and a multiple branched polymer, such as a dendrimer. In some embodiments, the composite particles have an average particle size of no more than about 2.5 microns. The collection of composite particles can be in a dry powder.

In other aspects, the invention relates to a collection of particles in a dry powder comprising a polymer-inorganic particle composite having an average particle size no more than about 10 microns and the inorganic particles having a selected average particle diameter of no more than about 100 nm, wherein the inorganic particles have an appearance of a particular color upon exposure to light. The inorganic particles can have size dependent color, i.e., absorption, such that the average particle size is selected yield the desired color and the particle collection has a suitable narrow particle size distribution. Suitable inorganic particles can comprise metal nitride particles, such as particles comprising aluminum nitride or $In_xGa_{1-x}N$, with $0 \leq x \leq 1$, or doped metal nitride particles. Furthermore, the color can result from contrasts in index of refraction since interfaces between different index materials results in particular wavelengths of reflection, absorption and transmission. Thus, the embedding of high index-of-refraction inorganic particles in a lower index polymer can result in the observation of color.

Moreover, the invention pertains to a collection of composite particles comprising inorganic particles and an ordered polymer blend. The ordered polymer blend can comprise a block copolymer, a blend of immiscible polymers, a gradient in polymer crosslinking with depth in the particle, or the like.

Furthermore, the invention can pertain to a method for the formation of composite particles comprising inorganic particles and a polymer. The method comprises spray drying a solution comprising the inorganic particles and a polymer precursor. The polymer precursor can comprise, for example, polymerizable monomers, crosslinkable oligomers, a polymer solution or the like. Generally, the spray is reacted in-flight to form a thermoplastic polymer binder.

In further embodiments, the invention pertains to a printed structure comprising a substrate and images printed on the substrate. The images have an average thickness of no more than about three microns. The covers a selected portion of the surface of the substrate in which the selected portion is less than the entire substrate surface. The images may be black and/or a particular visible color due to the composite's absorption, reflection and transmission properties. The substrate can be, for example, a sheet of paper. The image can be formed by printing the composite particles described herein.

In additional embodiments, the invention pertains to a method for forming a thin coating comprising a polymer-inorganic particle composite. The method comprises heating a substrate coated with a coating comprising composite particles. The composite particles comprise inorganic particles and a thermoplastic polymer. The heating can be performed to a temperature beyond the flow temperature of the polymer. The composite particles have an average particle diameter no more than about 2.5 microns. The corresponding composite coating can have a thickness of less than about 10 microns, in other embodiments less than about 5 microns, and in further embodiments less than about 2.5 microns.

In another aspect, the invention pertains to a method for the performance of in situ modification of inorganic particles formed within a reactive flow, the process comprising directing radiation, an organic or silicon-based coating composition, or a combination thereof to a product inorganic particle flow downstream from a reaction zone at which the inorganic particles are formed to form in situ modified inorganic particles. In some embodiments, a coating composition is directed at the inorganic particles to form of inorganic particles with a coating. The coating composition generally is an organic composition or a silicon-based composition and can be, for example, a surface modifier, a pigment, polymerizable monomers, crosslinkable oligomers, a polymer solution or the like.

The coating composition may or may not chemically react with the surface of the inorganic particles. For relevant embodiments, the deposition of a coating composition on the inorganic particles results in composite particles. The inorganic particles produced in the reactive flow can be cooled with an inert gas or other approach prior to the application of a coating composition.

Radiation can be used to modify the inorganic particle properties, such as crystallinity and/or purity, and/or radiation can be used to modify coating properties. Suitable radiation can be, for example, ultraviolet light, an electron beam, a corona discharge, x-rays, visible light, microwaves, infrared light, combinations thereof or the like. Radiation can be directed to the flow following the deposition of a coating composition to induce polymerization, crosslinking and/or other suitable modification of the coating composition.

The flow generally is initiated with a reactant delivery system that interfaces at an inlet nozzle with the reaction system. The reaction to form inorganic particles can be driven by an intense light beam to form the inorganic product particles within the flow. A reaction zone can be located at the intersection of a reactant flow and a light beam such that the inorganic particle production process involves a light induced pyrolysis, generally referred to as laser pyrolysis.

In a further aspect, the invention pertains to an apparatus comprising a reactant delivery system, a flow path, an energy source, a coating nozzle and a collection system. The reactant delivery system comprises precursors that react to form inorganic particles in response to suitable energy and can be configured, for example, to deliver vapor and/or aerosol reactants from an inlet nozzle. The energy source generally is configured deliver excitation energy to a reactant flow of inorganic particle precursors within a flow path from the reactant delivery system. The flow path generally is directed through a reaction chamber sealed from the ambient environment. The interaction of energy from the energy source and flow from the reactant delivery system establishes a reaction zone for inorganic particle formation. The reaction zone can correspond to a location at which thermally driven reactions take place. But in some embodiments of particular interest, the reactions are driven with energy from an intense light beam that intersects the reactant flow to induce reaction within the reaction zone. This process driven with an intense light beam has been termed laser pyrolysis, although an intense non-laser light source can be used. For light driven embodiments, the apparatus can comprise an optical path from an intense light source that intersects the reactant stream.

A product inorganic particle stream flows from the reaction zone as the reactant stream is converted into a product stream. The coating nozzle can be operably connected to a source, for example, of organic or silicon-based coating composition. The coating nozzle can be oriented to deliver the coating composition to intersect the inorganic particle product stream in the reaction chamber or within a collection conduit or other chamber. In some embodiments, the flow has an elongated dimension such that the a cross section perpendicular to the flow has an aspect ratio significantly greater than 1, such as greater than about 5, with a width generally no more than about the width of the light beam.

In other aspects, the invention pertains to an apparatus comprising a reactant delivery system, a flow path, an energy source, a radiation source and a collection system. The reactant delivery system comprises precursors that react to form inorganic particles in response to suitable energy and can be configured, for example, to deliver vapor and/or aerosol reactants from an inlet nozzle. The energy source is configured to deliver excitation energy to a reactant inorganic particle precursor flow from the reactant delivery system. The flow path generally is directed through a reaction chamber sealed from the ambient environment. The radiation source is configured to interact with the flow following the formation of inorganic particles. Interaction of the inorganic particles with radiation can result in a change in crystal structure and/or a change in oxidation state.

Additionally, the invention pertains to processes that combine in-flight a plurality of inorganic particle flows formed in separate reactive flows and that modify these inorganic particles to form corresponding composites. These processes take advantage of the ability to modify in-flight inorganic particles from a reactive flow. In this way, complex composites, such as submicron toner particles, can be formed completely with an in-flight process. The interaction of the independent inorganic particle flows can be designed to reduce agglomeration through the avoidance of interacting particles too close to their reaction zone so that the particles have cooled before they interact and through blending the particle flows at an oblique angle so that the relative momentum of the particles does not favor agglomeration.

In some embodiments, the plurality of independent inorganic particles flows is combined to form a blended inorganic particle flow prior to performing modifications with a coating composition or the like. In additional or alternative embodiments, the inorganic particles in one or more product flows can be modified prior to combining the particles with other inorganic product particle flows. A plurality of modification steps can be performed as appropriate to achieve the desired composite product.

In addition, the invention pertains to in-flight processing approaches in which there is a coating composition in-flight processing channel and a reactive inorganic particle production channel. In this context, coating composition processing is intended to include, for example, further processing of organic compositions, silicon-based compositions, oligomer processing, polymer processing and the like. The products from the separate channels are combined to form composite particles. The particles from the reactive inorganic particle production pathway can be modified with a coating composition, such as a surface modifier, prior to interacting with products from the organic in-flight processing channel. The coating composition in-flight processing channel can comprise a range of processing options, which can lead, for example, to pigmented polymer particles within the in-flight processing channel. The organic compositions can be subjected to electrons and/or ultraviolet radiation or other suitable radiation to induce polymerization and/or crosslinking of monomers, oligomers or polymers within the organic droplets either before and/or after combining the organic droplets with the inorganic particles. Suitable processes within the coating composition processing channel include, for example, drying, crosslinking, polymerization, chemical modification, combinations thereof and the like.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic depiction of a composite particle with a single inorganic particle.

Fig. 2 is a schematic depiction of a composite particle with a plurality of randomly dispersed inorganic particles.

Fig. 3 is a schematic depiction of a layered composite particle.

Fig. 4 is a schematic depiction of a composite particle with a surface with embedded inorganic particles.

Fig. 5 is a schematic depiction of a composite particle formed with ordered block copolymers.

Fig. 6 is a schematic, fragmentary side view of a modified inorganic particle production system.

Fig. 7 is a schematic side view of a laser pyrolysis reaction chamber with an elongated reactant inlet for a high throughput based on a sheet of flow.

Fig. 8 is a schematic diagram of a reactant delivery system with a gas/vapor precursor sources.

Fig. 9 is a schematic diagram of a reactant delivery system with a gas delivery subsystem, a vapor delivery subsystem and a mixing subsystem.

Fig. 10 is a sectional front view of an aerosol delivery system in which the section is taken along line 10-10 of the insert showing a top view of the aerosol delivery system.

Fig. 11 is a sectional side view of the aerosol delivery system of Fig. 10 taken along line 11-11 of the insert of Fig. 10.

Fig. 12 is a schematic view of three alternative configurations of a coating composition delivery nozzle relative to a product flow of inorganic particles.

Fig. 13 is a fragmentary top view of a coating composition delivery nozzle with two elements oriented around a product flow of inorganic particles.

Fig. 14 is a fragmentary top view of an embodiment with a coating composition delivery nozzle with four elements oriented around a product flow of inorganic particles.

Fig. 15 is a fragmentary top view of an embodiment with a coating composition delivery nozzle that surrounds a product flow of inorganic particles.

Fig. 16 is a front view of a panel of radiation sources aligned along the panel.

Fig. 17 is a partially cut-away perspective view of an embodiment of a reaction system with a coating composition delivery nozzle within a reaction chamber set up for the laser pyrolysis-based synthesis of inorganic particles, in which a wall of the reaction chamber is cut away to expose the interior of the reaction chamber.

Fig. 18 is a schematic perspective view of a flow system configured with a plurality of flow modification stations that can each comprise independently a radiation source or a coating composition delivery nozzle.

Fig. 19A is a fragmentary, sectional view through the wall of a reaction chamber adapted with a thin film delivery approach.

Fig. 19B is a fragmentary, perspective view of the joining of the inner walls of the reaction chamber walls shown in Fig. 19A.

Fig. 20A is a fragmentary, sectional view through the wall of a reaction chamber with an alternative embodiment adapted for a thin film delivery.

Fig. 20B is a fragmentary, perspective view of the joining of the inner walls of the reaction chamber of the reaction chamber walls shown in Fig. 20A.

Fig. 21A is a fragmentary, sectional view of another alternative embodiment of the wall of the reaction chamber configured for thin film delivery, in which the inner wall includes wall segments that are connected by spacers to form the inner wall. The cross section is taken through a section of chamber wall along a direction parallel to reactant flow in the chamber.

Fig. 21B is a fragmentary sectional view of the chamber wall shown in Fig. 21A, where the section is taken along line B-B.

Fig. 22 is a fragmentary, section view of the wall of the reaction chamber with a porous inner wall for the delivery of gas or vapor from a delivery channel within the wall.

Fig. 23A is a fragmentary sectional view of the wall of the reaction chamber with notches in the inner wall for the delivery of vapor into the reaction chamber from a delivery channel within the wall.

Fig. 23B is a fragmentary side view of a section of an inner, reaction chamber wall with notches for the delivery of inert gas.

Fig. 24 is a cut away perspective view of a laser pyrolysis apparatus configured to form two independent inorganic particle product streams.

Fig. 25 is a flow diagram indicating a general framework for forming composite particles.

Fig. 26 is a flow diagram indicating some specific embodiments of processes to form composite particles.

Fig. 27 is a flow diagram indicating the process steps in an embodiment involving complete in-flight formation of composite particles.

Fig. 28 is a flow diagram outlining various embodiments involving a plurality of in-flight processing streams with inorganic and/or organic/polymer channels.

Fig. 29 is a flow diagram indicating various optional processing steps for some representative embodiments of the processing approaches described herein for modifying in-flight inorganic particles within a flow.

Fig. 30 is a flow diagram depicting an embodiment of an in-flight process to form a coating composition for delivery to an inorganic particle flow.

Fig. 31 is a plot of infrared transmission as a function of frequency (inverse wavelength) for four different epoxy-silane modified rutile titanium dioxide nanoparticle powders.

Fig. 32 is a transmission electron micrograph of epoxy-silane modified rutile titanium oxide nanoparticles.

Fig. 33 is a plot of solution phase particle size measurements for two dispersed samples of epoxy-silane modified titanium dioxide samples.

DETAILED DESCRIPTION OF THE INVENTION

Improved composite particles in dry powder form can have reduced average particle diameters and/or improved particle structures, in which the particles comprise composites of polymer and inorganic particles. The polymers can be chemically bonded with the inorganic particles, or the polymer can otherwise function as a binder with respect to the inorganic particles, or the polymer can be physically adsorbed over the inorganic particles. Polymers can be organic or silicon-based polymers, and an ordered polymer can be useful to form more complex structures with desired properties. Improved processing approaches can be used efficiently to form desired materials. For example, in flight approaches can be used to modify particles following formation in a reactive stream. Also, aerosol approaches, such as spray drying, can be used to control particle formation in desirable ways to form composites with suitable properties. Composite particles with appropriate composition can be used as improved toners. The improved toner particles can be used to form sharper images with reduced amounts of material.

The composite particles generally comprise a polymer and inorganic particles in varying proportions selected as appropriate for the particular applications. Additional additives also can be incorporated into the particles. The polymer and inorganic particles can be randomly distributed within the particle, or the particles and polymer can be organized within a specific architecture that involves particular locations for the inorganic particles within the composite particles. In embodiments of particular interest, the composite particles have very small average particle sizes. Improved inorganic particle selection and processing approaches provide for formation of architectures and smaller particle sizes than were previously obtainable. In general, the average particle sizes can be less than 2.5 microns through the use of inorganic particles that can have submicron average particle sizes and extremely good dispersibility.

The composition of the composite particles can be selected for the particular application. For example, for toner particles, the inorganic particles can function as pigments, surface modifiers, reflectors, carriers and/or charge control agents. To act as surface modifiers, the inorganic particles can be concentrated along the surface of the particle. The polymer can function as a binder and can be selected to have a glass transition temperature suitable to have the polymer flow in response to appropriate temperatures. Similarly, the polymers should be stable at the temperature ranges to which the composite particles are subjected during use.

A range of polymers are suitable for incorporation into the composites, including both organic polymers and inorganic polymers, such as polysiloxanes. The polymers can be selected to have desired properties, such as the glass transition temperature T_g for amorphous polymers or the melting temperature T_m for crystalline polymer, which both correlate with the softening point of the polymer. Suitable polymers include block copolymers and polymer blends. Block copolymers can have compositions of the blocks such that the blocks order into separate phases. Thus, one block can associate with the inorganic particles while the other block segregates away from the inorganic particles. Immiscible polymer blends can function similarly to block copolymers that separate into different phases. The different blocks can have different physical properties, such as tackiness and/or T_g/T_m.

Dendrimers are highly branched polymer structures built upon a star-polymer. Dendrimers can be formed through the sequential reactions of polyfunctional monomers. The resulting structures are highly branched and can be formed with desired functional groups within the structure. Furthermore, dendrimer structures can be formed with structures that inherently form a shell with a core that can entrap small inorganic particles. Dendrimers are described further, for example, in U.S. Patent 6,794,327 to Youngs et al., entitled Supramolecular Structures And Process For Making The Same," and Published U.S. Patent Application 2003/0077635A1 to Lohse, entitled "Dendrimers and Methods For Their Preparation And use," both of which are incorporated herein by reference.

The inorganic particles generally include metal or metalloid elements in their elemental form or in metal /metalloid compounds. Specifically, the inorganic particles can include, for example, elemental metal or elemental metalloid, i.e. un-ionized elements, metal/metalloid oxides, metal/metalloid nitrides, metal/metalloid carbides, metal/metalloid sulfides, metal/metalloid silicates, metal/metalloid phosphates or combinations thereof. As used herein, inorganic particles include elemental carbon particles, such as fullerenes, carbon black, carbon nanotubes, graphite and combinations thereof. Inorganic particles excluding carbon particles can be referred to as non-carbon inorganic particles, which comprise a metal and/or a metalloid. Metalloids are elements that exhibit chemical properties intermediate between or inclusive of metals and nonmetals. Metalloid elements include silicon, boron, arsenic, antimony, and tellurium. While phosphorous is located in the periodic table near the metal elements, it is not generally considered a metalloid element. However, P_2O_5 and doped forms of P_2O_5 are good optical materials similar to some metalloid oxides, and other optical materials doped with phosphorous, e.g., in the form of P_2O_5, can have desirable optical properties. For

convenience, as used herein including in the claims, phosphorous is also considered a metalloid element.

The inorganic particles can be incorporated at a range of loadings into the blends. Particular loadings may be appropriate for specific applications. High inorganic particle loadings of up to about 50 weight percent or greater can be achieved with well dispersed particles. The composition of the components of the composite particles and the relative amounts of the components can be selected to yield desired properties in which the polymer functions as a binder. The inorganic particles can comprise a surface modifier that can facilitate dispersion or other functions. In some embodiments, the composite particles comprise mixtures of inorganic particles and polymers in which the polymer functions as a binder.

In other embodiments, the composite particles comprise polymer-inorganic particle composites with chemical bonding between the inorganic particles and the polymer, which may or may not involve a linker compound mediating the bonding of the polymer with the inorganic particle. A linker is a polyfunctional compound that binds with a first functional group with the inorganic particle and with a second functional group to the polymer. Chemical bonds, as used herein, generally has at least some covalent bond character and specific interactions, as distinguished from non-specific bonding, such as adhesive bonding, that involves a large number of weak, non-specific interactions and generally a significant entropic contribution. If the inorganic particles comprise a surface modifier, the surface modifier composition may or may not further function as a linker for bonding to the polymer. In addition, in embodiments involving chemically bonded composites, the amount of the linker compounds bonded to the inorganic particles can be adjusted to vary the degree of crosslinking obtained with the polymer.

In embodiments of the composite particles involving chemical bonding between the polymer and the inorganic particles, the polymer can be selected or modified to comprise appropriate functional groups to chemically bond with the inorganic particles or with functional groups of a linker compound. A linker compound can facilitate the formation of the resulting composite. Specifically, in these embodiments, the composites comprise a monomer/polymer component, inorganic particles, and linker compounds that bridge the inorganic particles and the monomer/polymer. In the case of monomer units being joined to the linker compound, a polymer is formed with the formation of the composite. For simplicity in notation, the monomer/polymer unit joined with the linker and assembled into the composite will be referred to generally as a polymer, although it is recognized that in some cases the unit

can be a monomer or polymer, such as a dimer, trimer or larger polymer structures. The molecular weights of the polymers can be selected to vary the properties of the resulting composite.

In some embodiments, it may be advantageous to use collections of inorganic particles having an average diameter of less than about 500 nanometers (nm). Suitable nanoparticles can be formed, for example, by flame synthesis, combustion, micelle/reverse micelle, or sol gel approaches. Methods for synthesizing inorganic particles in commercial quantities with particular high uniformity include, for example, light-based pyrolysis/laser pyrolysis in which light from an intense electromagnetic radiation source drives the reaction to form the particles. For convenience, this application refers to light-based pyrolysis and laser pyrolysis interchangeably, since a suitable intense source of electromagnetic radiation can be used in place of a laser. Laser pyrolysis is useful in the formation of particles that are highly uniform in composition, crystallinity and size. Furthermore, inorganic particles can be effectively formed, for example, using laser pyrolysis that results in particles that have desirable surface properties that lead to high dispersibility and ready incorporation into desired composites, although other sources of particles can be used.

The use of nanoscale particles within the polymer/inorganic particle blends can impart improved and/or desired properties for some applications. In particular, nanoparticles can provide desirable optical performance due to desirable optical properties, such as generally decreased scattering relative to larger inorganic particles. High-quality nanoparticles are desirable for the generation of homogeneously mixed nanoparticle-polymer blends with well-defined optical properties. Specifically, it is desirable to have particles in which the primary particles are not highly agglomerated such that the primary particles can be dispersed effectively to form the composite. High-quality nanoparticles to form nanocomposites can be produced on a commercial scale, as described in U.S. Patent 5,958,348 to Bi et al., entitled "Efficient Production of Particles By Chemical Reaction," incorporated herein by reference.

In some embodiments, the composite particles can comprise inorganic particles, a polymer and optionally other one or more additives. While in general, the relative amounts of the components can be selected to be suitable for particular application. For some applications, such as toner applications, it can be desirable to have at least about 25 volume percent polymer, in further embodiments at least about 35 volume percent and in additional embodiments from about 40 to about 95 volume percent polymer, such that the polymer can help to fix the printed particles. Suitable additives can be property modifiers, such as waxes

or antioxidants, or functional compositions, such as dyes. In general, the composite particles comprise no more than about 25 weight percent additives and in further embodiments no more than about 20 weight percent additives. Similarly, each additive is generally present in no more than about 15 weight percent and in other embodiments no more than about 10 weight percent. Inorganic particle compositions are discussed further above, and the remaining portion of the composite particles comprises the inorganic particles. A person of ordinary skill in the art will recognize that additional ranges of compositions within the explicit ranges above are contemplated and are within the present disclosure.

Since a wide range of inorganic particles and polymers can be incorporated into the composites described herein, the composites are suitable for a wide range of applications. For example, the composite particles can be used directly as free flowing particles or for the formation of coatings. In one application of interest, the particles are used as toner for application to a substrate surface using electrophotography and subsequently heated to bond the particles to the substrate surface. Toner applications are described herein in more detail, although all applications are contemplated for the improved composite particles. One significant advantage from the use of polymer-inorganic particle composites is the ability to control physical properties such as color, flow temperature, or electrical, magnetic or optical parameters over a wide range. A general discussion of polymer-inorganic particle composite compositions are described further U.S. Patent 6,599,631 to Kambe et al., entitled "Polymer-Inorganic Particle Composites," incorporated herein by reference and in copending U.S. Patent application 10/083,967 to Kambe et al., entitled "Structures Incorporating Polymer-Inorganic Particle Blends," incorporated herein by reference.

Generally, processing approaches for the formation of improved composite particles involve the effective dispersion of the inorganic particles. In some embodiments, the particles can be dispersed such that the secondary particle size, i.e., the effective particle size, is approximately equal to the primary particle size. The particles can be dispersed in the flow resulting in their formation or the particles can be dispersed following collection using a dispersant. It has been found that particles formed by laser pyrolysis can be well dispersed using organic dispersants, and thereby demonstrating that the primary particles are not hard fused, where the primary particle size and distribution of sizes are observed in a transmission electron micrograph. This is described further in U.S. Patent 6,599,631 to Kambe et al., entitled "Polymer-Inorganic Particle Composites," incorporated herein by reference. Formation of the polymer can be performed through combining the inorganic

particles with monomers and subsequently polymerizing the monomers, or by combining the inorganic particles directly with the polymer generally in solution. If the inorganic particles are combined directly with a polymer, the composite can be further crosslinked subsequent to forming the combination.

In some embodiments of particular interest, the inorganic particles are formed in reactive flows in which a reactant stream comprising particle precursors is initiated by a reactant delivery system, the reactant stream is reacted at a reaction zone and the product particles subsequently flow in a product stream. For example, the reaction zone can correspond with a light reaction zone at or near the intersection of a light beam with a reactant flow or with a flame reaction zone.

Based on the approaches described herein, inorganic particles synthesized within a flow can be modified in-flight before their collection. In particular, the inorganic particles can be interacted with radiation to modify the inorganic particle properties and/or the inorganic particles can be coated in flight. Performance of the processing steps in-flight significantly improves efficiency of processing for forming some composite materials since some difficult processing steps can be avoided. The inorganic particles in the reactive flow in which they are formed can be essentially well separated such that the processing of the particles can effectively modify the individual inorganic particles. Also, interacting the inorganic particles with appropriate radiation can alter the particle structures, for example, to alter the crystal structure, while the particles have not fully cooled. Inert gasses can also be delivered to the flow to cool the particles, if desired, as well as to further control the flow as it proceeds through the apparatus. Processing of the inorganic particles in the flow can involve pacifying the particle surfaces such that the collected particles are more easily dispersed for use.

The in-flight modification of the particles can involve contact of the particles with a composition that can provide a surface modifier, a linker compound, monomer compounds and/or polymer compounds. The composition may or may not further comprise a solvent or a dispersant.

A coating composition can be delivered to the product inorganic particles within the flow in the form of a vapor and/or aerosol. The coating composition can comprise, for example, organic compositions, organometalic compositions and/or silicon-based compositions. Through the selection of the inorganic particle compositions, the coating compositions, particle sizes and the relative amounts of the materials, composite particles with a wide range of properties can be formed. Some in-flight approaches can involve

combinations of inorganic particles from separate reactive flows. In additional or alternative embodiments, in-flight processing of organics can be performed prior to combining in flight the product organics with a flow of inorganic product particles. Radiation can be delivered to the flow to modify the inorganic particle properties and/or to modify coating compositions applied to the inorganic particles.

The apparatus can be configured to direct the coating composition relatively uniformly at the product inorganic particle flow. To accomplish this delivery of coating composition, one or more inlets can be used to deliver the coating composition into the flow. In some embodiments, the flow is in the form of a sheet with a relatively small thickness and a relatively large width, which can be visualized with a conceptual plane cutting through perpendicular to the flow. The coating composition inlets can be configured to approximately conform with this flow geometry to yield a more uniform coating over the inorganic particles. The nature of the coating composition inlet can be configured to yield the desired uniformity for the selected amount of coating composition without undesirably disrupting the flow.

The apparatus can be configured to deliver radiation to the flow relatively uniformly. In particularly, suitable radiation sources can be configured to roughly match the configuration of the flow. Suitable radiation sources can be selected to deliver electromagnetic radiation at a desired wavelength range, an electron beam, a corona discharge, or the like.

The coatings described herein are substantially different from sequential inorganic coatings. For example, U.S. Patent 6,803,073B to Doan, entitled Particle Forming Method," incorporated herein by reference, describes two sequential laser pyrolysis steps within a flow such that the reaction of a second precursor stream results in the nucleation of an inorganic coating composition over the initially formed core inorganic particles. The present approach is quite distinct since the inorganic particles do not flow through a light reactive zone with energy/heat sufficient to drive a laser pyrolysis process. In addition, the coatings described herein are distinct from the inorganic coatings described in the '073 Doan patent.

While the particles quench relatively rapidly in laser pyrolysis, with laser pyrolysis or other flowing reaction methods, it can be desirable to further cool the particles prior to the addition of a coating composition. In particular, the particles can be cooled by contacting the flow with a flow of inert gas, such as N_2. The degree of cooling can be adjusted to provide the particles with an appropriate temperature for combination with a coating composition.

In some embodiments based on spray processing, composite formation solutions can be formed using an appropriate solvent/ dispersant and subsequently subjected to an aerosol process to form composite particles within the spray. The polymer can be formed prior to the aerosol process and/or within the spray. Formation of the polymer within the spray can involve light induced polymerization, heat induced polymerization, polymerization that involves spontaneous reaction upon drying of the particles and/or reaction initiated with a catalyst that is introduced into the composite formation solution prior to, at the time of and/or subsequent to forming the aerosol. For example, the aerosol can be subjected to a UV light that initiates the polymerization process.

In some embodiments, conventional emulsion processes can be adapted for the production of improved materials. For example, pacifying inorganic particles can be deposited on the surfaces of suspended polymer particles to pacify the surface for subsequent drying. The surface can be pacified additionally or alternatively by crosslinking the outer surface of the toner particles. Similarly, the emulsion particles can be formed with a block copolymer with phase separated block having one phase along the composite particle surface and a second phase away from the composite particle surfaces. The outer polymer block can be crosslinked to pacify the surfaces of the composite particles for subsequent drying while leaving the inner blocks at a suitable melt temperatures for subsequent applications. Thus, for embodiments with pacification of the surfaces of the particles, undesirable agglomeration of the composite particles, as experienced in conventional processing, can be avoided upon drying from the emulsion. The dried particles can be milled to improve the flow properties of the dried powder.

In further embodiments, the polymers of the composite particles can be crosslinked following formation of the composite particles. Under sufficiently mild crosslinking conditions, the polymer at the surface of the particles may crosslink to a greater degree than the polymer deeper within the particles to provide a surface modification. Suitable crosslinking agents, such as chemical crosslinkers and radiation can be used to induce the crosslinking. The crosslinking can be performed in-flight if the composite particles are formed in-flight.

With respect to the formation of composite particles in-flight, the composite particles can comprise a single type of inorganic particles or a plurality of types of inorganic particles. Similarly, a separate organic assembly pathway can be used to form organic/polymer particles in-flight. In general, any of the composite particle architectures described herein can be formed with appropriate in-flight processes.

Processing of the organic particles in-flight can involve, for example, drying, crosslinking, polymerization, chemical modification, combinations thereof and the like. The polymer particles formed in-flight can be combined in-flight with inorganic particles formed in a reactive flow to form desired composite particles. Specifically, the flow from the organic reactive channel can be intersected with flow from the inorganic product flow to form the composites, in which the intersection can be performed within the inorganic particle reaction chamber or in a separate chamber. The inorganic particles in the product flow may or may not be modified in-flight prior to intersection with the organic product flows.

A range of composite particle architectures can be formed. In some embodiments, a majority of the composite particles comprise a single inorganic particle that is surrounded with a polymer material. The amount of polymer present correlates with the average thickness of the polymer coating over the particles, which can be selected as desired. In these embodiments, some of the particles, generally a small portion, in the composite may be inorganic particles alone and/or polymer particles free of inorganic particles.

In alternative embodiments, the inorganic particles are embedded generally randomly in a polymer matrix. The collection of particles has an average weight percent of polymer and inorganic particles, but the particular proportion in a composite particle can fluctuate around the average. The inorganic particles generally can be from a couple of nanometers in average diameter to roughly a micron or more in average diameter. If the particles are small enough, the composite particles on average can comprise a relatively large number of inorganic particles, such as on the order of tens of millions in contrast with the embodiments in which a single composite particle generally has a single inorganic particle.

In additional embodiments, the composite particles can have a core-shell structure. The embodiments with a single inorganic particle operating as a core with a shell of polymer can be considered one limit of such structures. In principle, there can be a plurality of layered shells with different compositions. More broadly, the core-shell structures can comprise one or more of differences between the core and shell(s) selected from different inorganic particles, different polymer compositions, different concentrations of inorganic particles, the presence or absence of inorganic particles, different additives, different degrees of crosslinking and/or the like. Generally, the core is formed first and subsequent shell layer(s) are sequentially added using the processing approaches described herein, such as in-flight processing, spray drying and the like or combinations thereof. However, in

some embodiments, block copolymers or the like can be used to form a defacto core/shell structure if the blocks of the copolymer segregated into different phases. The inorganic particles can associate with one phase of the segregated copolymer.

In further embodiments, the composite particles can have a surface layer of small inorganic particles. Depending on the degree of wetting of the inorganic particle by the polymer the degree that the particles are exposed at the surface can vary. If the particles are well wetted, these structures can be effectively a shell over a core as described above. In general, the inorganic particle layer can pacify the surface and/or provide functionality to the surface. These surface coatings of particles can be formed by colliding polymer particles with a flow of particles or by coating the polymer particles with well-dispersed inorganic particles in solution, and drying or spray drying the dispersion. Alternatively or additionally, the inorganic particles can be chemically bonded to the polymer on the surface of the particles to form a composite with surface inorganic particles. The inorganic particle coating can be applied to polymer particles or onto particles that are themselves polymer-inorganic particle composites, such as any of the polymer-inorganic particle composite architectures described above.

The improved composite particles can be used effectively in a range of applications. For example, due to the small size and relative uniformity of the particles, they can be used to make very thin composite coatings. For example, spray coating of a dispersion of the particles onto a surface can result in a very thin and very uniform coating of the particles. Due the processability of the particles, the particle coating can achieve very uniform coating with a very thin layer. The particle coating can be heated above the T_g or T_m of the polymer to obtain a resulting very thin layer of composite. The layer thickness can be as thin as or less than the average particle diameter. For example, these coatings can be used as optical coatings with the inorganic particles being used to increase the index-of-refraction of the composite or to provide ultraviolet light blocking capability. Other coatings can provide scratch resistance.

In some embodiments of particular interest, the composite particles can be used as toner particles. Toner particles are deposited using electrophotography in which the particles are attracted to selectively charged portions of a surface. The toner particles can incorporate additional additives if desired, such as pigments, dyes, charge moderators, waxes and the like. The polymers or a portion thereof can be selected to have an appropriate melting temperature for a polymer particle. If the surface of the composite can be modified to be less tacky, such as through the coating with inorganic particles, selected

crosslinking and/or a shell layer with a different polymer composition, the particles can be designed to melt or flow at lower temperatures such that a printed toner image can be developed onto the substrate surface at a lower temperature. In some embodiments, the particles have a low flow temperature as well as a non-tacky surface due to appropriate surface pacification approaches. Developing the image at a lower temperature correspondingly lowers the energy demands of the image production process and decreases unwanted side effects on the substrate from the heating process.

Composite Particle Structure, Architecture and Composition

The composite particles comprise inorganic particles and a polymer matrix such that the resulting composite particles incorporate aspects of both the inorganic particles and the polymer. The inorganic particles may or may not be chemically bonded to the polymer. The bonding of an inorganic particle to the polymer may or may not involve a linker that can be used to activate the surface of the inorganic particles for bonding with the polymer. Suitable composites can involve either low particle loadings or high particle loadings depending on the particular application. Similarly, the composition of the polymer component and the inorganic particle components can be selected to achieve desired properties of the resulting composite. The composite particles may exhibit a synergistic effect with respect to properties of the composite particles relative to those of the individual components. In some embodiments, the composites can comprise a plurality of different inorganic particles and/or a plurality of different polymers. Furthermore, the composite particles can comprise optional suitable additives that provide desired properties for processing and/or for use of the completed composite particles.

The inorganic particles can be incorporated at a range of loadings into the composite. Composites with low particle loadings can be produced with high uniformity if the inorganic particles are well dispersed. Low loadings, such as one or two weight percent or less, can be desirable for some applications. In addition, high inorganic particle loadings can be achieved with well-dispersed particles. In general, the inorganic particle loadings are from about 0.1 weight percent to about 90 weight percent, in other embodiments from about 1 weight percent to about 90 weight percent, in further embodiments from about 10 weight percent to about 85 weight percent, in additional embodiments from about 20 weight percent to about 85 weight percent and in some embodiments from about 30 to about 80 weight percent with respect to the composite particle weights. A person of skill in the art will recognize that other ranges within these explicit ranges are contemplated and are within the present disclosure. In addition, the

amount the linker compounds bonded to the inorganic particles can be adjusted to vary the degree of crosslinking obtained with the polymer.

In some embodiments, a collection of composite particles have an average particle size of no more than about 10 microns. In further embodiments, collections of the composite particles can have an average particle diameter no more than about 2.5 microns, in further embodiments from about 4 nanometers (nm) to about 2.0 microns, in additional embodiments from about 5 nm to about 1.0 micron, in other embodiments from about 5 nm to about 500 nm and in additional embodiments from about 5 nm to about 250 nm, although for certain particle architectures and/or compositions it may be desirable to have larger particle diameters. A person of ordinary skill in the art will recognize that additional ranges of average particle diameters within the explicit ranges above are contemplated and are within the present disclosure. While certain particles can be roughly spherical in shape other particles can have other shapes. For non-spherical particles, the particle diameter can be obtained from an average of the distance across the particle along the three principle axes of the particle. Particle diameters are evaluated using transmission electron microscopy or scanning electron microscopy. Generally, the particles have high particle uniformity with respect to size and shape.

In general, the composite particles can have any reasonable architecture or combinations of architectures. Examples of composite particle morphology are given in Figs. 1-4. Referring to Fig. 1, composite particle 60 comprises a single inorganic particle 62 and a polymer overcoat 64. Referring to Fig. 2, composite particle 66 comprises interspersed inorganic particles 68 and a polymer matrix 70. Inorganic particles 68 may or may not all have the same composition. In other words, the inorganic particles can comprise a blend of different compositions distributed within the polymer matrix. Similarly, the polymer matrix can comprise a single polymer or a blend of different polymers. The particles can be essentially randomly dispersed or there may be some alignment due to interactions within the materials, for example is the particles were magnetic or if the polymer tended to impose a structure on the composite.

If the composite particles generally comprise a plurality of inorganic particles, there generally will be a distribution of numbers of inorganic particle within the composite particles. In some embodiments, a majority of the composite particles have a plurality of inorganic particles and in further embodiments at least about 95 percent of the composite particles have a plurality of inorganic particles. In some embodiments, essentially all of the composite particles have a plurality of inorganic particles. A person of ordinary skill in the art will recognize that

additional ranges of composite particle composition within the explicit ranges above are contemplated and are within the present disclosure.

Referring to Fig. 3, composite particle 74 comprises a core shell structure with a core 76, a first shell 78 and an optional second shell 80, although additional optional shells can also be present. While core 76, first shell 78 and second shell 80 have different compositions from each other, the composition can vary between them in a range of ways, such as different inorganic particles based on particle composition or particle dimensions, different polymer compositions, different loadings of inorganic particles, presence or absence of inorganic particles, different additive compositions, combinations thereof and the like. If the polymers in different portions of the composite are the same or somewhat miscible with other, the precise boundary between the core and shell and/or between different shells may or may not only be specified on average, and may be inferred approximately from the production approach if no direct measure of the structure is available. One core shell structure of particular interest involves particles that have an outer shell comprising a crosslinked polymer.

The proportion of the particle volume attributed to the core and/or a specific shell may be selected as desired, although generally the core diameter and or layer thickness is generally at least about 1 nm. However, in some embodiments, the composition may have a gradient roughly as a function of radius. These structures would correspond to essentially continuously changing shells, although atomic sizes provide a physical limit to the gradient in shell structure/composition. For example, the crosslinking density can be a function of the radial distance if mild crosslinking conditions crosslink from the exterior surface inward and the crosslinking is limited such that there is greater crosslinking toward the surface of the particles.

Referring to Fig. 4, composite particle 84 comprises an inner particle 86 and surface embedded inorganic particles 88. Inner particle 86 may or may not include other or the same inorganic particles. If inner particle 86 comprises inorganic particles, inner particle 86 can have any of the structures shown in Figs. 1-3. Inorganic particles 88 are embedded along the surface of inner particle 86, and the polymer of inner particle 86 holds inorganic particle 86 on the surface. The degree in which the surface particles are embedded generally can depend on the surface properties of the particles, the composition of the polymer and the method for forming the composite particles. In some embodiments, it is desirable for the embedded inorganic particles to have an average secondary particle diameter of no more than about 250 nm, in further embodiments no more than about 100 nm and in further embodiments from about 2 nm to about 50 nm. Overlayers can be placed over the particles with structures as shown in Fig. 4, such as a polymer layer.

Toner particles can be coated with inorganic particles or coated inorganic particles. Forming coatings with fumed silica are described further in U.S. Patent 6,190,815 and 6,004,714 both to Ciccarelli et al., entitled "Toner Compositions," both of which are incorporated herein by reference. In contrast with these approaches, Applicants describe herein using substantially unagglomerated inorganic particles, such as silica. While silica can be suitable as a surface coating, a range of other inorganic particles can be desirable as surface coatings. In particular, the surface coating inorganic particles can have an average secondary particle size of no more than about 100 nm, and in further embodiments from about 2 nm to about 50 nm. In addition, the inorganic particles can have the uniformity described herein. A person of ordinary skill in the art will recognize that additional ranges of average secondary particle size are contemplated and are within the present disclosure.

Polymers and inorganic particle constituents of the composite particles are described further in the following sections. Depending on the application, it may be desirable to incorporate one or more additional additives into the particles. The amount of additive can be selected based on the type of additive and the particular application. In general, these other additives can be, for example, pigments, dyes, viscosity modifiers, surfactants, such as cationic, anionic and nonionic surfactants, waxes, softening agents, crosslinking agents, catalysts, charge retention agents, charge control agents, anti-oxidants, other processing aids, suitable combinations thereof and the like. For forming toner particles, it may be particularly desirable to have a dye or pigment for forming a color toner. The inorganic particles can function as a pigment, or an organic or inorganic pigment/dye can be used.

Suitable dyes and pigments are generally known in the art. In some embodiments, the composite particles comprise from about 0.1 weight percent pigment to about 50 weight percent pigment and/or dye, and in further embodiments from about 0.5 weight percent pigment and/or dye to about 40 weight percent pigment and/or dye. A person of ordinary skill in the art will recognize that additional ranges of pigment and/or dye concentrations within the explicit ranges are contemplated and are within the present disclosure. With respect to black pigments, suitable pigments include, for example, pigments known in the art, such as carbon black and magnetites, generally iron oxides. Commercially available magnetites include, for example, MO8029 and MO8060 from Mapico, Inc., St. Louis, MO, Pfizer magnetites (CB4799, CB5300, CB5600, MCX6369), Bayer magnetites (BAYFERROX™ 8600, 8610), Northern Pigments magnetites (NP-604, NP-608), Magnox magnetities (TMB-100, TMB-104).

Desired pigments/dyes for color application are generally primary colors cyan, magenta, yellow or combinations thereof. For example, suitable dyes and pigments include, for example, 2,9-dimethyl substituted quinacridone and anthraquinone dyes, copper tetra(octadecyl sulfonamido) phthalocyanine, x-copper phthalocyanine pigment (color index CI 74160), diarylide yellow 3,3-dichlorobenzidene acetoacetanilides (CI 12700), 2,5-dimethoxy-4-sulfonamide phenylazo-4'-chloro-2,5-dimethoxy acetoacentanilide as well as pigments from Paul Uhlich & Co., Inc. (HELIOGEN BLUE ™ L6900, D7080, D7020, PYLAM OIL BLUE™, PYLAM OIL YELLLOW™, PIGMENT BLUE 1™), Dominion Color Corp., Ltd., Toronto, Ontario Canada (Pigment Violet 1, Pigment Red 48, Lemon Chrome Yellow DDC 1026™, E. D. TOLUIDINE RED™, BON RED C™), Hoechst (NOVAPERM YELLOW FGL™, HOSTAPERM PINK E™) and DuPont (CINQUASIA MAGENTA™). The formation of submicron solid organic pigment particles is described further in U.S. Patent 6,749,980 to Cheng et al., entitled "Toner Processes," incorporated herein by reference.

Toner particles can comprise charge additives, generally in the amount from 0.1 to about 5 weight percent. In the embodiments described herein, the inorganic particles may function as a charge additive, such that other charge additives may not be needed. Suitable additional charge additives include, for example, charge additives known in the art, such as alkyl pyridinium halides, bisulfates, distearyl dimethyl ammonium methyl sulfate, behenyl trimethyl ammonium methyl sulfate, alkyldimethylbenzyl ammonium salts, 4-azo-1-azoniabicyclo (2.2.2) octane salts and alkoxylated amines. Charge additives are described further in U.S. Patent 4,560,635 to Hoffend et al., entitled "Toner Compositions With Ammonium Sulfate Charge Enhancing Additives," incorporated herein by reference.

Waxes can be incorporated into a toner particle generally in amounts no more than about 10 weight percent. Suitable waxes include waxes known in the art such as waxes and wax emulsions available from Allied Chemical (polypropylenes, polyethylenes, chlorinated polypropylenes and polyethylenes and mixtures thereof), Petrolite Corp. (polypropylenes, polyethylenes, chlorinated polypropylenes and polyethylenes and mixtures thereof), Michaelman Inc., Daniels Product Co., Eastman Chemical Products, Inc. (EPOLENE N-15™). Sanyo Kasei K. K. (VISCOL 55-P™ a low average molecular weight polypropylene), Micro Powder Inc. (AQUA SUPERSLIP™ 6550 and 6530, functionalized waxes and fluorinated waxes POLYFLUO™ 190, 200, 523XF, AQUA POLYFLUO™ 411, AQUA POLYSILK™ 19, POLYSILK™ 14, mixed fluorinated and functionalized waxes MICROSPERSION 19™), and S. C. Johnson Wax (functionalized acrylic polymer emulsions JONCRYL™ 74, 89, 130,

537, and 538). Other suitable waxes include, for example, solid paraffin wax, rice wax, amide wax, fatty acid wax, fatty acid metallic salt wax, fatty ester wax, partially-saponified fatty ester wax, silicon wax and carnauba wax.

Inorganic Particles

In general, any reasonable inorganic particles can be used to form the composites. In some embodiments, the particles have an average diameter of no more than about one micron. The composition of the particles generally is selected to impart desired properties to the composite. Thus, in the formation of toners for example, the color and electrical properties of the inorganic particles can be significant.

Small and uniform inorganic particles can provide processing advantages with respect to forming small and uniform composite particles. In addition, small inorganic particles have desirable properties for optical applications including, for example, a shifted absorption spectrum and reduced scattering. Suitable nanoparticles can be formed, for example, by laser pyrolysis, flame synthesis, combustion, or sol gel approaches. In particular, laser pyrolysis is useful in the formation of particles that are highly uniform in composition, crystallinity and size. Laser pyrolysis involves light from an intense light source that drives the reaction to form the particles. Laser pyrolysis is an excellent approach for efficiently producing a wide range of nanoscale particles with a selected composition and a narrow distribution of average particle diameters. Alternatively, submicron particles can be produced using a flame production apparatus such as the apparatus described in U.S. Patent 5,447,708 to Helble et al., entitled "Apparatus for Producing Nanoscale Ceramic Particles," incorporated herein by reference. Furthermore, submicron particles can be produced with a thermal reaction chamber such as the apparatus described in U.S. Patent 4,842,832 to Inoue et al., "Ultrafine Spherical Particles of Metal Oxide and a Method for the Production Thereof," incorporated herein by reference. In addition, various solution-based approaches can be used to produce some compositions of submicron particles, such as sol gel techniques.

Highly uniform particles can be formed by light-based pyrolysis, e.g., laser pyrolysis, which can be used to form submicron particles with extremely uniform properties with a variety of selectable compositions. For convenience, light-based pyrolysis is referred to as laser pyrolysis since this terminology reflects the convenience of lasers as a radiation source and is a conventional term in the art. Laser pyrolysis approaches discussed herein incorporate a reactant flow that can involve gases, vapors, aerosols or combinations thereof to introduce desired elements into the flow stream. The versatility of generating a reactant stream with

gases, vapor and/or aerosol precursors provides for the generation of particles with a wide range of potential compositions.

A collection of submicron/nanoscale particles may have an average diameter for the primary particles of less than about 500 nm, preferably from about 2 nm to about 100 nm, alternatively from about 2 nm to about 75 nm, or from about 2 nm to about 50 nm. A person of ordinary skill in the art will recognize that other ranges within these specific ranges are covered by the disclosure herein. Particle diameters are evaluated by transmission electron microscopy.

Particles refer to physical particles, which are unfused, so that any fused primary particles are considered as an aggregate, i.e. a physical particle. As noted more below, the particles are generally effectively the same as the primary particles, i.e., the primary structural element within the material. If there is hard fusing of some primary particles, these hard fused particles form secondary physical particles. The secondary particles, if any are present, are physical particles for the consideration of particle size. The particles can have a roughly spherical gross appearance, or they can have rod shapes, plate shapes or other non-spherical shapes. Upon closer examination, crystalline particles generally have facets corresponding to the underlying crystal lattice. Amorphous particles generally have a spherical aspect. Diameter measurements on particles with asymmetries are based on an average of length measurements along the principle axes of the particle.

Because of their small size, the particles tend to form loose agglomerates due to van der Waals and other electromagnetic forces between nearby particles. These loose agglomerates can be dispersed in a dispersant to a significant degree based on the primary particles, and in some embodiments approximately completely to form dispersed primary particles. The size of the dispersed particles can be referred to as the secondary particle size. The primary particle size, of course, is the lower limit of the secondary particle size for a particular collection of particles, so that the average secondary particle size preferably is approximately the average primary particle size. The secondary or agglomerated particle size may depend on the subsequent processing of the particles following their initial formation and the composition and structure of the particles. In some embodiments, the secondary particles have an average diameter no more than about 1000 nm, in additional embodiments no more than about 500 nm, in further embodiments from about 2 nm to about 300 nm, in other embodiments about 2 nm to about 100 nm, and alternatively about 2 nm to about 50 nm. A person of ordinary skill in the art will recognize that other ranges within these specific ranges are contemplated and are within the present disclosure. Secondary particles sizes within a

liquid dispersion can be measured by established approaches, such as dynamic light scattering. Suitable particle size analyzers include, for example, a Microtrac UPA instrument from Honeywell based on dynamic light scattering, a Horiba Particle Size Analyzer from Horiba, Japan and ZetaSizer Series of instruments from Malvern based on Photon Correlation Spectroscopy. The principles of dynamic light scattering for particle size measurements in liquids are well established.

Even though the particles may form loose agglomerates, the nanometer scale of the particles is clearly observable in transmission electron micrographs of the particles. The particles generally have a surface area corresponding to particles on a nanometer scale as observed in the micrographs. Furthermore, the particles can manifest unique properties due to their small size and large surface area per weight of material. For example, the absorption spectrum of crystalline, nanoscale TiO_2 particles is shifted into the ultraviolet.

The particles can have a high degree of uniformity in size. Laser pyrolysis generally results in particles having a very narrow range of particle diameters. Furthermore, heat processing under suitably mild conditions generally does not significantly alter the very narrow range of particle diameters. With aerosol delivery of reactants for laser pyrolysis, the distribution of particle diameters is particularly sensitive to the reaction conditions. Nevertheless, if the reaction conditions are properly controlled, a very narrow distribution of particle diameters can be obtained with an aerosol delivery system. As determined from examination of transmission electron micrographs, the particles generally have a distribution in sizes such that at least about 95 percent, and in some embodiments 99 percent, of the particles have a diameter greater than about 40 percent of the average diameter and less than about 160 percent of the average diameter. In embodiments of particular interest, the particles have a distribution of diameters such that at least about 95 percent, and in some embodiments 99 percent, of the particles have a diameter greater than about 60 percent of the average diameter and less than about 140 percent of the average diameter. A person of ordinary skill in the art will recognize that other ranges of uniformity within these specific ranges are covered by the disclosure herein.

Furthermore, in some embodiments no particles have an average diameter greater than about 5 times the average diameter, in other embodiments about 4 times the average diameter, in further embodiments 3 times the average diameter, and in additional embodiments 2 times the average diameter. In other words, the particle size distribution effectively does not have a tail indicative of a small number of particles with significantly larger sizes. This is a result of the small reaction region to form the inorganic particles and corresponding rapid quench of the

inorganic particles. An effective cut off in the tail of the size distribution indicates that there are less than about 1 particle in 10^6 have a diameter greater than a specified cut off value above the average diameter. High particle uniformity can be exploited in a variety of applications.

In addition, the nanoparticles for incorporation into the composite particles may have a very high purity level. Furthermore, crystalline nanoparticles, such as those produced by laser pyrolysis, can have a high degree of crystallinity. Similarly, the crystalline nanoparticles produced by laser pyrolysis can be subsequently heat processed to improve and/or modify the degree of crystallinity and/or the particular crystal structure. Impurities on the surface of the particles may be removed by heating the particles to achieve not only high crystalline purity but high purity overall.

A basic feature of successful application of laser pyrolysis for the production of desirable inorganic nanoparticles is the generation of a reactant stream containing one or more metal/metalloid precursor compounds, a radiation absorber and, in some embodiments, a secondary reactant. The secondary reactant can be a source of non-metal/ metalloid atoms, such as oxygen, required for the desired product and/or can be an oxidizing or reducing agent to drive a desired product formation. A secondary reactant may not be used if the precursor decomposes to the desired product under intense light radiation. Similarly, a separate radiation absorber may not be used if the metal/metalloid precursor and/or the secondary reactant absorb the appropriate light radiation. The reaction of the reactant stream is driven by an intense radiation beam, such as a light beam, e.g., a laser beam. As the reactant stream leaves the radiation beam, the inorganic particles are rapidly quenched.

A laser pyrolysis apparatus suitable for the production of commercial quantities of particles by laser pyrolysis has been developed using a reactant inlet that is significantly elongated in a direction along the path of the laser beam. This high capacity laser pyrolysis apparatus, e.g., 1 kilogram or more per hour, is described in U.S. Patent 5,958,348, entitled "Efficient Production Of Particles By Chemical Reaction," incorporated herein by reference. Approaches for the delivery of aerosol precursors for commercial production of particles by laser pyrolysis is described in copending and commonly assigned U.S. Patent 6,193,936 to Gardner et al., entitled "Reactant Delivery Apparatus," incorporated herein by reference.

In general, nanoparticles produced by laser pyrolysis can be subjected to additional processing to alter the nature of the particles, such as the composition and/or the crystallinity. For example, the nanoparticles can be subjected to heat processing in a gas atmosphere prior to use. Under suitably mild conditions, heat processing is effective to modify the characteristics of the particles without destroying the nanoscale size or the narrow particle size distribution of

the initial particles. For example, heat processing of submicron vanadium oxide particles is described in U.S. Patent 5,989,514 to Bi et al., entitled "Processing Of Vanadium Oxide Particles With Heat," incorporated herein by reference.

A wide range of simple and complex submicron and/or nanoscale particles have been produced by laser pyrolysis with or without additional heat processing. In general, the inorganic particles generally include metal or metalloid elements in their elemental form or in compounds. Specifically, the inorganic particles can include, for example, elemental metal or elemental metalloid, i.e. un-ionized elements such as silver or silicon, metal/metalloid oxides, metal/metalloid nitrides, metal/metalloid carbides, metal/metalloid sulfides or combinations thereof. In addition, there is the capability for producing nano-particulate carbon materials. Complex systems of ternary and quaternary compounds have also been made. In addition, uniformity of these high quality materials can be substantial. These particles generally can have a very narrow particle size distribution. Availability of a wide range of compositions and crystal structures of nanoparticles provides a corresponding significant range in potential combinations between nanoparticles and polymers as well as properties for the resulting composites.

With respect to the electrical properties of the particles, some particles include compositions such that the particles are electrical conducting, electrical insulators or electrical semiconductors. Suitable electrical conductors include, for example, elemental metals and some metal compositions. Electrical conductors, such as metals, generally have a room temperature resistivity of no more than about 1×10^{-3} Ohm-cm. Electrical insulators generally have a room temperature resistivity of at least about 1×10^{5} Ohm-cm. Electrical semiconductors include, for example, silicon, GaN, CdS and InP. Semiconducting crystals can be classified to include so called, II-VI compounds, III-V compounds and group IV compounds, where the number refers to the group in the periodic table. Semiconductors are characterized by a large increase in conductivity with temperature in pure form and an increase in electrical conductivity by orders of magnitude upon doping with electrically active impurities. Semiconductors generally have a band gap that results in the observed conductivity behavior. At room temperature, the conductivity of a semiconductor is generally between that of a metal and a good electrical insulator.

Several different types of nanoscale particles have been produced by laser pyrolysis. Elemental carbon particles generally may or may not be considered inorganic materials. As used herein, carbon particles as carbonaceous solids, such as fullerenes, nanotubes, graphite, and carbon black are not considered inorganic particles and are considered distinguishable

from both inorganic materials and organic materials for clear separate identification. Selected inorganic particles can generally be characterized as comprising a composition with a number of different elements that are present in varying relative proportions, where the number and the relative proportions are selected based on the application for the nanoscale particles. Materials that have been produced (possibly with additional processing, such as a heat treatment) or have been described in detail for production by laser pyrolysis include, for example, carbon particles, silicon, SiO_2, doped SiO_2, titanium oxide (anatase and rutile TiO_2), MnO, Mn_2O_3, Mn_3O_4, Mn_5O_8, vanadium oxide, silver vanadium oxide, lithium manganese oxide, aluminum oxide (γ-Al_2O_3, delta-Al_2O_3 and theta-Al_2O_3), doped-aluminum oxide (alumina), tin oxide, zinc oxide, rare earth metal oxide particles, rare earth doped metal/metalloid nitride particles, rare earth metal/metalloid sulfides, rare earth doped metal/metalloid sulfides, silver metal, iron, iron oxide, iron carbide, iron sulfide ($Fe_{1-x}S$), cerium oxide, zirconium oxide, barium titanate ($BaTiO_3$), aluminum silicate, aluminum titanate, silicon carbide, silicon nitride, and metal/metalloid compounds with complex anions, for example, phosphates, silicates and sulfates. The production of a range of particles by laser pyrolysis is described further in copending U.S. Patent Application serial number 10/195,851 to Bi et al., entitled "Nanoparticle Production and Corresponding Structures," incorporated herein by reference.

Submicron and nanoscale particles can be produced with selected dopants using laser pyrolysis and other flowing reactor systems. Amorphous powders and crystalline powders can be formed with complex compositions comprising a plurality of selected dopants. The powders can be used to form optical materials and the like. Amorphous submicron and nanoscale powders and glass layers with dopants, such as rare earth dopants and/or other metal dopants, are described further in copending and commonly assigned U.S. Patent 6,849,334 to Horne et al., entitled "Optical Materials And Optical Devices," incorporated herein by reference. Crystalline submicron and nanoscale particles with dopants, such as rare earth dopants, are described further in copending and commonly assigned U.S. Patent Application serial number 09/843,195 to Kumar et al., entitled "High Luminescence Phosphor Particles," incorporated herein by reference.

The dopants can be introduced at desired quantities by varying the composition of the reactant stream. The dopants are introduced into an appropriate host material by appropriately selecting the composition in the reactant stream and the processing conditions. Thus, submicron particles incorporating one or more metal or metalloid elements as host composition with selected dopants, including, for example, rare earth dopants and/or complex blends of

dopant compositions, can be formed. For embodiments in which the host materials are oxides, an oxygen source should also be present in the reactant stream. For these embodiments, the conditions in the reactor should be sufficiently oxidizing to produce the oxide materials.

Furthermore, dopants can be introduced to vary properties of the resulting particles. For example, dopants can be introduced to change the optical properties of the particles that are subsequently incorporated into polymer-inorganic particle composite particles. For optical applications, the index-of-refraction can be varied to form specific optical devices that operate with light of a selected frequency range or dopants can introduce fluorescent or phosphorescent properties to the particles such that they can function as phosphors. Dopants can also be introduced to alter the processing properties of the material. Furthermore, dopants can also interact within the materials. For example, some dopants are introduced to increase the solubility of other dopants.

In some embodiments, the one or plurality of dopants are rare earth metals or rare earth metals with one or more other dopant elements. Rare earth metals comprise the transition metals of the group IIIb of the periodic table. Specifically, the rare earth elements comprise Sc, Y and the Lanthanide series. Other suitable dopants comprise elements of the actinide series. For optical glasses, the rare earth metals of particular interest as dopants comprise, for example, Ho, Eu, Ce, Tb, Dy, Er, Yb, Nd, La, Y, Pr and Tm. Generally, the rare earth ions of interest have a +3 ionization state, although Eu^{+2} and Ce^{+4} are also of interest. Rare earth dopants can influence the optical absorption properties that can alter the application of the materials for the production of optical amplifiers and other optical devices. Suitable non-rare earth dopants for various purposes include, for example, Bi, Sb, Zr, Pb, Li, Na, K, Ba, B, Si, Ge, W, Ca, Cr, Ga, Al, Mg, Sr, Zn, Ti, Ta, Nb, Mo, Th, Cd and Sn.

As noted above, laser pyrolysis has been used to produce a range of powder compositions. The compositions can include multiple metal/metalloid elements. A representative sample of references relating to some of these powder materials is presented in the following.

As a first example of nanoparticle production, the production of silicon oxide nanoparticles is described in copending and commonly assigned U.S. Patent Application Serial Number 09/085,514 to Kumar et al., entitled "Silicon Oxide Particles," incorporated herein by reference. This patent application describes the production of amorphous SiO_2. The synthesis by laser pyrolysis of silicon carbide and silicon nitride is described in copending and commonly assigned U.S. Patent Application Serial No. 09/433,202 to Reitz et al. filed on November 5, 1999, entitled "Particle Dispersions," incorporated herein by reference. The

production of silicon particles by laser pyrolysis is described in an article by Cannon et al., J. of the American Ceramic Society, Vol. 65, No. 7, pp. 330-335 (1982), entitled Sinterable Ceramic Particles From Laser-Driven Reactions: II, Powder Characteristics And Process Variables," incorporated herein by reference.

The production of titanium oxide nanoparticles and crystalline silicon dioxide nanoparticles is described in copending and commonly assigned, U.S. Patent Application Serial Number 09/123,255 to Bi et al., entitled "Metal (Silicon) Oxide/Carbon Composites," incorporated herein by reference. In particular, this application describes the production of anatase and rutile TiO_2. The production of aluminum oxide nanoparticles is described in copending and commonly assigned, U.S. Patent Application Serial Number 09/136,483 to Kumar et al., entitled "Aluminum Oxide Particles," incorporated herein by reference. In particular, this application disclosed the production of γ-Al_2O_3. Suitable liquid, aluminum precursors with sufficient vapor pressure of gaseous delivery include, for example, aluminum s-butoxide ($Al(OC_4H_9)_3$). Also, a number of suitable solid, aluminum precursor compounds are available including, for example, aluminum chloride ($AlCl_3$), aluminum ethoxide ($Al(OC_2H_5)_3$), and aluminum isopropoxide ($Al[OCH(CH_3)_2]_3$).

Furthermore, mixed metal nitride nanoparticles have been produced by laser pyrolysis along with or without subsequent heat processing, as described in copending and commonly assigned U.S. Patent Applications Serial No. 09/188,768 to Kumar et al., entitled "Composite Metal Oxide Particles," and 09/334,203 to Kumar et al., entitled "Reaction Methods for Producing Ternary Particles," and U.S. Patent 6,136,287 to Horne et al., entitled "Lithium Manganese Oxides and Batteries," all three of which are incorporated herein by reference. The formation of submicron and nanoscale particles comprising metal/metalloid compounds with complex anions is described in copending and commonly assigned U.S. Patent Application serial number 09/845,985 to Chaloner-Gill et al., entitled "Phosphate Powder Compositions And Methods For Forming Particles With Complex Anions," incorporated herein by reference. Suitable complex anions include, for example, phosphates, silicates and sulfates.

As noted above, the inorganic particles can function as pigments, either black or a specific color, charge control agents and/or surface modifiers. Suitable charge control agents and/or surface modifiers include, for example, SiO_2, TiO_2 and Al_2O_3. Suitable colorants include, for example, doped compounds, including doped phosphor compositions. Phosphor compositions that can be used as colorants are described further, for example, in U.S. Patent 6,692,660 to Kumar et al., entitled "High Luminescent Phorphor Particles,"

incorporated herein by reference. Also, quantum confined particles can be used as colorants in which quantum confined particles has very small and uniform particle diameters with a controlled particle size such that the inorganic particle size itself determines the color of the particles. Quantum confined particles of CdS and CdSe are described in U.S. Patent 5,505,928 to Alivisatos et al., entitled "Preparation of III-V Semiconductor Nanocrystals," incorporated herein by reference.

Furthermore, the composition of mixed metal oxides can be varied to select the color of the resulting inorganic particles. $In_xGa_{1-x}N$ is one mixed metal composition of particular interest. These particles can be formed using laser pyrolysis. Suitable precursors of In include, for example, indium trichloride, and suitable precursors for Ga include, for example, gallium metal, organometallic gallium, gallium oxide, and/or gallium trifluoride. The nitride can be formed using laser pyrolysis using a nitrogen precursor, such as ammonia, in the absence of oxygen atoms. The band gap of the semiconductor is a function of the value of x, i.e., the ration of In to Ga. The value of x of the particles can be selected through the selection of the amounts of the metal precursors in the reactive flow. For example, $In_{0.1}Ga_{0.9}N$ yields a material with a violet color while $In_{0.4}Ga_{0.6}N$ yields a material with a red color.

Polymers and Internal Material Structure

As noted above, the polymer-inorganic particle composites may or may not involve chemical bonding between the inorganic particles and the polymers. Chemical bonding is considered to broadly cover bonding with some covalent character with or without partial ionic bonding character and can have properties of ligand-metal bonding. Covalent bonding refers broadly to covalent bonds with sigma bonds, pi bonds, other delocalized covalent bonds and/or other covalent bonding types, and may be polarized bonds with or without ionic bonding components and the like. In other embodiments, the inorganic particles are simply embedded within the polymer matrix by the physical properties of the matrix. For convenience, blends not involving chemical bonding between the inorganic particles and the polymer matrix are called polymer-inorganic particle mixtures, while blends having chemical bonding between at least a portion of the inorganic particles and the polymer are called bonded composites. Of course, polymer-inorganic particle mixtures generally involve non-bonding electrostatic interactions, such as van der Waals interactions, between the polymer and the inorganic particles.

While mixtures are suitable in many contexts, the formation of polymer-inorganic particle bonded composites can have advantages with respect to stability and uniformity of the blend. Specifically, high particle loadings can be achieved in a bonded composite without significant agglomeration of the particles, provided that the particles are functionalized with groups that do not easily bond to themselves, which can result in the formation of hard agglomerates. In addition, in relevant embodiments, the amount the linker compounds bonded to the inorganic particles can be adjusted to vary the degree of crosslinking obtained with the polymer.

The composites with bonding between the polymer and the inorganic particles comprise a monomer/polymer component, inorganic particles, and optional linker compounds that bridge the inorganic particles and the monomer/polymer. In the case of monomer units being joined to the linker compound, a polymer can be formed with the formation of the composite. For simplicity in notation, the monomer/polymer unit joined with the linker and assembled into the composite can be referred to generally as a polymer, although it is recognized that in some cases the unit can be a monomer or polymer, such as a dimer, trimer or larger polymer structures.

The linker compounds have two or more functional groups. One functional group of the linker is suitable for chemical bonding to the inorganic particles. One functional group can be selected based on the composition of the inorganic particle. Another functional group of the linker is suitable for covalent bonding with the polymer. Convenient linkers include, for example, functionalized organic molecules.

Various structures can be formed based on embodiments involving the formation of chemically bonded polymer/inorganic particle composites. The structures obtained will generally depend on the relative amounts of polymer/monomers, linkers and inorganic particles as well as the synthesis process itself. Linkers may be identified also as coupling agents or crosslinkers. Furthermore, in some embodiments, polymer-inorganic particle bonded composites, as well as polymer-inorganic particle mixtures, can comprise a plurality of different polymers and/or a plurality of different inorganic particles. Similarly, if a poly-inorganic particle blend comprises a plurality of different polymer and/or a plurality of different inorganic particles, all of the polymer and/or inorganic particles can be chemically bonded within the composite or, alternatively, only a fraction of the polymers and inorganic particles can be chemically bonded within the composite. If only a fraction of the polymer and/or inorganic particles are chemically bonded, the fraction bonded can be a random portion or a specific fraction of the total polymer and/or inorganic particles.

To form the desired bonded composites, the inorganic particles can be modified on their surface by chemical bonding to one or more linker molecules. The ratio of linker composition to inorganic particles can be at least one linker molecule per inorganic particle. The linker molecules surface modify the inorganic particles, i.e., functionalize the inorganic particles. While the linker molecules can bond to the inorganic particles, they can be, but are not necessarily, bonded to the inorganic particles prior to bonding to the polymers. They can be bonded first to the polymers and only then bonded to the particles. Alternatively, they can bond to the two species simultaneously. Similarly, the inorganic particles can be surface modified with compositions that interact, and generally chemically bond, with the surface of the inorganic particles but do not have functional groups that bond with the polymer. However, surface modification alone can be useful to aid with dispersion and/or to provide other processing advantages.

In some embodiments, the linker is applied to form at least a significant fraction of a monolayer on the surface of the particles. In particular, for example, at least about 20% of a monolayer can be applied to the particles, and in other embodiments, at least about 40% of a monolayer can be applied. Based on the measured BET surface areas of the particles, a quantity of linker can be used corresponding up to coverage about 1/2, 1 and 2 of the particle surface relative to a monolayer of the linker. A person of ordinary skill in the art will recognize that other ranges within these explicit ranges are contemplated and are within the present disclosure. A monolayer is calculated based on measured surface area of the particles and an estimate of the molecular radius of the linker based on accepted values of the atomic radii. Excess linker reagent can be added because not all of the linker binds and some self-polymerization of the linker reagent can take place. To calculate the coverage, the linker can be assumed to bond to the particle normal to the surface. This calculation provides an estimate of the coverage.

The inorganic particles can be bonded through the linker compound into the polymer structure, or the particles can be grafted to polymer side groups. The bonded inorganic particles can, in most embodiments, crosslink the polymer. Specifically, most embodiments involve star crosslinking of a single inorganic particle with several polymer groups. The structure of the composite can generally be controlled by the density of linkers, the length of the linkers, the chemical reactivity of the coupling reaction, the density of the reactive groups on the polymer as well as the loading of particles and the molecular weight range of the polymer (i.e., monomer/polymer units). In alternative embodiments, the polymer has functional groups that bond directly with the inorganic particles, either at terminal sites or at

side groups. In these alternative embodiments, the polymer includes functional groups comparable to appropriate linker functional groups for bonding to the inorganic particles.

A range of polymers is suitable for incorporation into the composites, including, without limitation, organic polymers, inorganic polymers, such as polysiloxanes, and combinations and copolymers thereof. If the polymers are formed prior to reacting with the functionalized inorganic particles, the molecular weights of the polymers can be selected to vary to properties of the resulting composite. The polymer is selected or synthesized to include appropriate functional groups to covalently bond with functional groups of the linker compound.

The frame of the linker supporting the functional groups is generally an organic compound, although it may also include silyl and/or siloxy moieties. The organic linker frame can comprise any reasonable organic moiety including, for example, linear or branched carbon chains, cyclical carbon moieties, saturated carbon moieties, unsaturated carbon moieties, aromatic carbon units, halogenated carbon groups and combinations thereof. The structure of the linker can be selected to yield desirable properties of the composite. For example, the size of the linker is a control parameter that may affect the periodicity of the composite and the self-organization properties.

Many different types of polymers are suitable for incorporation into the composites. In bonded composite embodiments, the polymers generally can have terminal groups and/or side groups capable of bonding to a linker or directly to the inorganic particles. Whether or not the polymers are chemically bonded to the inorganic particles, suitable organic polymers include, for example, polyamides (nylons), polyimides, polycarbonates, polyurethanes, polyacrylonitrile, polyacrylic acid, polyacrylates, polyacrylamides, polyvinyl alcohol, polyvinyl chloride, heterocyclic polymers, polyesters, modified polyolefins and copolymers and mixtures thereof. Composites formed with nylon polymers, i.e., polyamides, and inorganic nanoparticles can be called Nanonylon™. Suitable polymers include conjugated polymers within the polymer backbone, such as polyacetylene, and aromatic polymers within the polymer backbone, such as poly(p-phenylene), poly(phenylene vinylene), polyaniline, polythiophene, poly(phenylene sulfide), polypyrrole and copolymers and derivatives thereof. Some polymers can be bonded to linkers at functional side groups. The polymer can inherently include desired functional groups, can be chemically modified to introduce desired functional groups or copolymerized with monomer units to introduce portions of desired functional groups. Similarly, some composites include only a single polymer/monomer composition bonded into the composite. Within a crosslinked structure, a polymer is

identifiable by 3 or more repeat units along a chain, except for hydrocarbon chains which are not considered polymers unless they have a repeating side group or at least about 50 carbons - carbon bonds within the chain.

Suitable silicon-based polymers include polysilanes, polysiloxane (silicone) polymers, such as poly(dimethylsiloxane) (PDMS) and copolymers and mixtures thereof as well as copolymers and mixtures with organic polymers. Polysiloxanes are particularly suitable for forming composites with grafted inorganic particles. To form these grafted composites, the polysiloxanes can be modified with amino and/or carboxylic acid groups. Polysiloxanes are desirable polymers because of their transparency to visible and ultraviolet light, high thermal stability, resistance to oxidative degradation and its hydrophobicity. Other inorganic polymers include, for example, phosphazene polymers (phosphonitrile polymers).

Appropriate functional groups for binding with the polymer depend on the functionality of the polymer. Generally, the functional groups of the polymers and the linker can be selected appropriately based on known bonding properties. For example, carboxylic acid groups bond covalently to thiols, amines (primary amines and secondary amines) and alcohol groups. As a particular example, nylons can include unreacted carboxylic acid groups, amine groups or derivatives thereof that are suitable form covalently bonding to linkers. In addition, for bonding to acrylic polymers, a portion of the polymer can be formed from acrylic acid or derivatives thereof such that the carboxylic acid of the acrylic acid can bond with amines (primary amines and secondary amines), alcohols or thiols of a linker. The functional groups of the linker can provide selective linkage either to only particles with particular compositions and/or polymers with particular functional groups. Other suitable functional groups for the linker include, for example, halogens, silyl groups ($-SiR_{3-x}H_x$), isocyanate, cyanate, thiocyanate, epoxy, vinyl silyls, silyl hydrides, silyl halogens, mono-, di- and trihaloorganosilane, phosphonates, organometalic carboxylates, vinyl groups, allyl groups and generally any unsaturated carbon groups (-R'-C=C-R"), where R' and R" are any groups that bond within this structure. Selective linkage can be useful in forming composite structures that exhibit self-organization.

Upon reaction of the polymer functional groups with the linker functional groups, the identity of initial functional groups is merged into a resultant or product functional group in the bonded structure. A linkage is formed that extends from the polymer. The linkage extending from the polymer can include, for example, an organic moiety, a siloxy moiety, a sulfide moiety, a sulphonate moiety, a phosphonate moiety, an amine moiety, a carbonyl moiety, a hydroxyl moiety, or a combination thereof. The identity of the original functional groups may

or may not be apparent depending on the resulting functional group. The resulting functional groups generally can be, for example, an ester group, an amide group, an acid anhydride group, an ether group, a sulfide group, a disulfide group, an alkoxy group, a hydrocarbyl group, a urethane group, an amine group, an organo silane group, a hydridosilane group, a silane group, an oxysilane group, a phosphonate group, a sulphonate group or a combination thereof.

If a linker compound is used, one resulting functional group generally is formed where the polymer bonds to the linker and a second resulting functional group is formed where the linker bonds to the inorganic particle. At the inorganic particle, the identification of the functional group may depend on whether particular atoms are associated with the particle or with the functional group. One or more atoms of the inorganic particle are involved in forming the bond between the linker and the inorganic particle. It may be ambiguous if an atom in the resulting linkage originates from the linker compound or the inorganic particle. This is just a nomenclature issue, and a person of skill in the art can identify the resulting structures without concern about the particular allocation of atoms to the functional group. In any case, a resulting or product functional group is formed joining the linker molecule and the inorganic particle. The resulting functional group can be, for example, one of the functional groups described above resulting from the bonding of the linker to the polymer. As a specific example, the bonding of a carboxylic acid with an inorganic particle may result in a group involving bonding with a non-metal/metalloid atom of the particle; however, an oxo group is generally present in the resulting functional group regardless of the composition of the particle. Ultimately, a bond extends to a metal/ metalloid atom.

Appropriate functional groups for bonding to the inorganic particles depends on the character of the inorganic particles. U.S. Patent 5,494,949 to Kinkel et al., entitled "SURFACE-MODIFIED OXIDE PARTICLES AND THEIR USE AS FILLERS AND MODIFYING AGENTS IN POLYMER MATERIALS," incorporated herein by reference, describes the use of silylating agents for bonding to metal/metalloid oxide particles. The particles have alkoxy modified silane for bonding to the particles. For example, preferred linkers for bonding to metal/metalloid oxide particles include $R^1R^2R^3$-Si-R^4, where R^1, R^2, R^3 are alkoxy groups, which can hydrolyze and bond with the particles, and R^4 is a group suitable for bonding to the polymer. Trichlorosilicate (-$SiCl_3$) functional groups can react with an hydroxyl group at the metal oxide particle surface by way of a condensation reaction.

Generally, thiol groups can be used to bind to metal sulfide particles and certain metal particles, such as gold, silver, cadmium and zinc. Carboxyl groups can bind to other metal particles, such as aluminum, titanium, zirconium, lanthanum and actinium. Similarly, amines

and hydroxide groups would be expected to bind with metal oxide particles and metal nitride particles, as well as to transition metal atoms, such as iron, cobalt, palladium and platinum.

In some embodiments, the polymer incorporates the inorganic particles into the polymer network. This can be performed by reacting a functional group of the linker compound with terminal groups of a polymer molecule. Alternatively, the inorganic particles can be present during the polymerization process such that the functionalized inorganic particles are directly incorporated into the polymer structure as it is formed. In other embodiments, the inorganic particles are grafted onto the polymer by reacting the linker functional groups with functional groups on polymer side groups. In any of these embodiments, the surface modified/functionalized inorganic particles can crosslink the polymer if there are sufficient linker molecules, i.e., enough to overcome energetic barriers and form at least two or more bonded links to the polymer. Generally, an inorganic particle has many linkers associated with the particle. Thus, in practice, the crosslinking depends on the polymer-particle arrangement, statistical interaction of two crosslinking groups combined with molecular dynamics and chemical kinetics.

Block copolymers can be used such that the different blocks of the polymer segregate, which is a conventional property of selected block copolymers. Suitable block copolymers include, for example, polystyrene-block-poly(methyl methacrylate), polystyrene-block-polyacrylamide, polysiloxane-block-polyacrylate and mixtures thereof. These block copolymers can be modified to include appropriate functional groups to bond with the linkers, if desired. For example, polyacrylates can be hydrolyzed or partly hydrolyzed to form carboxylic acid groups, or acrylic acid moieties can be substituted for all or part of the acrylated during polymer formation if the acid groups do not interfere with the polymerization. Alternatively, the ester groups in the acrylates can be substituted with ester bonds to diols or amide bonds with diamines such that one of the functional groups remains for bonding with a linker. Block copolymers with other numbers of blocks and other types of polymer compositions can be used.

The inorganic particles can be associated with only one of the polymer compositions within the block such that the inorganic particles are segregated together with that polymer composition within the segregation block copolymer. For example, an AB di-block copolymer can include inorganic particles only within block A. Segregation of the inorganic particles can have functional advantages with respect to taking advantage of the properties of the inorganic particles. Similarly, tethered inorganic particles may separate relative to the polymer by analogy to different blocks of a block copolymer if the inorganic particles and the

corresponding polymers have different solvation properties. In addition, the nanoparticles themselves can segregate relative to the polymer to form a self-organized structure. The block copolymers can have more than two blocks, such as ABC or ABA triblock copolymers.

The segregation of different polymer blocks can result in self-organization within the composite particles. For example, the segregated layers can result in a functional core-shell structure. A schematic diagram of a segregated block copolymer composite within a composite particle 90 is shown in Fig. 5. For illustration, a first polymer block 92 within core 94 is depicted with sharp bend, while a second polymer block 96 within shell 98 is depicted with curves. In this embodiment, inorganic particles 100 are depicted in association with first polymer block 92, although other configurations can be found in other embodiments. For example, the inorganic particles can be associated with the second polymer block in the shell, or the same or different inorganic particles can be associated with both blocks. The structure in Fig. 5 has some analogies with the structure in Fig. 3. Dashed lines schematically indicate a rough separation of core 94 from shell 98 and other exterior surface of composite particle 90.

Other ordered copolymers include, for example, graft copolymers, comb copolymers, star-block copolymers, dendrimers, mixtures thereof and the like. Ordered copolymers of all types can be considered a polymer blend in which the polymer constituents are chemically bonded to each other. Dendrimers in particular can have advantageous structures for the formation of composite particles. Specifically, dendrimers are highly branched polymers that can form structures with cavities that can hold inorganic particles. Dendrimers can be functionalized as appropriate.

Physical polymer combinations may also be used and may also exhibit self-organization. Polymer combinations involve mixtures of chemically distinct polymers. The polymers can segregate into a core-shell structure as shown in Fig. 3. The inorganic particles may bond to only a subset of the polymer species, as described above for block copolymers. Physical polymer combinations can exhibit self-organization similar to block copolymers. The presence of the inorganic particles can sufficiently modify the properties of the composite that the interaction of the polymer with inorganic particles interacts physically with the other polymer species differently than the native polymer alone. In particular, the presence of nanoparticles within the polymer-inorganic particle blends can result in a blend that is sensitive to weak fields due to the small particle size. This sensitivity can be advantageously used in the formation of devices. Processes making use of small particles generally can be referred to as a soft matter approach.

Exemplary embodiments of polymer-inorganic particle composites are described further in copending and commonly assigned U.S. Patent 6,599,631 to Kambe et al., entitled "Polymer-Inorganic Particle Composites," incorporated herein by reference, and copending U.S. Patent Application serial number 10/083,967 to Kambe et al., entitled "Structures Incorporating Polymer-Inorganic Particle Blends," incorporated herein by reference.

Apparatus For In-Flow Processing

A reaction apparatus for in-flight processing accommodates a flow path that provides for a reaction to form the inorganic particles as well as for application of a coating composition and/or for the application of radiation to the flow following formation of the inorganic particle. A reactant delivery portion initiates a flow comprising precursors for the formation of the inorganic particles. Also, the reaction apparatus generally interfaces with auxiliary systems, such as systems to delivery a coating composition and/or radiation to the flow within the reaction system. Once, the final modified inorganic particles are formed, a collector separates the product modified inorganic particles from the flow to terminate the in-flight process. The distinct steps for the formation of the ultimate modified inorganic particles can be performed in the same compartment, in a separate compartment for each step, or in a plurality of compartments with multiple steps performed in one or more compartments. However, regardless of the particular reactor design, the apparatus generally is configured to synthesize inorganic particles from appropriate precursors and to modify the inorganic particles in-flight.

As described above, flow relates to a net movement of mass from one point to another. Generally, the flow path within the apparatus relating to in-flight processing extends from one or more inorganic particle reactant precursor inlets to the collector. Along the flow, the inorganic particles are synthesized and the inorganic particles are modified. Generally, a negative pressure device is used to maintain the flow through the apparatus along the flow path, although flow can be maintained from the positive pressure generated form composition delivery into the apparatus. Suitable negative pressure devices include, for example, a pump, a blower, an aspirator/venturi, compressor, ejector or the like. If there is a plurality of inorganic particle precursor inlets, flow from these can be combined either prior to inorganic particle production and/or after inorganic particle such that there are different flow of product inorganic particles. If different flows are combined, these are different branches of a flow path that combine along a flow path to a collector.

In some embodiments, the apparatuses are designed for the performance of laser pyrolysis for the formation of the core inorganic particles. Laser pyrolysis has become the standard terminology for flowing chemical reactions driven by an intense radiation, e.g., light, with rapid quenching of product inorganic particles after leaving a reaction region formed by the radiation intersecting with the reactant flow. The name, however, is a misnomer in the sense that radiation from non-laser sources, such as a strong, incoherent light or other electromagnetic beam, can replace the laser. Also, the reaction is not a pyrolysis in the sense of a thermal pyrolysis. The laser pyrolysis reaction is not solely thermally driven by the exothermic combustion of the reactants. In fact, in some embodiments, laser pyrolysis reactions can be conducted under conditions where no visible light emissions are observed from the reaction, in stark contrast with pyrolytic flames.

The reaction conditions can determine the qualities of the particles produced by laser pyrolysis. The reaction conditions for laser pyrolysis can be controlled relatively precisely in order to produce inorganic particles with desired properties. For example, the reaction chamber pressure, flow rates, composition and concentration of reactants, radiation intensity, radiation energy/wavelength, type and concentration of inert diluent gas or gases in the reaction stream, temperature of the reactant flow can affect the composition and other properties of the product particles, for example, by altering the time of flight of the reactants/products in the reaction zone and the quench rate. Thus, in a particular embodiment, one or more of the specific reaction conditions can be controlled. The appropriate reaction conditions to produce a certain type of particles generally depend on the design of the particular apparatus. Some general observations on the relationship between reaction conditions and the resulting particles can be made.

Increasing the light power results in increased reaction temperatures in the reaction region as well as a faster quenching rate. A rapid quenching rate tends to favor production of higher energy phases, which may not be obtained with processes near thermal equilibrium. Similarly, increasing the chamber pressure also tends to favor the production of higher energy phases. Also, increasing the concentration of the reactant serving as the oxygen source, nitrogen source, sulfur source or other secondary reactant source in the reactant stream favors the production of particles with increased amounts respectively of oxygen, nitrogen, sulfur or other secondary reactant.

Reactant velocity of the reactant gas stream is inversely related to particle size so that increasing the reactant velocity tends to result in smaller particle sizes. A significant factor in determining particle size is the concentration of product composition condensing into product

particles. Reducing the concentration of condensing product compositions generally reduces the particle size. The concentration of condensing product can be controlled by dilution with non-condensing, e.g., inert, compositions or by changing the pressure with a fixed ratio of condensing product to non-condensing compositions, with a reduction in pressure generally leading to reduced concentration and a corresponding reduction in particle size and vice versa, or by combinations thereof, or by any other suitable means.

Light power during laser pyrolysis also influences the inorganic particle sizes with increased light power favoring smaller particle formation, especially for higher melting temperature materials. Also, the growth dynamics of the particles have a significant influence on the size of the resulting particles. In other words, different forms of a product composition have a tendency to form different size particles from other phases under relatively similar conditions. Similarly, under conditions at which populations of particles with different compositions are formed, each population of particles generally has its own characteristic narrow distribution of particle sizes.

Inorganic particles of interest include, for example, amorphous particles, crystalline particles, combinations thereof and mixtures thereof. Amorphous inorganic particles possess short-range order that can be very similar to that found in crystalline materials. In crystalline materials, the short-range order comprises the building blocks of the long-range order that distinguishes crystalline and amorphous materials. In other words, translational symmetry of the short-range order building blocks found in amorphous materials creates long-range order that defines a crystalline lattice. In general, the crystalline form is a lower energy state than the analogous amorphous form. This provides a driving force towards formation of long-range order. In other words, given sufficient atomic mobility and time, long-range order can form. For convenience, the structures of the inorganic particles are referred to as mineral structures to distinguish these materials from the coating materials, which are referred to as having non-mineral structures, although the inorganic particles do not necessarily have structures corresponding to natural minerals.

In laser pyrolysis, a wide range of inorganic particles can be formed in the reactive process. Based on kinetic principles, higher quench rates favor amorphous particle formation while slower quench rates favor crystalline particle formation as there is time for long-range order to develop. Faster quenches can be accomplished with a faster reactant stream velocity through the reaction zone. In addition, some precursors may favor the production of amorphous particles while other precursors favor the production of crystalline particles of similar or equivalent stoichiometry. The formation of amorphous metal oxides particles and

crystalline metal oxide particles with laser pyrolysis is described further in U.S. Patent 6,106,798 to Kambe et al., entitled "Vanadium Oxide Nanoparticles," incorporated herein by reference.

To form a desired composition in the reaction process, one or more precursors generally supply the one or more metal/metalloid elements that are within the desired composition. The reactant stream generally would comprise the desired metal element(s) and, additionally or alternatively, metalloid element(s) to form the host material and, optionally, dopant(s)/additive(s) in appropriate proportions to produce product particles with a desired composition. Furthermore, additional appropriate precursor(s)/reactant(s) can supply other element(s) for incorporation into the product inorganic particles. The composition of the reactant stream can be adjusted along with the reaction condition(s) to generate desired product particles with respect to composition and structure. Based on the particular reactants and reaction conditions, the product particles may not have the same proportions of metal/metalloid elements as the reactant stream since the elements may have different efficiencies of incorporation into the particles, i.e., yields with respect to unreacted materials. However, the amount of incorporation of each element is a function of the amount of that element in the reactant flow, and the efficiency of incorporation can be empirically evaluated based on the teachings herein to obtain desired compositions. The designs of the reactant nozzles for radiation driven reactions described herein are designed for high yields with high reactant flows.

Referring to Fig. 6, modified inorganic particle production system 110 comprises a laser pyrolysis section 112, flow/modification section 114, and collection system 116. Laser pyrolysis section 112 comprises a reaction chamber 120, an intense light delivery apparatus 122, a reactant delivery portion 124 and an optional particle modifying section 126. Reaction chamber 120 confines the reaction for the formation of the inorganic core particles. Reaction chamber 120 comprises a reactant inlet 130, a light inlet conduit 132, a light outlet conduit 134 which forms a light beam path 136 with light beam inlet 132, a reaction zone 138 in the vicinity of and generally overlapping with the intersection of a light beam path 136 and the flow path of reactants from reactant inlet 130. Reaction chamber 120 can interface with particle modification section 126 at one and/or more modification elements 140, which can be coating composition nozzles or radiation sources. Appropriate flame reactors, thermal reactors or other flow based inorganic particle synthesis reactors can be constructed for in-flight modification of synthesized inorganic particles by a person of ordinary skill in the art based on the disclosure herein.

Laser pyrolysis systems suitable for producing commercial quantities of product particles can have an inlet elongated along the direction of the light beam propagation such that a sheet of reactants flow into the reaction zone to form a sheet of product particle in a product flow. Generally, essentially the entire reactant flow passes through the light beam. Large throughputs are achievable with these systems, which are able to efficiently produce high quality particles over appropriately long run time. Reaction chamber designs for large throughputs are described further in U.S. Patent 5,958,348 to Bi et al., entitled "Efficient Production of Particles By Chemical Reaction," incorporated herein by reference.

A diagram of a high throughput laser pyrolysis reaction chamber is shown schematically in Fig. 7, which has an elongated reaction chamber 150 for generating a sheet of product flow 151 from a sheet of reactant flow 153. This chamber is shown without displaying any coating components for simplicity with respect to other reactor components and can be adapted for modifying the product inorganic particles in-flight, as described further below with respect to other embodiments. A reactant inlet 152 leads to main chamber 154. Reactant inlet 152 conforms generally to the shape of main chamber 154. Reactant inlet 152 is generally connected to a reactant delivery portion. Main chamber 154 comprises an outlet 156 along the reactant/product stream for removal of the flow with product particles, any unreacted gases and inert gases. Shielding gas inlets 158 can be located on both sides of reactant inlet 152. Shielding gas inlets are used to form a blanket of inert gases on the sides of the reactant stream to inhibit contact between the chamber walls and the reactants or products.

The dimensions of elongated reaction chamber 154 and reactant inlet 152 can be designed for highly efficiency product composition production. The reaction zone is located within the reaction chamber in the vicinity of the intersection of the reactant flow with the light beam path. Reasonable elongated dimensions or widths for reactant inlet 152, when used with a CO_2 laser with a power in the several kilowatt range, are from about 5 mm to about 2 meters or in further embodiments from about 2 centimeters to about 1 meter. In general, the inlet generally has a thickness from about 1 mm to about 10 centimeters (cm) and in further embodiments from about 2 mm to about 2 cm. Furthermore, the aspect ratio of the inlet opening, which is the width divided by the thickness, can range from about 2 to about 1000 and in other embodiments from about 5 to about 200. A person of ordinary skill in the art will realize that additional ranges of inlet dimensions and aspect ratios are contemplated and are within the present disclosure. While shown as a rectangular inlet, the edges and corners can be rounded somewhat while maintaining the general nature of an elongated flow. The resulting flows through the system have dimensions reflecting the initial reactant flow, although

spreading can expand the flow and shielding gas and baffles can be used to limit spreading and/or further constrain the flow. In alternative embodiments, a circular inlet can be used, which can be suitable for flame reactors and thermal reactors. Alternative configurations for high throughput laser pyrolysis, which can be adapted for in flight modification of the inorganic particles, are described in Published U.S. Patent Application 2005/020036 to Mosso et al., entitled "Particle Production Apparatus," incorporated herein by reference.

Referring to Fig. 7, tubular sections 160, 162 extend from the main chamber 154. Tubular sections 160, 162 hold windows 164, 166, respectively, to define a light beam path 168 through the reaction chamber 150. Tubular sections 160, 162 can comprise inert gas inlets 170, 172 for the introduction of inert gas into tubular sections 160, 162. Inert gas inlets 170, 172 generally are connected to a suitable inert gas source.

Referring to Fig. 6, intense light delivery apparatus 122 generally can comprise an intense light source 180 and suitable optics, which are connected to light inlet conduit 132. A beam dump 182 can be connected to light outlet conduit 134 to terminate the light beam path. Laser pyrolysis can be performed with a variety of optical frequencies, using either a laser or other intense radiation source, such as a focused arc lamp. Some desirable light sources operate in the infrared portion of the electromagnetic spectrum, although other wavelengths can be used, such as the visible or ultraviolet regions of the spectrum. Excimer lasers can be used as intense ultraviolet light sources. CO_2 lasers are particularly convenient sources of light. Commercial CO_2 lasers are available in the watt to many kilowatts ranges. Suitable beam dumps/power meters are also commercially available. Light delivery apparatus 122 can further comprise suitable optical components, such as mirrors, lenses, widows and the like. In particular, the light inlet path from intense light source 180 into reaction chamber 120 can comprise a cylindrical lens that focuses the light in one dimension, generally the dimension along the flow of the reactants, such that in the beam is thinner in the dimension shown in Fig. 6 along the flow of reactants from the bottom of the page toward the top of the page. In the embodiment of Fig. 6 with a cylindrical lens, the beam would not be focused perpendicular to the plane of the page so that a thicker flow of reactants can pass through the light beam to increase throughput.

Reactant delivery portion 124 is configured to interface with reactant inlet 130 to deliver a flow of reactants into reaction chamber 120. Reactant delivery portion 124 can comprise suitable reservoirs, nozzles, injectors and the like to deliver gaseous reactants, vapor reactants, aerosol reactants or a combination thereof. Many precursor compositions, such as metal/metalloid precursor compositions, can be delivered into the reaction chamber as

a gas/vapor. Appropriate precursor compositions for gaseous delivery generally include compositions with reasonable vapor pressures, i.e., vapor pressures sufficient to get desired amounts of precursor gas/vapor into the reactant stream. The vessel holding liquid or solid precursor compositions can be heated (cooled) to increase (decrease) the vapor pressure of the precursor, if desired. Solid precursors generally are heated to produce a sufficient vapor pressure. A carrier gas can be bubbled through a liquid precursor to facilitate delivery of a desired amount of precursor vapor. Similarly, a carrier gas can be passed over the solid precursor to facilitate delivery of the precursor vapor. Alternatively or additionally, a liquid precursor can be directed to a flash evaporator to supply a composition at a selected vapor pressure. The use of a flash evaporator to control the flow of non-gaseous precursors can provide a high level of control on the precursor delivery into the reaction chamber.

However, the use of exclusively gas/vapor phase reactants can be challenging with respect to the types of precursor compositions that can be used conveniently. Thus, techniques have been developed to introduce aerosols containing precursors, such as metal/metalloid precursors, into laser pyrolysis chambers. Improved aerosol delivery apparatuses for flowing reaction systems are described further in U.S. Patent 6,193,936 to Gardner et al., entitled "Reactant Delivery Apparatuses," incorporated herein by reference. In some embodiments, the aerosol is entrained in a gas flow, which can comprise an inert gas(es) and/or a gaseous reactant(s). Suitable aerosol generators generally include, for example, ultrasonic nozzle, an electrostatic spray system, a pressure-flow atomizer, an effervescent atomizer, a gas atomizer, a pressure flow atomizer, a spill-return atomizer, a gas-blast atomizer, a two fluid internal mix atomizer, a simplex atomizer, a two fluid external mix atomizer, a Venturi-based atomizer or combination thereof. Ultrasonic nozzles with atomization surfaces and suitable broadband ultrasonic generators are available from Sono-Tek Corporation, Milton, NY, such as model 8700-120. Suitable gas atomizers are available from Spraying Systems, Wheaton, IL.

For embodiments involving a plurality of metal/metalloid elements, the metal/metalloid elements can be delivered all as vapor, all as aerosol or as any combination thereof. If a plurality of metal/metalloid elements is delivered as an aerosol, the precursors can be dissolved/dispersed within a single solvent/dispersant for delivery into the reactant flow as a single aerosol. Alternatively, the plurality of metal/metalloid elements can be delivered within a plurality of solutions/dispersions that are separately formed into an aerosol. The generation of a plurality of aerosols can be helpful if convenient precursors are not readily soluble/dispersible in a common solvent/dispersant. The plurality of aerosols can be introduced into a common gas flow for delivery into the reaction chamber through a common

nozzle. Alternatively, a plurality of reactant inlets can be used for the separate delivery of aerosol and/or vapor reactants into the reaction chamber such that the reactants mix within the reaction chamber prior to entry into the reaction zone. Multiple reactant inlets for delivery into a laser pyrolysis chamber are described further in copending U.S. Patent Application serial number 09/970,279 to Reitz et al., entitled "Multiple Reactant Nozzle For A Flowing Reactor," incorporated herein by reference.

In addition, for the production of highly pure materials, it may be desirable to use a combination of vapor and aerosol reactants. In some embodiments, vapor/gas reactants generally can be supplied at higher purity than is readily available at low cost for aerosol delivered compositions. At the same time, some elements, especially rare earth dopant(s)/additive(s), alkali metals and alkali earth metals as well as some transition metals, cannot be conveniently delivered in vapor form. Thus, in some embodiments, a majority of the material for the product compositions can be delivered in vapor/gas form while other elements are delivered in the form of an aerosol. The vapor and aerosol can be combined for reaction, for example, prior to introduction into the reaction chamber and/or following delivery through a single reactant inlet or a plurality of inlets into the reaction chamber.

Also, secondary reactants can be used in some embodiments to alter the oxidizing/reducing conditions within the reaction chamber and/or to contribute non-metal/metalloid elements or a portion thereof to the reaction products. The particles, in some embodiments, further comprise one or more non-(metal/metalloid) elements. For example, some compositions of interest are oxides, nitrides, carbides, sulfides or combinations thereof. For the formation of oxides, an oxygen source should also be present in the reactant stream, and other appropriate sources of non-(metal/metalloid) elements can be supplied to form the other compositions.

Suitable secondary reactants serving as an oxygen source for the formation of oxides include, for example, O_2, CO, N_2O, H_2O, CO_2, O_3 and the like and mixtures thereof. Molecular oxygen can be supplied as air. In some embodiments, the metal/metalloid precursor compositions comprise oxygen such that all or a portion of the oxygen in product particles is contributed by the metal/metalloid precursors. Similarly, liquids used as a solvent/dispersant for aerosol delivery can similarly contribute secondary reactants, e.g., oxygen, to the reaction. In other words, if one or more metal/metalloid precursors comprise oxygen and/or if a solvent/dispersant comprises oxygen, a separate secondary reactant, e.g., a vapor reactant, may not be needed to supply oxygen for product particles. The conditions in the reactor should be sufficiently oxidizing to produce the metal/metalloid oxide particles.

Generally, a secondary reactant composition should not react significantly with the metal/metalloid precursor(s) prior to entering the radiation reaction zone since this can result in the formation of larger particles and/or damage the inlet nozzle. Similarly, if a plurality of metal/metalloid precursors is used, these precursors should not significantly react prior to entering the radiation reaction zone. If the reactants are spontaneously reactive, a metal/metalloid precursor and the secondary reactant and/or different metal/metalloid precursors can be delivered in separate reactant inlets or nozzles into the reaction chamber such that they are combined just prior to reaching the light beam.

Infrared absorber(s) for inclusion in the reactant stream include, for example, C_2H_4, isopropyl alcohol, NH_3, SF_6, SiH_4 and O_3. O_3 and isopropyl alcohol can act as both an infrared absorber and as an oxygen source. The radiation absorber(s), such as the infrared absorber(s), can absorb energy from the radiation beam and distribute the energy to the other reactants to drive the pyrolysis.

An inert shielding gas can be used to reduce the amount of reactant and product molecules contacting the reactant chamber components. Inert gases can also be introduced into the reactant stream as a carrier gas and/or as a reaction moderator. Appropriate inert gases generally include, for example, Ar, He, N_2 (for many reactions), other gases suitably inert for particular reactions, or combinations thereof.

An embodiment of a reactant delivery unit suitable for the delivery of vapor reactants to reactant inlet 130 of Fig. 6 is shown schematically in Fig. 8. Referring to Fig. 8, a reactant delivery unit 190 comprises a source 192 of a precursor compound, which can be a liquid, solid or gas. For liquid or solid reactants, an optional carrier gas from one or more carrier gas sources 194 can be introduced into precursor source 192 to facilitate delivery of the reactant. Precursor source 192 can be a liquid holding container, a solid precursor delivery apparatus or other suitable container. The carrier gas from carrier gas source 194 can be, for example, an infrared absorber, a secondary reactant, an inert gas or mixtures thereof. In alternative embodiments, precursor source 192 is a flash evaporator that can deliver a selected vapor pressure of precursor without necessarily using a carrier gas. A flash evaporator can deliver a selected partial pressure of a precursor vapor into the reaction chamber, and other components leading to the reaction chamber can be heated, if appropriate, to reduce or eliminate condensation of the vapor prior to entry into the reaction chamber. Thus, a plurality of flash evaporators can be used to deliver selected amounts of a plurality of vapor reactants into the reaction chamber.

The gases/vapors from precursor source 192 can be mixed with gases from infrared absorber source 196, inert gas source 198 and/or gaseous reactant source 200 by combining the gases/vapors in a single portion of tubing 202. The gases/vapors are combined a sufficient distance from the reaction chamber such that the gases/vapors become well mixed prior to their entrance into the reaction chamber. The combined gas/vapor in tube 202 passes through a duct 204 into channel 206, which is in fluid communication with a reactant inlet, such as 130 in Fig. 6.

An additional reactant precursor can be supplied as a vapor/gas from second reactant source 208, which can be a liquid reactant delivery apparatus, a solid reactant delivery apparatus, a flash evaporator, a gas cylinder or other suitable container or containers. As shown in Fig. 8, second reactant source 208 delivers an additional reactant to duct 204 by way of tube 202. Alternatively, second reactant source can deliver the second reactant into a second duct such that the two reactants are delivered separately into the reaction chamber where the reactants combine at or near the reaction zone. Thus, for the formation of complex materials and/or doped materials, a significant number of reactant sources and, optionally, separate reactant ducts can be used for reactant/precursor delivery. For example, as many as 25 reactant sources and/or ducts are contemplated, although in principle, even larger numbers could be used. Mass flow controllers 210 can be used to regulate the flow of gases/vapors within the reactant delivery system of Fig. 8.

An alternative embodiment of a reactant delivery unit is shown schematically in Fig. 9. As shown in Fig. 9, reactant delivery unit 220 comprises a gas delivery subsystem 222 and a vapor delivery subsystem 224 that both join a mixing subsystem 226. Gas delivery subsystem 222 can comprise one or more gas sources, such as a gas cylinder or the like for the delivery of gases into the reaction chamber. As shown in Fig. 9, gas delivery subsystem 222 comprises precursor gas sources 230, 232, 234, and an optional light absorbing gas source 236, which can supply a light absorbing gas for laser pyrolysis if a reaction precursor does not sufficiently absorb the intense light. In other embodiments, the gas delivery subsystem can comprise a different number of gas sources such that desired precursors can be selected as desired. The gases combine in a gas manifold 238 where the gases can mix. Gas manifold can have a pressure relief valve 240 for safety. Inert gas source 234 can be also used to supply inert gas within the chamber adjacent the windows/lenses 242, 234 used to direct light from an external light source into chamber 236.

Vapor delivery subsystem 224 comprises a plurality of flash evaporators 250, 252, 254. Although shown with three flash evaporators, vapor delivery subsystem can comprise, for

example, one flash evaporator, two flash evaporators, four flash evaporators or more than four flash evaporators to provide a desired number of vapor precursors that can be selected for delivery into the reactor to form desired inorganic particles. Each flash evaporator can be connected to a liquid reservoir to supply liquid precursor in suitable quantities. Suitable flash evaporators are available from, for example, MKS Equipment or can be constructed from readily available components. The flash evaporators can be programmed to deliver a selected partial pressure of the particular precursor. The vapors from the flash evaporator are directed to a manifold 256 that directs the vapors to a common feed line 258. The vapor precursors mix within common feed line 258.

The gas components from gas delivery subsystem 222 and vapor components from vapor delivery subsystem 224 are combined within mixing subsystem 226. Mixing subsystem 226 can be a manifold that combines the flow from gas delivery subsystem 222 and vapor delivery subsystem 224. In the mixing subsystem 226, the inputs can be oriented to improve mixing of the combined flows of different vapors and gases at different pressures. The mixing block can have a slanted termination to reduce backflow into lower pressure sources. A conduit 270 leads from mixing subsystem 226 to reaction chamber 236. Reactant delivery unit 220 can be configured to deliver a selected reactant composition based on a supply with a range of precursors and other reactants to tune a particular inorganic particle composition without refitting the unit since a number of precursors supplies can be integrated together within the unit simultaneously.

Referring to Fig. 9, a heat controller 272 can be used to control the temperature of various components through conduction heaters or the like throughout the vapor delivery subsystem, mixing subsystem 226 and conduit 270 to reduce or eliminate any condensation of precursor vapors. A suitable heat controller is model CN132 from Omega Engineering (Stamford, CT). Overall precursor flow can be controlled/monitored by a DX5 controller from United Instruments (Westbury, NY.). The DX5 instrument can be interfaced with mass flow controllers (Mykrolis Corp., Billerica, MA) controlling the flow of one or more vapor/gas precursors. The automation of the unit can be integrated with a controller from Brooks-PRI Automation (Chelmsford, MA).

As noted above, the reactant stream can comprise one or more aerosols. The aerosols can be formed within the reaction chamber or outside of the reaction chamber prior to injection into the reaction chamber. If the aerosols are produced prior to injection into the reaction chamber, the aerosols can be introduced through reactant inlets comparable to those used for gaseous/vapor reactants. For the formation of inorganic particles with complex compositions,

additional aerosol generators and/or vapor/gas sources can be combined to supply the desired precursor compositions within the reactant stream.

Using aerosol delivery apparatuses, solid precursor compositions can be delivered by dissolving the compositions in a solvent. Alternatively, powdered precursor compositions can be dispersed in a liquid/solvent for aerosol delivery. Liquid precursor compositions can be delivered as an aerosol from a neat liquid, a multiple liquid dispersion or a liquid solution. Aerosol reactants can be used to obtain a significant reactant throughput. A solvent/dispersant can be selected to achieve desired properties of the resulting solution/dispersion. Suitable solvents/dispersants include water, methanol, ethanol, isopropyl alcohol, other organic solvents, metal/metalloid precursors themselves and mixtures thereof. The solvent should have a desired level of purity such that the resulting particles have a desired purity level. Some solvents, such as isopropyl alcohol, are significant absorbers of infrared light from a CO_2 laser such that no additional light absorbing composition may be needed within the reactant stream if a CO_2 laser is used as a light source.

The precursor compositions for aerosol delivery are dissolved in a solution generally with a concentration in the range(s) greater than about 0.1 molar. Generally, increasing the concentration of precursor in the solution increases the throughput of reactant through the reaction chamber. As the concentration increases, however, the solution can become more viscous such that the aerosol may have droplets with larger sizes than desired. Heating the solution can increase solubility and lower the viscosity to increase production rate without increasing aerosol droplet size. Thus, selection of solution concentration can involve a balance of factors in the selection of a suitable solution concentration.

If precursors are delivered as an aerosol with a solvent present, the solvent generally can be rapidly evaporated by the radiation (e.g., light) beam in the reaction chamber such that a gas phase reaction can take place. In addition, solvent generally can also evaporate prior to reaching the light beam during delivery. Under appropriate conditions, the resulting particles may not be highly porous, in contrast to other approaches based on aerosols in which the solvent cannot be driven off rapidly. Thus, the fundamental features of the laser pyrolysis reaction can be essentially unchanged by the presence of an aerosol. Nevertheless, the reaction conditions are affected by the presence of the aerosol. The use of aerosol reactants for laser pyrolysis particle production is described further in U.S. Patent 6,849,334 to Horne et al., entitled "Optical Materials And Optical Devices," incorporated herein by reference.

An embodiment of a reactant delivery nozzle configured to deliver an aerosol reactant along with gas/vapor is shown in Figs. 10 and 11. Inlet nozzle 280 connects with a reaction

chamber at its lower surface 282. Inlet nozzle 280 comprises a plate 284 that bolts into lower surface 282 to secure inlet nozzle 280 to the reaction chamber. Inlet nozzle 280 comprises an inner nozzle 286 and an outer nozzle 288. Inner nozzle 286 can have, for example, a twin orifice internal mix atomizer 290 at the top of the nozzle. Suitable gas atomizers are available from Spraying Systems, Wheaton, IL. The twin orifice internal mix atomizer 290 has a fan shape to produce a thin sheet of aerosol and gaseous compositions. Liquid is fed to the atomizer through tube 292, and gases for introduction into the reaction chamber are fed to the atomizer through tube 294. Interaction of the gas with the liquid assists with droplet formation.

Outer nozzle 288 comprises a chamber section 296, a funnel section 298 and a delivery section 300. Chamber section 296 holds the atomizer of inner nozzle 286. Funnel section 298 directs the aerosol and gaseous compositions into delivery section 300. Delivery section 300 leads to a rectangular reactant opening 302, shown in the insert of Fig. 10. Reactant opening 302 forms a reactant inlet into a reaction chamber for laser pyrolysis. Outer nozzle 288 comprises a drain 304 to remove any liquid that collects in the outer nozzle. Outer nozzle 288 is covered by an outer wall 306 that forms a shielding gas opening 308 surrounding reactant opening 302. Inert shielding gas is introduced through tube 310. Additional embodiments for the introduction of an aerosol with one or more aerosol generators into an elongated reaction chamber is described in U.S. Patent 6,193,936 to Gardner et al., entitled "Reactant Delivery Apparatuses," incorporated herein by reference.

For the performance of laser pyrolysis, the energy absorbed from the light beam increases the temperature at a tremendous rate, many times the rate that heat generally would be produced by exothermic reactions under controlled condition(s). While the process generally involves nonequilibrium conditions, the temperature can be described approximately based on the energy in the absorbing region. The laser pyrolysis process is qualitatively different from the process in a combustion reactor where an energy source initiates a reaction, but the reaction is driven by energy given off by an exothermic reaction. Thus, while the light driven process for particle collection is referred to as laser pyrolysis, it is not a traditional pyrolysis since the reaction is not driven by energy given off by the reaction but by energy absorbed from a radiation beam. In particular, spontaneous reaction of the reactants generally does not proceed significantly, if at all, back down the reactant flow toward the nozzle from the intersection of the radiation beam with the reactant stream. If necessary, the flow can be modified such that the reaction zone remains confined.

With suitable high throughput reactor designs, high inorganic particle production rates can be achieved. The particle production rate based on reactant delivery configurations

described herein can yield particle production rates in the range(s) of at least about 0.1g/h, in some embodiments at least about 10 g/h, in some embodiments at least about 50 g/h, in other embodiments in the range(s) of at least about 100 g/h, in further embodiments in the range(s) of at least about 250 g/h, in additional embodiments in the range(s) of at least about 1 kilogram per hour (kg/h) and in general up in the range(s) up to at least about 10 kg/h. A person of ordinary skill in the art will recognize that additional values of particle production rate within these specific values are contemplated and are within the present disclosure.

In general, these high production rates can be achieved while obtaining relatively high reaction yields, as evaluated by the portion of metal/metalloid nuclei in the flow that are incorporated into the product inorganic particles. In general, the yield can be in the range(s) of at least about 30 percent based on the limiting reactant, in other embodiments in the range(s) of at least about 50 percent, in further embodiments in the range(s) of at least about 65 percent, in other embodiments in the range(s) of at least about 80 percent and in additional embodiments in the range(s) of at least about 95 percent based on the metal/metalloid nuclei in the reactant flow. A person of ordinary skill in the art will recognize that additional values of yield within these specific values are contemplated and are within the present disclosure.

Referring to Fig. 6, particle modification section 126 can comprise one or more modification elements 140, each of which can be a coating nozzle or a radiation source. Coating nozzles can be operably connected to a coating composition supply system. A coating nozzle can be oriented to deliver the coating composition with a desired momentum to the flow with product inorganic particles. This is shown schematically in Fig. 12 with a sheet of inorganic particle reaction product flow. A product flow of inorganic particles 320 can have a cross sectional width "w" and a thickness "t" resulting in an aspect ratio of w/t for a cross section of the flow. The dimensions of the product flow relate back to the shape of the inorganic precursor reactant inlet, which can be referenced as a specific feature of the apparatus, although the product flow may involve some spreading or other alteration of the flow.

Three different coating nozzle embodiments 322, 324, 326 are superimposed for comparison in Fig. 12. Nozzle 322 is oriented to deliver a coating composition with an average momentum component along the inorganic particle product flow indicated with a flow arrow 328. Nozzle 324 is oriented to deliver a coating composition with an average momentum component perpendicular to the average flow direction of the inorganic particle product flow. Nozzle 326 is oriented to deliver a coating composition with an average momentum component against the average flow direction of the inorganic particle product

flow to generate a larger relative momentum between the two flows. Other configurations in addition to the representative embodiments in Fig. 12 can be used as appropriate. In general, for any processing steps involving the combination of flows from different sources, the flow can be controlled to avoid the introduction of excessive turbulence that can destabilize the flow in undesirable ways.

It may be desirable to have a more symmetrical coating composition delivery with any of the orientations in Fig. 12 or with other orientations. Referring to a top sectional view in Fig. 13, a coating composition inlet has two nozzle components 330, 332 disposed on the two sides of product inorganic particle flow 334. Nozzle components 330, 332 can have a width somewhat larger than the width of inorganic particle flow 334 to reduce any edge effects. Another embodiment is shown in Fig. 14. In this embodiment, coating composition inlet has four nozzle components 336, 338, 340, 342 with nozzle components 336, 338 along the face of the inorganic particle sheet 344 and nozzle components 340, 342 along the edges of the inorganic particle sheet 344. The flow rates through the nozzle components can be adjusted to yield more uniform composite particles. The nozzle configuration can be generalized further to have coating composition delivered completely encircling the flow, as shown in Fig. 15 with nozzle 346 surrounding inorganic particle flow 348. Variations on these specific embodiments in Figs. 13-15 can be used to obtain a desired level of coating uniformity.

In general, reactant delivery components suitable for the delivery of inorganic particle precursors/reactants can be adapted for the delivery of coating compositions. In particular, in some embodiments the coating composition inlet is elongated, as shown in Figs. 12 and 13, to intersect with an elongated inorganic particle product flow. Suitable coating composition reactant delivery systems can be used for the delivery of a vapor and/or aerosol coating compositions along an elongated inlet(s). Specifically, particular embodiments of delivery systems are shown in Figs. 8-11, which can be adapted to deliver coating compositions.

As noted above with respect to Fig. 6, particle modification section 126 can comprises one or more radiation sources that are placed to direct radiation within the reaction chamber to modify the properties of the inorganic particles and/or to modify the coating properties. Suitable radiation sources include, for example, an electron beam, a corona discharge or a source of electromagnetic radiation. Klystrons or other electron beam sources can be adapted for these applications. Suitable electromagnetic radiation can be used, such as infrared, visible, microwave, ultraviolet, x-rays and combinations thereof. Suitable light sources can be used to deliver desired wavelengths, such as ultraviolet light emitting diodes, as described in U.S.

Patent 6,734,033 to Emerson et al., entitled "Ultraviolet Light Emitting Diode," incorporated herein by reference; a wide range of diodes and other light sources in the visible; infrared diodes, as described in U.S. Patent 6,783,260 to Machi et al., entitled "IR Laser Based High Intensity Light," incorporated herein by reference; and microwaves, as described in Published U.S. Patent Application 2004-0245932A to Durand, entitled "Microwave Generator With Virtual Cathode," incorporated herein by reference. Infrared and/or microwave radiation can be used to heat the flow to evaporate solvent, induce crosslinking or other thermally driven reactions and/or induce other thermal processes. Ultraviolet light and/or visible light can be used to induce crosslinking or other specific reactions. Electron beams can be used to crosslink samples or induce other property changes.

While a single element can be used for the radiation source, the radiation source can be similar configured with one or a plurality of elements roughly in a way corresponding to the coating nozzle configurations as shown in Figs. 13-15, for the more uniform irradiation of the flow. In some embodiments, the radiation source can have an extended element or group of elements to generate radiation along an extended panel. For example, as shown in Fig. 16, a radiation emitting panel 350 can comprise a plurality of elements 352, which can be diodes, klystrons, or the like.

An alternative embodiment of a reaction chamber is shown in Fig. 17 with a single coating composition nozzle. Referring to Fig. 17, reaction chamber 380 comprises a light tube 382 that connects to an intense light source, such as a CO_2 laser, and a light tube 384 connected to a beam dump 386. An inlet tube 388 connects with a precursor delivery portion that delivers vapor reactants and carrier gases. Suitable reactant delivery portions are described above. Inlet tube 388 leads to reactant nozzle 390. An exhaust transport tube 392 connects to process chamber 380 along the flow direction from reactant nozzle 390. Exhaust transport tube 392 leads to a product filtration chamber 394 with a filer element. Product filtration chamber 394 connects to a vacuum pump or the like at pump connector 396. Coating nozzle 400 is configured to direct a coating composition just above a reaction zone within chamber 380. Coating nozzle 400 is operably connected to a coating composition feed line 402, which is in fluid communication with coating composition reservoir 404.

With respect to Fig. 6, if particle modification section 126 comprises a plurality of coating nozzles and/or radiation sources, each coating nozzle can be configured independently, for example, with a suitable configuration as shown in Figs. 12-15, and each radiation source can be similarly independently configured. The spacing and relative positioning of the coating nozzles and radiation sources can be configured to yield the

desired product particles. Similarly, a radiation source can be configured to irradiate the flow before or after delivery of a coating composition depending on whether or not the radiation is intended to alter the properties or induce reaction of the coating compositions.

As a specific example, we can assume as a representative example, that the three modification elements 140 are two coating nozzles and one radiation source. The radiation source can be placed first along the flow to modify the inorganic particles prior to coating the particles. Alternatively, the radiation source can be placed upstream from both coating nozzles so that the radiation is directed at the particles in the flow after receiving coating materials from both coating nozzles. In another alternative configuration, the radiation source can be positioned between the two coating nozzles so that the radiation interacts with the particles after the deposition of a first coating composition but before the deposition of a second coating composition.

In summary, reaction chamber 120 of Fig. 6 is shown with three modification elements while reaction chamber 380 of Fig. 17 has a single modification element, which is a coating nozzle. Similarly, reaction chambers can have no modification elements, two modification elements, four modification or more than four modification elements. Also, each element can be a radiation source or a coating nozzle. The positioning and order of the modification elements can be selected as desired to achieve the appropriate results of the modification process. For embodiments with a plurality of coating composition delivery inlets, these can be spaced an appropriate amount within the coating chamber such that the coating processes interact with each other to a selected degree. Also, an apparatus with a fixed number and position of modification elements can be reconfigured for different coating compositions and/or radiation sources for a particular desired product. With such an apparatus, each modification element may or may not be used for any particular run through the apparatus to produce desired product particles.

Referring to Fig. 6, flow/modification section 114 connects the laser pyrolysis system with the collector system. In the embodiment of Fig. 17, the flow/modification system is a conduit directing the flow to a filter based collector. If flow/modification section 114 does not comprise any modification elements, all particle modification is initiated with the reaction system, e.g., the laser pyrolysis chamber or other inorganic particle synthesis chamber. The flow/modification section 114, as with exhaust transport tube 392 of Fig. 17, then conveys the particles from the reaction chamber to the collector system without further modifying the particles. However, in other embodiments, flow/modification section 114 comprises one or more modification elements.

In particular, in some embodiments, referring to Fig. 6, flow/modification section 114 comprises one or more modification elements involved with the delivery of one or more coating compositions and/or interaction with radiation from a radiation source at one or more locations. For any of these embodiments, the flow/modification element further comprises a conduit and/or chambers. Flow/modification section 114 can be distinguished from the reaction section 112 due to a change in direction of the flow or due to a change in cross sectional area available to the flow, such as a constriction. A conduit can be straight, or it can be curved to redirect the flow as appropriate to reach the collection system. Thus, the cross sectional dimensions may or may not remain relatively constant between the inorganic particle synthesis reactor and the flow/modification section, and the conduit can have a circular cross section even if the reaction chamber flow is elongated.

For the embodiment of the particle production system in Fig. 17, flow/modification section 114 corresponds with exhaust transport tube 392. Exhaust transport tube 392 only transports particles and does not comprise elements to modify the particles. Once the modified particles exit reaction chamber 380, the particles proceed to collector without being subjected to further modification conditions.

An embodiment of a flow/modification section configured with processing stations for modifying the particles in the flow is shown in Fig. 18. Flow/modification section 420 is operably connected between inorganic particle reaction chamber 422 and collector 424. As shown in Fig. 18, flow/coating system 420 comprises 6 modification elements 426, 428, 430, 432, 434, 436 along conduit 438. Each modification element can comprise a coating composition delivery nozzle or a radiation source. Each coating delivery nozzle can be configured, for example, as described above with respect to Figs. 12-15. Specifically, the orientation of a coating nozzle can be configured to deliver the particular coating composition with a desired momentum with respect to the flow. Similarly, the configuration of the coating composition nozzle around the flow can be designed to deliver a more uniform distribution of coating composition with a configuration of Figs. 13-15. Each coating composition nozzle generally is in fluid communication with a coating composition supply element having a reservoir to deliver a vapor and/or aerosol comprising the desired coating composition. Suitable radiation sources are described above in detail, and these can be oriented around the flow as desired, for example using the configurations shown in Figs. 13-15. Panels of radiation source can be configured as shown in Fig. 16.

While Fig. 18 shows a flow/modification section with 6 modification elements, flow/modification sections can be configured with 1, 2, 3, 4, 5, 7, 8, 9, 10 or more

modification elements. The number of modification elements, their relative positioning and the configuration of individual modification elements can be designed to achieve desired coating properties. In general, the length along the flow of the flow/coating system can be selected to provide desired space for placement of desired modification elements. Factors for consideration in selecting the order and positioning of the modification elements for placement within the reaction chamber generally are similarly relevant for evaluating the order and placement within the flow/modification section.

In addition, Fig. 18 shows flow/modification section 420 having conduit 438 with approximately constant cross section perpendicular to the flow along the conduit, although conduit 438 changes direction. However, a flow/modification section can change cross section perpendicular to the flow to accomplish particular processing objectives. For example, the flow/modification section can open into a processing chamber or taper to constrict the flow. Tapering can increase the density within the flow, which can result in some controlled agglomeration of the particles within the flow. If desired, the flow can be controlled to effectively form a fluidized bed reactor to result in further controlled agglomeration prior to collection of the particles.

As noted above, it can be desirable to add inert gas to the flow following formation of the inorganic particles. In particular, inert gas can be used to cool the inorganic particles prior to further modification, especially coating, of the particles. Similarly, inert gas can be used to cool the particles after they are irradiated within the flow. Furthermore, inert gas can be introduced to constrain the flow of the product particles and to shield the walls of the apparatus. To deliver inert gas, a coating nozzle within the reaction chamber and/or within the flow/modification section can be configured to deliver inert gas rather than a coating composition.

In alternative embodiments, a film of inert gas can be delivered through small openings or pores in the wall of the reaction chamber or through the walls of the flow/modification section. Furthermore, these constructions can also be used to deliver a coating composition. Representative wall modifications for the delivery of inert gas and/or modification compositions are shown in Figs. 19-23. With respect to the figures, portions of the apparatus having fluid delivery through the walls are referred to as components, e.g., the reaction chamber or the flow/modification section.

Referring to Figs. 19A and 19B, a first approach for thin film fluid delivery is depicted. The walls comprise an outer wall 452. The inner wall comprises two or more overlapping sections, comprising first section 454 and second section 456, which extend around the

circumference of the component to form the inner wall of the particular component. First section 454 has a smaller diameter around the circumference of the wall compared with second section 456 such that they can overlap as shown in Figs. 19 and 20. A delivery channel 458 is located between outer wall 452 and inner walls 454, 456. Delivery channel 458 is connected to a source of inert shielding gas or other fluid composition. Inner wall 456 has a bend 460 to connect to flange 462 that is welded or otherwise secured against inner wall 464. The overlapping region between inner walls 464, 466 forms a channel 464 that directs a thin film of shielding gas along inner wall 456. Fluid can pass into channel 464 through openings 466.

An alternative embodiment of a thin film system is shown in Figs. 20A and 20B. In this embodiment, openings 470 are located along bend 460 such that shielding gas impinges on inner wall 454 to distribute flow within channel 464 so that flow is more or less uniform as it exits channel 464 along inner wall 456. While the flow arrows in Figs. 19A and 20A indicate an overall flow within delivery channel 458 from left-to-right, the flow within delivery channel 458 can be in the opposite direction from right-to-left. The pressure in delivery channel 458 is higher than the pressure in the component such that inert gas flows into channel 464.

In Figs. 19-20 only one film directing channel 464 extending the circumference of the component is shown. Additional film directing channels can be formed along the direction of flow within the reaction chamber using additional sections of inner wall, if desired for the efficient delivery of selected fluid. These series of channels 464, each extending around the circumference of the component, can be repeated along the length of the component.

An alternative embodiment is shown in Figs. 21A and 21B. The shielding gas delivery conduit 480 is formed by outer wall 482 and inner wall 484. Inner wall 484 is formed by a series of wall sections 486. Each wall section 486 extends around the circumference of the component. Wall sections are secured to adjacent sections by spacers 488 to form the inner wall. Shielding gas delivery channels 490 are formed between wall sections 486. The dimensions of wall sections 486 and spacers 488 are selected to yield desired dimensions for channels 490.

In another alternative embodiment, the chamber walls along the direction of the reactant flow comprise an inert gas channel 500 between an inner wall 502 and an outer wall 504, as shown in Fig. 22. All or a portion of inner wall 502 can be a porous metal such that fluid, such as inert gas, permeates into the interior of the component. Thus, a film of fluid lines the porous metal along the wall of the component.

In a similar embodiment, the component walls comprise an inert gas channel 510 between an inner wall 512 and an outer wall 514, as shown in Figs. 23A and 23B. Inner wall

512 is formed from stamped metal that has louvers 516 along inner wall 512 that form openings through inner wall 512. Some inert gas flowing within channel 510 flows through louvers 516 into the component along inner wall 512. Additional variations on this approach can be used to deliver a thin film of fluid along the inner wall of the component. Thin film delivery of shielding gases is described further in Published PCT Application WO 01/07155 to Mosso et al., entitled "Particle Production Apparatus," incorporated herein by reference, and in U.S. Patent 5,827,370 to Gu, entitled "Method And Apparatus For Reducing Build-Up Of Material On Inner Surface Of Tube Downstream From Reaction Furnace," incorporated herein by reference.

Referring to Fig. 6, collection system 116 can comprise a collector 450, a negative pressure device 452 and a scrubber 454 with appropriate conduits connecting the flow between these components. Collector 450 can be, for example, a filter, an electrostatic collector or the like. Suitable filters include, for example, flat filters or cylindrical filters. In some embodiments of interest, the collector can be a bag collector for continuous collection without disrupting particle production, such as describe in U.S. Patent 5,874,684 to Parker et al., entitled "Nanocrystalline Materials," and U.S. Patent 6,270,732 to Gardner et al., entitled Particle Collection Apparatus And Associated Methods, both of which are incorporated herein by reference. Suitable negative pressure devices include, for example, pumps, blowers, an aspirator/venturi, compressor, ejector or the like. Vacuum pumps are commercially available, such as available from Leybold Vacuum Products, Export, PA or a dry rotary pump from Edwards, such as model QDP80. Optional scrubber 454 can be used to remove environmentally harmful compounds from the filtered flow to reduce their release into the atmosphere. Suitable scrubbers include, for example, in-line Sodasorb® (W.R. Grace) chlorine traps.

The pressure in the reaction chamber generally can be measured with a pressure gauge. For example, a manometer can be used as a pressure gauge. Manometers provide accurate linear responses with respect to pressure. In some embodiments, the pressure gauge is connected to a controller. The controller can be used to monitor the pressure in reaction chamber and maintain the pressure in reaction chamber within a specified range using a feedback loop with the collection system. The operation of the feedback loop depends on the structural design of the collection system, and may involve, for example, the adjustment of a valve, pumping speed and/or filter pulsing rates, with automatic adjustment by the controller. Suitable automatic valves for interfacing with the controller are available from Edwards

Vacuum Products, Wilmington, MA. If manual values are used, the controller can notify an operator to adjust the manual valve appropriately.

As noted above, separate reaction pathways for the formation of inorganic particles can be incorporated into the apparatus. At a selected point in the processing, the different product inorganic particle flows can be combined with or without having modified the inorganic particles within the different synthetic flows. For the in-flight formation of composites with a plurality of inorganic particles, reactive flows originating from two or more independent reactant inlet nozzles generally are used to form the corresponding two or more product inorganic particle streams. To form the two or more independent inorganic particle streams, the independent reactions can be performed in a single reaction chamber and/or in a plurality of reaction chambers with appropriate exit channels to facilitate the modification and combination of the inorganic particle streams to form the desired composite particles. For example, the different inorganic particle product flows can be directed to respective conduits that are combined at a suitable manifold. In other embodiments, the reactive flows can be formed in a single reactive chamber with independent reactant inlets and independent reaction zones and appropriately combined for further processing.

One embodiment of an apparatus to perform the combination of two inorganic reactive flows is shown schematically in Fig. 24. Laser pyrolysis reaction chamber 530 comprises two independent reactant inlets 532, 534, each being connected to a reactant delivery system. Shielding gas from shielding gas inlets around the reactant inlets can be used to entrain the reactant flows. Flow from independent reactant inlets 532, 534 intersects light beams from light sources, e.g., lasers, 536, 538, respectively at independent light reaction zones 540, 542. However, the flows are configured to gradually result in the intersection of the independent reactive flow at some point after the light reaction zones 540, 542. The ultimately merged flows exit a single outlet 544 to enter a conduit system for further processing and/or collection. Furthermore, addition of further reactants to the flow of product inorganic particles can be performed within the reaction chamber. The exit from the reaction chamber may or may not have a clear demarcation and may be identified by some redirection of the flow or other change in the flow environment.

Processing to form Composite Particles

In some embodiments, inorganic particles from an appropriate source or synthesis approach are incorporated into a process for the formation of the composite material, which

can involve more than one processing step. In further embodiments, the inorganic particles are synthesized in a flow based process, and one or more aspects of the further processing are incorporated into an in-flight processing of the inorganic particles prior to their collection. In some embodiments, the entire process can be completed in-flight such that the first material collected comprises composite particles with inorganic particles and a polymer. Also, there can be an in-flight organic composition/droplet processing channel prior to association with inorganic particles, which is also generally in-flight. Alternatively, other processing approaches can be based on flow-based methods such as spray drying or the like, to form composite particles from a dispersion/solution comprising inorganic particles and polymers and/or polymer precursors. Other composite particle synthesis approaches can be based on reactions within a solution/ dispersion, such as emulsion synthesis approaches. In general, it may be desirable to pacify the surface of the composite particles, chemically or physically through separation at the point of drying, at the last stage of the process such that the formation of the composite particles involves the formation of free flowing composite particles without significant hard agglomeration.

The general organization of the process is shown in the flow diagram of Fig. 25. The process 550 is depicted with three milestones, formation of inorganic particles 552, collection of inorganic particles 554 and collection of dry composite particles 556. The transitions between the milestones involve optional in-flight processing 558 and optional post collection processing 560. These are both indicated as optional in the sense that all of the processing between milestones can be performed in-flight or all of the processing to form the composite can be performed following collection of the inorganic particles. If there is no in-flight processing 558, the transition between the formation of the inorganic particles and the collection of the inorganic particles simply involves collection, and if there is no post collection processing, the collection of the inorganic particles and the collection of the dry composite particles collapse into the same event.

As noted above, the formation of inorganic particles 552 can involve processes based on a reactive flow, such as laser pyrolysis and flame pyrolysis, or processes performed in solution, such as sol-gel condensation and miscelle/reverse miscelle approaches. For solution based processes, it may be desirable to collect the particles prior to performing further processing steps since the composition of the particles can be influenced by solvation effects. For example, it may be desirable to calcify with a heat treatment the particles produced by solution based method prior to further processing. However, if the particles have desired crystallinity and composition in solution following

sysnthesis, the additional processing steps can be performed without harvesting the inorganic particles. In particular, a portion of the composite particle processing steps can be performed in the original inorganic particle synthesis solution prior to collecting the particles. For example, the inorganic particles in solution can be contacted with a linker compound and/or monomers/polymers prior to collecting the inorganic particles to pacify the surface of the particles.

In embodiments of particular interest, the inorganic particles are prepared in a reactive flow, for example, using flame pyrolysis or laser pyrolysis. These particles can be collected from the flow, or the particles can be modified using an in-flight process 558. For example, the particles can be flowed through a vapor and/or aerosol comprising a linker/surface modifier, such as those described above. The linker/surface modifier can condense onto the surface of the inorganic particles as they pass through the vapor/aerosol. The linker/surface modifier can be supplied continuously to present an effective steady state concentration such that the modification of the particles is consistent with corresponding uniform results. Similarly, the inorganic particles can be intersected with a vapor/aerosol comprising monomers and/or solvated polymers. The monomers can be subjected to heat and/or radiation, such as UV light, to induce polymerization following association with the inorganic particles. Similarly, a polymer can be crosslinked using heat and/or radiation, such as UV light, following association with the inorganic particles. Generally, these embodiments involving in-flight polymer association with the inorganic particles result in a composite with an architecture shown in Fig. 1.

The delivery of the linker/surface modifier can be performed at a selected location along the particle flow between the reaction zone at which the inorganic particles are formed and the particle collector. A plurality of modification stations can be used along this path. For example, at one location a linker can be added, at a second location a monomer is added and at a third location the flow is irradiated to polymerize the monomer. Similarly, other desirable combinations of in-flight processing steps can be used to form desired processed particles.

At step 554, the inorganic particles are collected. The harvested inorganic particles can be unmodified inorganic particles, surface modified inorganic particles with associated linkers or other surface modifiers, or polymer-inorganic particle composite particles. If the inorganic particles are not the final composite particles, post-collection processing 560 can be performed. The dry composite particles are collected 556 after any post-collecting processing 560 of the inorganic particles.

Suitable processing of the inorganic particles can include, for example, solution-based processes, spray-drying processes or combinations thereof. Also, a plurality of processing steps can be used. Post collection processing generally comprises suspending the inorganic particles in a fluid, generally a liquid. The formation of the dispersion can involve, for example, the selection of an appropriate dispersant and vigorous mixing to well disperse the particles. Dispersing aids, such as surfactants and other functionalized surface modifying compositions, can be used to facilitate the dispersion. Suitable surface modifiers include, for example, linker compounds described above or linker compounds lacking a plurality of functional groups such that the compounds only bond with the particle surface. If a surface modifier was associated with the inorganic particles in-flight associated with the inorganic particle synthesis, generally no further surface modification would be used. It has been found that inorganic particles formed by laser pyrolysis generally have excellent dispersion capabilities under appropriate dispersion conditions. The dispersion and association with a linker compound with respect to inorganic particles formed using laser pyrolysis is described further in U.S. Patent 6,599,631 to Kambe et al., entitled "Polymer-Inorganic Particle Composites," incorporated herein by reference. Alternatively or additionally, the dispersed particles can be contacted with a polymer composition or monomers to form a composite forming suspension.

The dispersed inorganic particles with or without a surface modifier can be introduced into a processing step for introduction of polymer. The conditions and processing steps can be used to obtain desired particle architecture corresponding to the examples in Figs. 1-5. For example, to get a layered structure as in Fig. 3, each layer can be applied sequentially in separate processing steps. Similarly, concentrations and processing conditions can be used to select between the architectures of Figs. 1 and 2.

In some embodiments, the suspended inorganic particles can be subjected to emulsion polymerization. In emulsion polymerization, the polymer is formed in the presence of suspended inorganic particles with or without a surface modifier. For example, the polymerization can be based on a free radical mechanism. The polymers condense onto the suspended inorganic particles and may nor may not chemically bond to the inorganic particles or linkers on the surface of the inorganic particles. The concentrations and polymerization conditions can be controlled to select the polymer molecular weights and the relative amounts of polymer and inorganic particles as well as the composite particle size. In emulsion polymerization processes, generally the polymer precursors, the inorganic particles or both are in an organic solvent/dispersant and are added to an aqueous solution

for the polymerization reaction. A commercial stirred reactor vessel can be adapted for these processes. After the composite particles are formed in the emulsion polymerization process, the composite particles can be collected and milled to form the collection of dry composite particles. Emulsion polymerization processes are described further in U.S. Patent 6,946,229 to Suzuki et al., entitled "Toner For Forming Color Image, Image Forming Apparatus, And Toner Container," incorporated herein by reference, and in U.S. Patent 6,787,280 to Yamashita et al., entitled "Electrophotographic Toner And Method Of Producing Same," incorporated herein by reference.

Additionally or alternatively, in some embodiments, a spray process is involved in the formation of the composite particles. The spray process can be a spray drying process or the like. In general, a dispersion is fed to an aerosol generator that directs an aerosol spray into a drying chamber. The temperature at the aerosol nozzle and/or within the drying chamber can be set to a value such that supplied heat evaporates the solvent/dispersant. For example, heated inert gas can be fed into the drying chamber to facilitate solvent/dispersant evaporation. Additionally or alternatively, the spray can be interacted with radiation within the drying chamber to initiate chemical reaction of compositions associates with the particles. For example, ultraviolet light can be used to initiate polymerization or crosslinking of polymer precursors within the composite particles. Similarly, for some polymer precursors, drying of the particles can induce polymerization and/or crosslinking reactions. Furthermore, the solvent/dispersant evaporation results in the formation of dry composite particles, which are collected from the apparatus. Commercial spray dryer apparatuses are available, such as Mobile Minor™ available from GEA Niro, Inc., Columbia, MD. Also, other spray drying apparatuses are available for facilitating the formation of unagglomerated particles, such as described in U.S. Patent 6,962,006 to Chickering, III et al., entitled "Methods and Apparatus for Making Particles Using Spray Dryer and Inline Jet Mill," incorporated herein by reference.

To improve the flowability and dispersability of the composite particles, the materials can be milled following their formation. A range of commercial mills can be adapted for this purpose. However, it may be desirable alternatively or additionally to form the particles using a process in which the surfaces of the particles do not significantly associate, especially with respect to hard fusing, such that the particles are inherently highly flowable. The surface pacification can be chemical or physical in nature. With respect to physical pacification, the particles can be formed, for example, in a spray dry approach such that the particles are in physical isolation when they are formed. Once the dry particles are

collected, the dried polymer generally does not migrate to bind with the polymer of the neighboring particles if the polymer composition is appropriately selected with respect to composition. Furthermore, the chemical pacification can be performed by crosslinking the surface of the composite particles such that the surfaces of the particles do not mingle when the solvent is removed.

In other embodiments, inorganic particles are embedded on the surface of the composite particle. The polymer, optionally composite, particles can be combined with well dispersed inorganic particles. The polymer particles can comprise a composition with appropriate functional groups along the particle surface that forms chemical bonds with the inorganic particles or with a linker associated with the inorganic particles. Thus, the inorganic particles with or without a surface modifier can associate with the polymer particle surface due to non-bonding or bonding interactions. The various pacification approaches can be combined if desired.

Further details for representative specific processes are described further with respect to Figs. 26 and 27. Fig. 26 is directed to inorganic particle production in a reactive flow. Specifically, Fig. 26 refers to an NPM™ process, which is a commercial scale laser pyrolysis approach, such as covered under U.S. Patent 5,958,348 to Bi et al., entitled "Efficient Production of Particles By Chemical Reaction," incorporated herein by reference and other high throughput laser pyrolysis synthesis approaches, although other reactive flow based synthesis approaches can be substituted for the NPM™ process. The formation of inorganic particles is performed in the first step of alternative pathways A, B, and C. Pathways A, B and C provide alternative approaches for forming, optionally modifying and collecting inorganic particles. Pathways D and E are alternative approaches for completing the formation of the composite particles.

In pathway A, inorganic particles are synthesized by laser pyrolysis 600, and no additional in-flight processing is performed such that the inorganic particles are collected and incorporated into a process for the composite formation. The inorganic particles in this pathway can be selected to function as pigments, magnetic particles, charge modifying particles, fillers and/or to provide other desirable functionalities. For example, in some embodiments, the particles can be semi-conductor materials or phosphor particles. The collected particles are introduced into the D or E processing steps to associate the inorganic particles with a binder system.

In pathway B, an in-flight modification is performed on the inorganic particles. As specified in Fig. 26, the modification is a surface modification involving the coating with an

organic pigment. In the in-flight process, inorganic particles are synthesized using laser pyrolysis 602. In parallel, an organic pigment is vaporized 604. The organic pigment vapor is contacted with the inorganic particle flow 606 to form coated inorganic particles through vapor condensation. The inorganic particles function as a substrate for the condensation of the organic pigment, and the inorganic particles function as a core of the resulting pigment particles. The pigment coated particles are collected for incorporation into processing steps D or E where they are associated with a binder.

In pathway C, the inorganic particles are synthesized with laser pyrolysis 608 and collected. There is no in-flight processing of the as-synthesized inorganic particles. However, in process C, the post-collection processing of the inorganic particles involves at least two separate steps. In this process, inorganic particles and pigment precursors are dispersed 610 together in a slurry. Then, pigment compositions are formed in the presence of the inorganic particles 612 such that they become associated with the inorganic particles upon formation. The precipitation of the pigment onto the inorganic particles can take place as a result of solvation effects, solvent removal, bonding to the inorganic particles or the like. In pathway C, the inorganic particles again serve as a substrate for pigment condensation, but in contrast with pathway B, the condensation in pathway C is performed from a dispersion. The formation of pigments in the presence of a silica, i.e., silicon dioxide, core is described further in U.S. Patent 4,566,908 to Nakatani et al., entitled "Azoic Pigments Having a Silica Core," incorporated herein by reference.

Following completion of the A, B or C process steps, the modified or unmodified inorganic particles are incorporated into the alternative composite forming steps of D and E. Both process D and process E involve a spray based approach. In the spray step of each process, a solution/dispersion is atomized using a suitable atomizer. Suitable atomizers include, for example, rotary atomizers that accelerate the liquid to a wheel edge using centrifugal forces, a two-fluid atomizers that uses kinetic energy from a gas stream to generate a shear force for atomization, and a pressure nozzle atomizer that generates a mechanical shear force at the orifice to atomize the droplets. Solvents/dispersants can be, for example, organic solvents, aqueous solvents or combinations thereof. In some embodiments, the solvent/dispersant or a portion thereof is recovered in the spray dry process. The spray generally is directed within a chamber. The composite particles are formed in-flight within the spray chamber, and the dry composite particles are collected from the chamber. The particles can be collected with a cyclone collector or a bag-type collection similar to bag collectors used for continuous recovery of laser pyrolysis generated

particles. Process D and process E differ from each other with respect to the composition of the solution/dispersion sprayed and the in-flight processing of the spray.

In process D, the inorganic particles with or without surface modification are mixed 620 with oligomers and/or monomers as well as any other additives. The resulting solution/dispersion is sprayed 622, and the aerosol spray is subjected to polymerization conditions 624 within the spray chamber. Suitable polymerization conditions may be dependent on the composition of the oligomers/monomers. For example, the polymerization can be induced thermally with an appropriately heated chamber and/or with radiation, such as UV light and/or other energy source that induces the reaction. Generally, the polymer precursors have suitable functional groups for further polymerization and/or crosslinking. Similarly, the aerosol can be formed to combine a catalyst solution with the reaction solution when the aerosol is formed such that the catalyst induces the polymerization reaction. The composite particles are then collected 626 and can be used as desired.

In process E, the inorganic particle with or without surface modification are mixed 630 in a solution/dispersion with a dissolved polymer and any other additives. The resulting solution/dispersion is then sprayed 632 as an aerosol into the spray chamber. The evaporation of the solvent/dispersant within the spray chamber 634 results in desired composite particles, which are collected 636 to obtain a collection of the dry composite particles.

A fully in-flight processing approach is outlined in a flow diagram of Fig. 27. With respect to composite particle formation performed in-flight, inorganic nanoparticles are formed 650, for example, using NPM™ laser pyrolysis. Suitable precursors are delivered 652 to the inorganic particle production step. These inorganic particles can be, for example, pigment particles, such as semiconductor inorganic pigment particles. A series of in-flight processing steps are shown in Fig. 27. Generally, any particular step after synthesis of the inorganic particles 650 is optional, except for one monomer/oligomer delivery step. The inorganic particles can be contacted with a surface modifying agent 654 which are delivered from a source of a first surface modifying agent 656. A surface charge can be applied 658, for example, with a corona discharge, a charged beam, electrodes or the like. Depending on the particular circumstances, surface charge may be conducive to controlled aggregation or may inhibit undesirable aggregation. Thus, modification of surface charge can be used to control aggregation.

A monomer and/or oligomer can be delivered 670 to the flow. The monomers/ oligomers are delivered 672 from a reservoir to the flow, such as using vapor deposition, aerosol deposition, combinations thereof or the like. The monomers/oligomers can be cured 674, i.e., polymerized and/or crosslinked, in-flight after being condensed onto the particles in the flow. In some embodiments, the polymerization is performed in the gas phase, as the vapor deposition process is taking place, while in other embodiments, the curing takes place in a condensed phase of droplets in the flow. The curing of an oligomer/polymer can involve evaporation of a solvent, but in other embodiments a reaction to cure the monomer/oligomer can be induced thermally, such as with infrared heating, or with radiation, such as ultraviolet light, other light, corona discharge, an electron beam, or the like or combinations thereof. For radiation induced curing, the radiation can be applied as a narrow beam or within a particular zone of the flow to control the reaction in a desired way to produce polymer with desired properties. Similar, to induce the curing process, a catalyst can be introduced to the flow in-flight at the time of the application of the monomer/oligomer or subsequently.

Referring to Fig. 27, a property enhancing agent can then be associated 676 with the particles in the flow. The property enhancing agent can be delivered from a reservoir 678. Suitable additives include, for example, wax, pigment or a charge control agent.

A second in-flight coating with a monomer and/or oligomer can be deposited 680 onto the particles in the flow. These additional polymeric materials may or may not form a separate layer in the final composite particles, such as shown in Fig. 3. Referring to Fig. 27, the second quantity of monomer/oligomer can be delivered 682 from a reservoir of second monomer/oligomer compositions, which may be the same or different from the first quantity of monomer/oligomer compositions delivered at step 670. The second quantity of monomers/oligomers can be cured in-flight 684. This can be performed using heat, appropriate radiation or the like as described above with respect to step 674. In additional embodiments, further additives and/or additional coatings of monomer/oligomer can be added subsequent to step 680, as desired.

If desired, controlled aggregation can be performed prior to final collection, although controlled aggregation can similarly be performed after collection and storage with a continuous or batch design. In an embodiment of an in-flight approach, the flow is modified to increase the density of the flow to effectively form a fluidized bed, or directed into a fluidized bed reactor structure, to induce controlled agglomeration 690. An aggregation promoter such as a solvent, vapor, crosslinking agent, monomer or the like can

be added 692 to the fluidized bed reactor to promote controlled aggregation of the composite particles from the flow. The conditions, such as the addition of heat and/or an aggregation promoter, in the fluidized bed portion of the flow can be adjusted to yield desired aggregation. Fuidized bed reactors generally involve suspension of particles in a fluid for supplying controlled reaction conditions. Controlled reactions in fluidized bed reactors are described further, for example, in U.S. Patent Application Publication Number 2005/0267269A to Hagerty et al., entitled Polymerization Process," and U.S. Patent 4,548,138 to Korenberg, entitled "Fast Fluidized Bed Reactor and Method of Operating the Reactor," both of which are incorporated herein by reference. The product composite particles are separated 694 from the flow in the fluidized bed reactor to separate the resulting aggregates 696 from the waste exhaust 698. Final separation of the product can involve, for example, filtration or other suitable approaches. High volume particle collectors are described further, for example, in U.S. Patent 6,270,732 to Gardner et al., entitled "Particle Collection Apparatus And Associated Methods," incorporated herein by reference. The exhaust can be scrubbed as appropriate to remove toxic or environmentally damaging materials and to meet appropriate regulatory standards.

In additional embodiments, the order of the processing steps in Fig. 27 may be modified, particular steps can be repeated and other steps can be added, as appropriate. Also, additional monomer/oligomer coating layers can be added with or without additional additive composition(s). Additional additive(s) can be added at various points in the process.

As noted above, in some embodiments, a plurality of inorganic particles can be formed independently and combined in-flight. Also, as noted above, non-mineral droplets can be formed in-flight for subsequent processing into composites. A general diagram is shown in Fig. 28 broadly indicating optional approaches for in-flight processing with a plurality of inorganic particle channels and a non-mineral droplet processing channel. Herein, the description of non-mineral processing includes, for example, organic processing as well as silicon-based composition processing, and/or surface modification composition processing. Non-mineral droplet processing is in contrast with the inorganic particle processing in which the inorganic particles can be ceramic and generally have a mineral like composition. Generally, the non-mineral droplets are deformable such that they can coat or envelope the inorganic particles.

Referring to Fig. 28, Channels I and II are inorganic particle production and processing channels, and Channel III is an organic droplet/particle production and

processing channel. Channels II and III are optional, and additional inorganic processing channels and/or organic processing channels can be added as appropriate. In general, inorganic processing channels I and II can involve processing steps as shown in Fig. 27 with particular steps added or removed as desired. As shown in Fig. 28, the processing steps are shown more succinctly with steps shown as addition of compositions, delivery of energy or controlled aggregation.

Channel I comprises inorganic particle synthesis 700 with optional modification. In-flight composition addition 712 can comprise addition of monomers/oligomers and/or the addition of other additives, such as organic pigments, surface modifiers, wax, charge control agents or the like or combinations thereof. In-flight energy delivery 714 can involve energy delivery for curing, and/or the addition of surface charge and/or the like. Similarly, controlled aggregation 716 can involve application of surface charge, altering flow density and/or the like. These processing steps can be omitted or repeated as appropriate, and the order of these processing steps can be selected as desired. Channel II similarly comprises inorganic particle synthesis 730, optional in-flight composition addition 732, optional in-flight energy delivery 734 and optional controlled aggregation 736.

Non-mineral processing channel III generally can be initiated with droplet formation 750. Techniques have been developed to form well collimated and entrained aerosol flows. See, for example, U.S. Patent 6,193,936 to Gardner et al., entitled "Reactant Delivery Apparatuses," incorporated herein by reference, which can be adapted for flows without inorganic precursors. Initial droplets can comprise polymer/monomers/oligomers, solvent and/or other organic or silicon-based composition(s), such as pigments or property modifiers. Once the initial droplets are formed, one or more additional processing steps can be performed, as desired. For example, one or more additional compositions can be added 752 to the flowing droplets, for example, using vapor deposition and/or aerosol deposition. Similarly, one or more steps involving the addition of energy/radiation 754, such as a corona discharge, infrared light, ultraviolet light, or the like, or combinations thereof. Furthermore, controlled aggregation can be performed 756, such as through modifications in the flow and/or through adjustments in the surface charges of the droplets. These processing steps can be omitted or repeated as appropriate, and the order of these processing steps can be selected as desired.

Flows from channels II, III or others can be combined with the flow from channel I. For example, with respect to combining multiple inorganic particles in the composite particles, it may be desired, for example, to combine an inorganic semiconductor pigment

with a magnetic inorganic particle. Use of surface exposed magnetic iron oxide particles for toner production is described further, for example in U.S. Patent 6,875,549 to Yamazaki et al., entitled "Dry Toner Production Process, Image Formation Method and Process Cartridge," incorporated herein by reference. Each flow from channels II or III can be combined with the flow in channel I independently at one or more selected stages in the channel I processing. This is indicated schematically with dashed lines in Fig. 28. However, of course, the processing steps themselves in channel I of Fig. 28 can have fewer steps, additional steps, a different order, etc., such that schematic depiction in Fig. 28 for alternative combining orders for the different channels are only a representative sampling of the possibilities. To combine the flows, in some embodiments, the flows can be directed to intersect along a common conduit, although alternative approaches for combining the flows can be used. For these various embodiments, the composite particles are ultimately collected 758, for example, using one of the various collectors described herein.

The reference to in-flight processing refers to a process in which the intermediates are continuously in motion relative to a fixed frame of reference, which generally is the apparatus and the room or room(s) in which that apparatus is located. The rate of the flow with respect to either mass per unit time or net velocity can change along the flow path due to modification in the flow parameters and/or the addition of materials to the flow, but the particles within the flow do not come to a rest until the final product particles are collected. All of the processing can be performed in a single chamber, or one or more processing steps can be performed in separate flow passageways or other chambers. A particular chamber can be identified using conventional understandings on these issues with respect to narrowing or nozzle structures indications of leaving a chamber or widening or similar demarcations indicating entrance into a chamber.

A representative example of the possible processes represented in Fig. 28 is depicted in Fig. 29. In Fig. 29, the process has three branches, processing of a first inorganic particle flow 770, processing of second inorganic particle flow 772 and processing of combined stream 774. As discussed further below, there may only be one inorganic particle processing stream or there may be more than two inorganic particle processing streams. In its simplest form, the overall process only needs to have three processing steps, a synthesis of inorganic particles, a coating or modifying step, and the collection step, although one or more additional steps can be used to accomplish a desired objective.

Referring to Fig. 29, processing of first inorganic particle flow 770 can comprise the synthesis of inorganic particles 780, the modification of inorganic particles 782, a coating

step 784 and a modification of the coated particles 786. Modification step 782, coating step 784 and modification step 786 are individually optional such that none, one, two or all three steps may be performed. Similarly, Modification step 782, coating step 784 and modification step 786 individually can be repeated any number of reasonable times and in any desired order to form desired processed inorganic particle flow from process branch 770.

While coating step 784 generally can involve the delivery of a composition from a reservoir, in some embodiments, coating step 784 itself may comprise optionally a plurality of in-flight processing steps to form a coating composition. Referring to Fig. 30, a representative embodiment of in-flight processing to form a coating composition is presented. In this embodiment, coating step 784 comprises initiating a coating composition flow 790, modifying the flow 792, addition of compositions to the coating composition flow 794, modifying the combined flow 796 and directing the coating composition to a coating nozzle 798. Initiating a coating composition flow 790 can comprise directing a gas, vapor and/or aerosol along a flow channel. Modification 792 of the flow can comprise directing radiation or heat to the flow. Addition of a composition to the flow 794 can comprise addition of a composition that reacts with existing components of the flow or a composition that is inert to the compositions already in the flow. Modification of the combined coating composition flow can comprise addition of radiation and/or heat to the flow, which may initiate a reaction, such as crosslinking or polymerization, within the flow. In general, in these embodiments, only one of steps 792, 794 and 796 may be present. On the other hand, the modification steps 792, 796 and addition of composition steps 794 can be repeated independently a reasonable number of times in a desired order to achieve a desired resulting coating composition. The coating nozzle directs the completed coating composition to an inorganic particle flow.

Referring to Fig. 29, processing of second inorganic particle flow 772 may be completely absent. If processing branch 772 is present, processing branch 772 comprises a step of synthesizing the inorganic particles 810 and can further comprise a modification of inorganic particles 812, a coating step 814 and a modification of coated inorganic particles 816. Modification of inorganic particles 812, coating step 814 and modification of coated particles 816 are individually optional. Similarly, the steps of modification of inorganic particles 812, coating step 814 and modification of coated particles 816 can be individually repeated any reasonable number of times in any desired order to form a desired modified second inorganic particle flow.

Referring to Fig. 29, processing of combined streams 774 comprises combining flows 818, modifying the combined flows 820, applying a coating composition 822, modifying the coated particles 824 and collecting the produce particles 826. Combining flows 818 comprises directing particles from the first inorganic particle flow and the second inorganic particle flow to merge in-flight to form a combined flow. The particles from the two inorganic particle flows may be separately processed in-flight as described above with respect to the many options for this processing. Again, modification step 820, coating step 822 and modification step 824 are individually optional such that none, one, two or all three steps may be performed. Similarly, modification step 820, coating step 822 and modification step 824 individually can be repeated any number of reasonable time and in any desired order to form desired processed mixed inorganic particle flow from process branch 774. The collection of the particles 826 terminates the in-flight processing as it terminates the flow.

As shown in Fig. 29, two separate inorganic particle flows are combined, and it is noted above that appropriate processes may have only a single inorganic particle synthesis step and corresponding processing branch. However, in alternative embodiments, three or more inorganic particle flows can be combined. The third or higher inorganic particle flow can be combined also at step 818 or they can be introduced at any selected later step after the first two inorganic particle flows have been combined, and the third inorganic particle flow can be subjected to some form of modification, such as interaction with radiation or a coating composition. Similarly, a fourth inorganic particle flow need not be combined at the same step as the third, and so on for any further inorganic particle flows.

Uses and Structures Formed from the Composite Particles

The composite particles can be used essentially in any application in which the properties of the composite particles are advantageous. In particular, the small composite particles are suitable for forming coatings and for printing applications. As noted above, the small size of the composite particles provides improved performance as toner since sharper images can be formed, and generally the images can be formed at lower temperatures due to the smaller particle sizes. Toner particles can be printed, for example, using established electrophotographic processes. In addition, the small size of the composite particles can be advantageous for forming thin coatings.

For the formation of thin coatings, in some embodiments, the composite particles can be suspended in a dispersant and coated onto a substrate surface using, for example,

spray coating, spin coating, dip coating, extrusion or other suitable coating approach. The spray coating can be performed to provide a desired thickness of the composite particles upon the removal of the dispersant. For example, roughly a monolayer equivalent of composite particles can be deposited uniformly over a substrate, although thicker layers can be similarly formed as desired. The amount of composite material can be controlled through the adjustment of the concentration of the dispersion and the spray conditions. After depositing the composite particle coating, the coating can be heated to flow the polymer within the composite particles. The flow can result in a layer of composite material in contrast with a layer of distinguishable particles. Through this approach, very thin layers of polymer-inorganic particle composite material can be deposited. In some embodiments, the layer can have an average thickness of no more than about five microns, in other embodiments, no more than about a micron, in some embodiments no more than about 500 nm and in further embodiments from about 5 nm to about 250 nm. A person of ordinary skill in the art will recognize that additional ranges of average coating thicknesses within the explicit ranges above are contemplated and are within the present disclosure.

The composite particles can be printed onto a substrate to form images on the substrate. To form images, generally the coating is applied to selected portion of the substrate less than the entire substrate surface. The printed material can form characters or other desired images. The image can be black and/or desired colors. In some embodiments, the images where applied, have an average thickness of no more than about 3 microns and in further embodiments no more than about 2 microns. A person of ordinary skill in the art will recognize that additional ranges within the explicit ranges of average image thickness are contemplated and are within the present disclosure. To set the image, the coated substrate can be heated above the flow temperature of the polymer within the composite particles.

Coatings of various thicknesses whether or not subsequently heated can be useful for a range of applications, such as optical applications, protective coatings, electromagnetic shielding and thermal conduction. With respect to optical coatings, the index of refraction of the composite can be selected to yield desirable properties for antireflective coatings, UV absorbing coatings, optical filters and the like. Protective coatings can be used if the composite is a hard material that can protect a softer substrate. Electromagnetic shielding coatings can be formed with magnetic inorganic particles, such as iron oxides or iron carbides, as described further in U.S. Patent 5,938,979 to Kambe et al., entitled "Electromagnetic Shielding," incorporated herein by reference. Good thermal conducting

coatings can be formed with aluminum nitride (AlN) particles, which is a very good thermal conductor.

The composite particles described herein are well suited for a range of printing applications. For example, the composite particles can be directly used as dry toner for electrophotographic printing. Dry toners are used in laser printers, photocopiers, fax machines, combinations thereof and the like. Similarly, the composite particles can be dispersed in a liquid for use as a liquid toner. Liquid toner compositions can be substituted for dry toners for electrophotographic printing. The use of liquid toners with solid toner particles is described further, for example, in U.S. Patent 6,132,922 to Fukae et al., entitled "Liquid Developer For Electrophotographic Printing Apparatus," incorporated herein by reference.

The composite particles can also be incorporated into inks for ink jet printing, lithographic printing, gravure printing, screen printing and the like. The composite particles can function as pigments and/or property modifiers to facilitate the formation of a stable image. Due to the small particle size, sharper images can be formed with less material. The use of printing inks with particulate colorants for newspaper publishing is described in U.S. Patent 5,981,625 to Zou et al., entitled "Non-Rub Off Printing Inks," incorporated herein by reference.

EXAMPLE - In Situ Silanization of Rutile Titanium Oxide

This example demonstrates the ability to surface modify rutile titanium oxide particles formed by laser pyrolysis, in-flight prior to collection of the particles.

The laser pyrolysis was performed in an apparatus essentially as shown in Fig. 17. As shown in Fig. 17, an epoxy trimethoxy silane is introduced into the coating nozzle 400 through a conduit. In some alternative embodiments, the apparatus has been modified for the delivery of epoxy trimethoxy silane composition into the chamber along a baffle leading to the exit nozzle.

Reaction conditions were set to produce rutile titanium dioxide with BET surface areas of roughly either 100 m^2/g or 150 m^2/g. The reaction conditions to form rutile titanium dioxide is discussed further in U.S. Patent 6,599,631 to Kambe et al., entitled "Polymer-Inorganic Particle Composites," incorporated herein by reference.

The epoxy trimethoxy silane ($(CH_3O)_3SiCH_2CH_2CH_2OCH_2CHOCH_2$) was delivered by bubbling dry nitrogen gas through a heated liquid of the silane. The particle stream was cooled and maintained at a temperature below the silane decomposition temperature of

150°C by diluting the flow with nitrogen gas. The particle modification was performed in different runs at several silane flows.

Results are presented in the Fig. 31 for the infrared spectra of four samples of silane modified titanium dioxide particles. For comparison, a spectrum for the silane itself is presented. As the silane flow is increased from samples 1 to 4, clear evidence of the presence of silane on the particles is evident. At least samples 3 and 4 exhibit peaks evidencing silane. A transmission electron micrograph of the particles is shown in Fig. 32. A halo around the particles seems to correspond to the epoxy silane coating around the particles.

The surface modified particles were dispersed. Measurements of volume percent as a function of particle diameter in the dispersion are plotted for two samples in Fig. 33. A majority of the particles were well dispersed with particle diameters in solution of roughly 15 nanometer and an extremely narrow distribution. A second peak indicates a small amount of some higher agglomerates.

The embodiments above are intended to be illustrative and not limiting. Additional embodiments are within the claims. In addition, although the present invention has been described with reference to particular embodiments, those skilled in the art will recognize that changes can be made in form and detail without departing from the spirit and scope of the invention. Any incorporation by reference of documents above is limited such that no subject matter is incorporated that is contrary to the explicit disclosure herein.

What is claimed is:

1. A collection of composite particles having an average particle size of no more than about 2.5 microns, wherein each of at least about 95 percent of the composite particles comprise a thermoplastic polymer binder and a plurality of inorganic particles.

2. The collection of composite particles of claim 1 wherein the inorganic particles have an average particle size of no more than about 250 nm.

3. The collection of composite particles of claim 1 wherein the composite particles comprise a surface modifier chemically bonded to the surface of the inorganic particles.

4. The collection of composite particles of claim 1 wherein at least about 90 percent of the composite particles have an aspect ratio of no more than about 1.8.

5. The collection of composite particles of claim 1 wherein the composite particles further comprise a pigment, a phosphor or a dye.

6. The collection of composite particles of claim 1 wherein the composite particles further comprise a charge modulator.

7. The collection of composite particles of claim 1 wherein the composite particles comprise a magnetic inorganic particle.

8. The collection of composite particles of claim 1 wherein the composite particles comprise a particle comprising a semi-conducting inorganic material.

9. The collection of composite particles of claim 1 wherein the composite particles comprise on average at least about 50 volume percent polymer binder.

10. The collection of composite particles of claim 1 wherein the inorganic particles are essentially randomly distributed within the composite particle.

11. The collection of composite particles of claim 1 wherein a majority of the particles comprise a plurality of layers having distinct compositions from each other.

12. The collection of composite particles of claim 1 wherein a majority of composite particles comprise a plurality of inorganic particles embedded along the surface of the composite particles.

13. A collection of composite particles having an average particle size of not more than about 2.5 microns wherein a majority of the composite particles have an inorganic particle core surrounded by the polymer binder and wherein the surface of the composite particles have a higher degree of crosslinking relative to the interior of the particles.

14. A collection of composite particles comprising inorganic particles and a polymer wherein a majority of the composite particles comprise a core comprising the polymer and the inorganic particles are embedded along the surface of the composite particles, the composite particles having an average particle size no more than about 10 microns.

15. The collection of composite particle of claim 14 wherein the polymer comprises a thermoplastic polymer binder and wherein the inorganic particles have an average particle size of no more than about 100 nm.

16. The collection of composite particles of claim 14 further comprising a polymer layer over the embedded inorganic particles.

17. A collection of composite particles comprising inorganic particles and a polymer having a multiple branched structure.

18. The collection of composite particles of claim 17 wherein the polymer comprises a dendrimer.

19. The collection of composite particles of claim 17 wherein the inorganic particles are chemically bonded to the polymer.

20. The collection of composite particles of claim 19 wherein a surface modifier links the inorganic particles and the polymer wherein the surface modifier is chemically bonded to the inorganic particles and the surface modifier is covalently bonded to the polymer.

21. A collection of composite particles comprising inorganic particles and a coating comprising an organic or silicon-based compound, wherein the composite particles have an average particle size of no more than about 10 microns, wherein the inorganic particles have an average particle size of no more than about 100 nanometers and wherein the inorganic particles are phosphors, metal nitrides, metal carbides, metal sulfides, metalloid nitrides, metalloid carbides, metalloid sulfides, doped particles, combinations thereof or mixtures thereof.

22. The collection of composite particles of claim 21 wherein the inorganic particles comprise a phosphor with a host crystalline lattice and an activator dopant.

23. The collection of composite particles of claim 21 wherein the coating comprises a surface modifier chemically bonded to the inorganic particles.

24. The collection of composite particles of claim 21 wherein the coating comprises a thermoplastic polymer binder.

25. A collection of composite particles having a layered structure having distinct compositions from each other, the composite particles comprising inorganic particles and a thermoplastic polymer binder, wherein the composite particles have an average particle size of no more than about 10 microns and wherein each layer of the composite particles comprises a polymer.

26. The collection of composite particles of claim 25 wherein a first layer of the composite particles comprises first inorganic particles and the thermoplastic polymer binder and a second layer comprises second inorganic particles different from the first inorganic particles and a polymer.

27. The collection of composite particles of claim 25 wherein an outer layer of the composite particles comprise crosslinked polymer.

28. A method for forming composite particles comprising a composite of inorganic particles and a polymer, the method comprising spray drying a solution comprising the inorganic particles and a polymer precursor wherein the spray is reacted in-flight to form a thermoplastic polymer binder.

29. The method of claim 28 wherein the in-flight reaction is initiated through irradiation with electromagnetic radiation.

30. The method of claim 29 wherein the electromagnetic radiation comprises ultraviolet light.

31. The method of claim 28 wherein the in-flight reaction is initiated thermally.

32. The method of claim 28 wherein the composite particles are substantially dispersible with an average particle size of no more than about 2.5 microns.

33. A printed structure comprising a substrate and images printed onto the substrate wherein the image has a thickness of no more than about 3 microns and wherein the image covers a selected portion of a surface of the substrate, the selected portion being less than the entire substrate surface.

34. The printed structure of claim 33 wherein the substrate comprises paper.

35. The printed structure of claim 33 wherein the image comprises inorganic particles and a thermoplastic polymer binder.

36. A method for the formation of a thin coating comprising a polymer-inorganic particle composite, the method comprising heating a substrate coated with a coating comprising a collection of composite particles comprising inorganic particles and a thermoplastic polymer binder, the collection of composite particles having an average particle size no more than about 2.5 microns, wherein the heating is performed to a temperature beyond the flow temperature of the polymer.

37. The method of claim 36 wherein the coating is printed to cover a portion of the substrate less than the entire substrate surface.

38. The method of claim 36 wherein the composite particles further comprise a pigment, a phosphor or a dye.

39. The method of claim 36 wherein each of at least about 95 percent of the composite particles comprises a plurality of inorganic particles.

40. The method of claim 36 wherein the resulting coating has an average thickness of no more than about 3 microns.

41. A method for the in-flight modification of inorganic particles formed within a reactive flow, the method comprising directing an organic or silicon-based coating composition to contact an inorganic particle flow downstream from a reaction zone where the inorganic particles were formed, to modify the particles in the flow.

42. The method of claim 41 wherein the inorganic particles are formed in a reaction driven by an intense light beam.

43. The method of claim 41 further comprising intersecting the flow of inorganic particles with an inert gas to cool the inorganic particles downstream from the reaction zone, prior to directing the coating composition at the inorganic particle flow.

44. The method of claim 41 wherein the directing of a coating composition comprises directing an organic coating composition at the flow of inorganic particles.

45. The method of claim 41 wherein the coating composition comprises a surface modification agent that chemically bonds to the particle surfaces.

46. The method of claim 41 wherein the coating composition comprises a polymer.

47. The method of claim 41 wherein the coating composition comprises a polymer precursor.

48. The method of claim 41 wherein the coating composition comprises a dye.

49. The method of claim 41 further comprising directing radiation at the flow of inorganic particles after directing the coating composition at the flow of inorganic particles wherein the radiation induces a reaction of the coating composition.

50. The method of claim 41 further comprising forming a second independent flow of product inorganic particles at a second reaction zone and subsequently combining this second flow of product inorganic particles with the inorganic particles before or after they are contacted with the coating composition.

51. The method of claim 41 wherein the coating composition is formed in an aerosol and modified by radiation or with another composition prior to directing the coating composition to contact the inorganic particle flow.

52. A method for the in-flight modification of inorganic particles formed within a reactive flow, the method comprising directing incoherent radiation from a radiation source to an inorganic particle flow downstream from a reaction zone where the inorganic particles were formed, to modify the inorganic particles.

53. The method of claim 52 wherein the directing of radiation comprises directing infrared light, ultraviolet light, visible light or electron beam radiation at the flow of inorganic particles.

54. The method of claim 52 wherein the modification of the inorganic particles comprises a change in crystal structure.

55. The method of claim 52 wherein the modification of the inorganic particles comprises a change in oxidation state.

56. The method of claim 52 further comprising applying an organic or silicon-based coating composition to the inorganic particles following the modification of the inorganic particles by the radiation.

57. A reaction apparatus comprising a reactant delivery portion, a reaction chamber, an energy source, a coating nozzle and a collector, wherein the reactant delivery portion is configured to deliver precursors for inorganic particle formation through an inlet into the reaction chamber, wherein the reaction chamber is configured to have a flow path from the inlet of the reactant delivery system to the collector, wherein the energy source is configured to deliver excitation energy to a flow of inorganic particle precursors within the flow path to establish a reaction zone, wherein the coating nozzle is operably connected to a reservoir of organic or silicon-based coating nozzle and wherein the coating nozzle is configured to deliver a coating composition to the flow path at a coating location downstream from the reaction zone.

58. The reaction apparatus of claim 57 wherein the reactant delivery portion is configured to deliver vapor precursors for inorganic particle formation.

59. The reaction apparatus of claim 57 wherein the reactant delivery portion is configured to deliver aerosol precursors for inorganic particle formation.

60. The reaction apparatus of claim 57 wherein the energy source comprises an intense light source that is configured to project a beam of light through the reaction chamber to intersect the flow path.

61. The reaction apparatus of claim 60 wherein the intense light source comprises a laser.

62. The reaction apparatus of claim 57 wherein the collector comprises a continuous collector such that collected powders can be removed from the apparatus without stopping production.

63. The reaction apparatus of claim 62 wherein the collector comprises:

a collection chamber having a collector inlet, a gas outlet, and a particle drain, wherein the gas outlet is connected to a pump;

a filter within the collection chamber, wherein the filter is configured to obstruct flow paths from the collector inlet to the gas outlet and wherein particles dislodged from the filter flow to the particle drain;

a particle removal section that is configured to apply force to the filter to dislodge particles from the filter; and

a particle drain at the bottom of the collection chamber.

64. The reaction apparatus of claim 57 wherein the coating location is within the reaction chamber downstream from the reaction zone.

65. The reaction apparatus of claim 57 further comprising an outlet conduit connecting the reaction chamber and the collector with a configuration to have the flow path extending through the outlet conduit to the collector, wherein the coating location is within the outlet conduit.

66. The reaction apparatus of claim 57 wherein the coating nozzle comprises an aerosol generator.

67. The reaction apparatus of claim 57 further comprising a radiation source configured to direct radiation to intersect the flow path.

68. The reaction apparatus of claim 67 wherein the radiation source is configured to direct radiation to intersect the flow path upstream from the coating location.

69. The reaction apparatus of claim 67 wherein the radiation source is configured to direct radiation to intersect the flow path downstream from or at an overlapping position with the coating location.

70. The reaction apparatus of claim 57 wherein the inlet has an elongated configuration characterized with a major axis and a minor axis wherein the major axis is at least a factor of three greater than the minor axis to form a flow path that is correspondingly elongated and wherein the coating nozzle has an elongated configuration oriented to intersect the elongated flow path with an elongated stream of coating composition such that the elongated dimensions approximately coincide.

71. The reaction apparatus of claim 57 further comprising an inert gas inlet operably connected to an inert gas reservoir wherein the inert gas inlet is configured to deliver inert gas to the flow path between the reaction zone and the coating location.

72. The reaction apparatus of claim 57 wherein the coating nozzle is operably connected to a coating conduit operably connected to two separate reservoirs with a configuration to mix compositions from the two separate reservoirs for delivery through the coating nozzle.

73. A reaction apparatus comprising a reactant delivery portion, a reaction chamber, an energy source, a radiation source and a collector, wherein the reactant delivery portion is configured to deliver precursors for inorganic particle formation through an inlet into the reaction chamber, wherein the reaction chamber is configured to have a flow path from the inlet of the reactant delivery system to the collector, wherein the energy source is configured to deliver excitation energy to a flow of inorganic particle precursors within the flow path to establish a reaction zone, wherein the radiation source is configured to deliver radiation to the flow path at a transformation location downstream from the reaction zone and wherein the radiation source directs incoherent infrared light, microwave radiation, visible light, x-ray radiation, an electron beam, a corona discharge or a combination thereof.

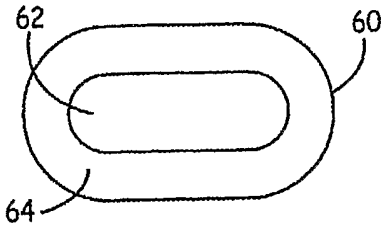


FIG. 1

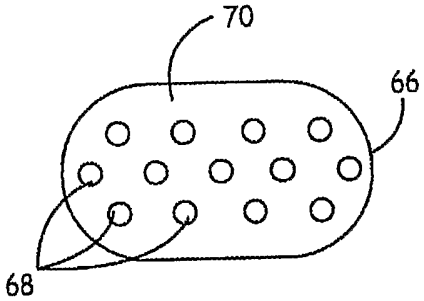


FIG. 2

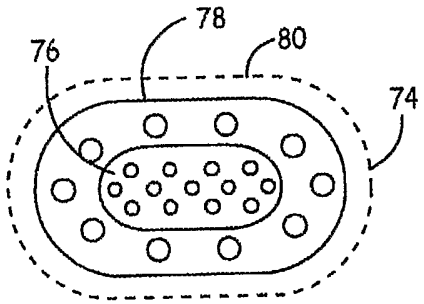


FIG. 3

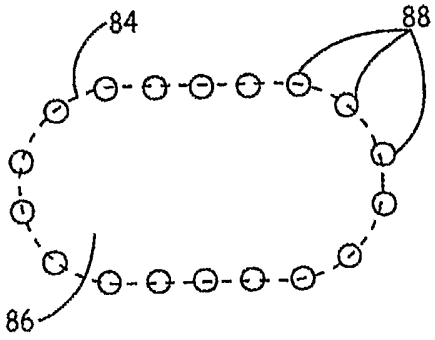


FIG. 4

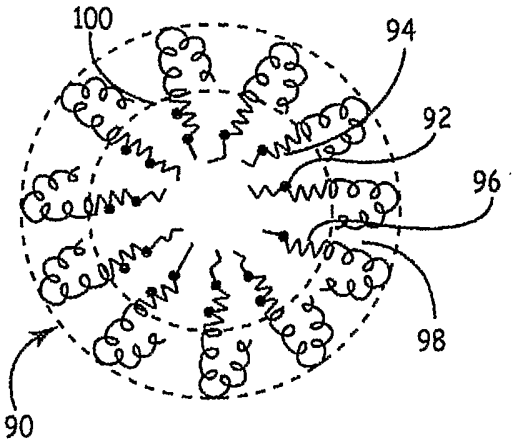

100
94
92
96
98
90

FIG. 5

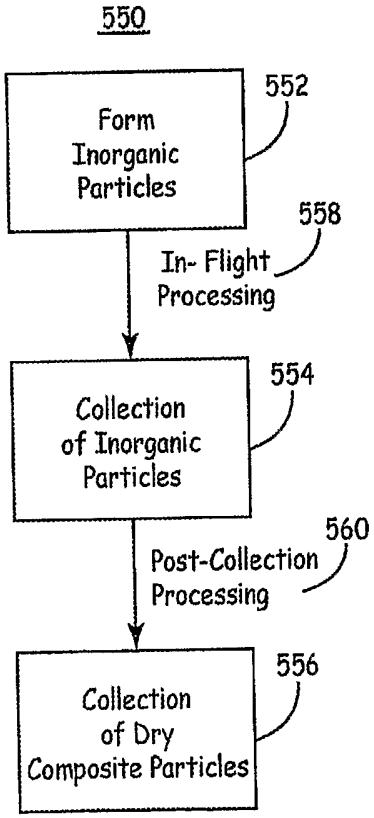

550
Form Inorganic Particles
552
In- Flight Processing
558
Collection of Inorganic Particles
554
Post-Collection Processing
560
Collection of Dry Composite Particles
556

FIG. 25

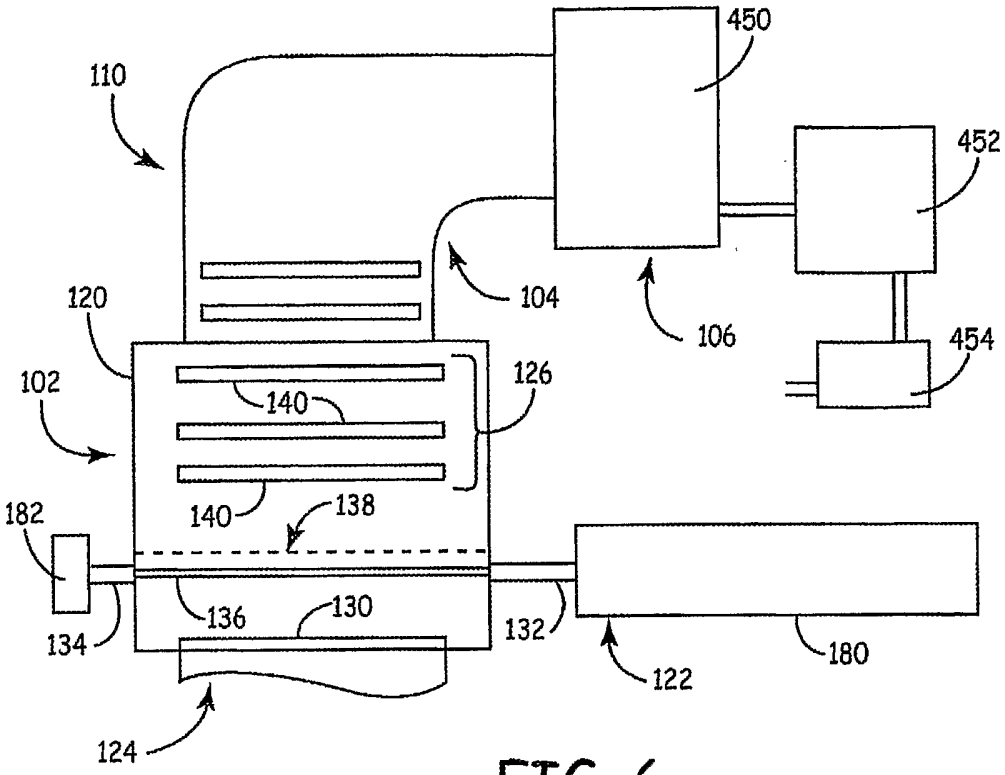

450
110
452
104
106
120
454
102
126
140
140
138
182
136
130
134
132
122
180
124

FIG. 6

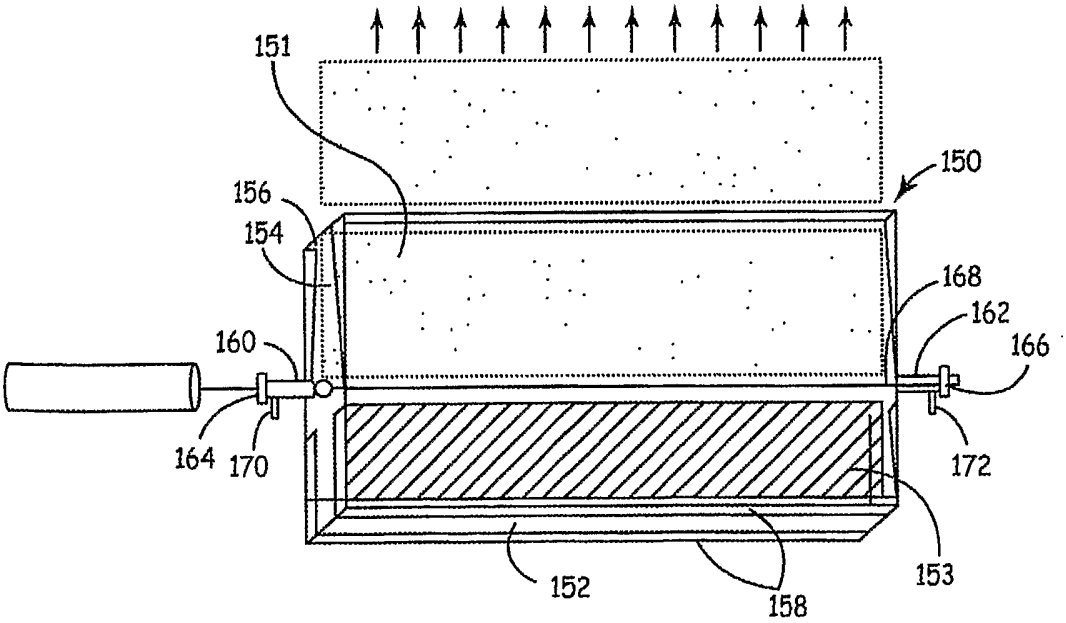

151
150
156
154
168
162
160
166
164
170
172
153
152
158

FIG. 7

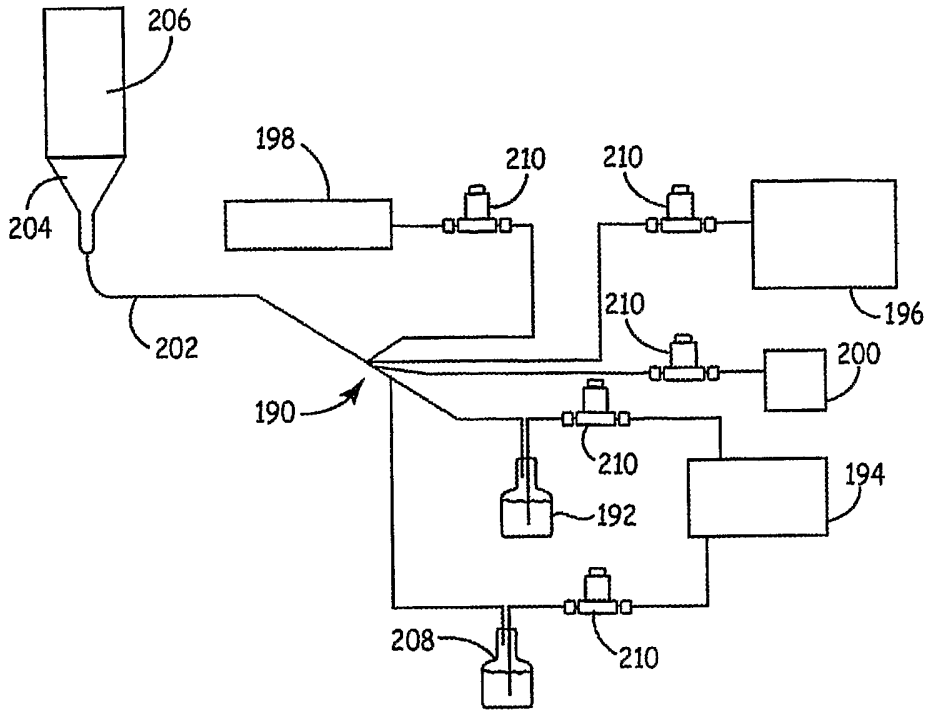

206
198
210
210
204
196
202
210
200
190
210
194
192
208
210

FIG. 8

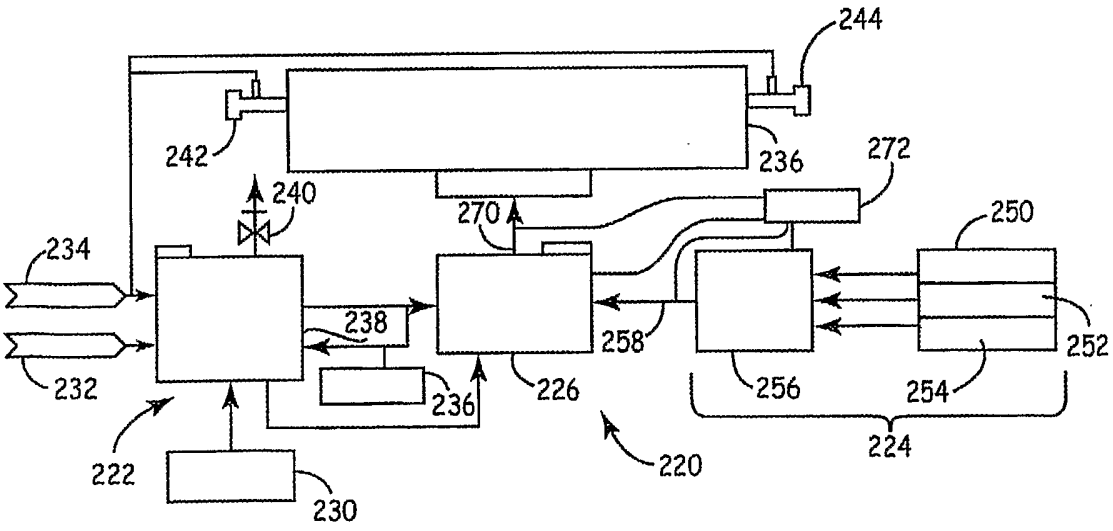

244
242
236
272
240
270
250
234
238
258
252
232
236
226
256
254
222
220
224
230

FIG. 9

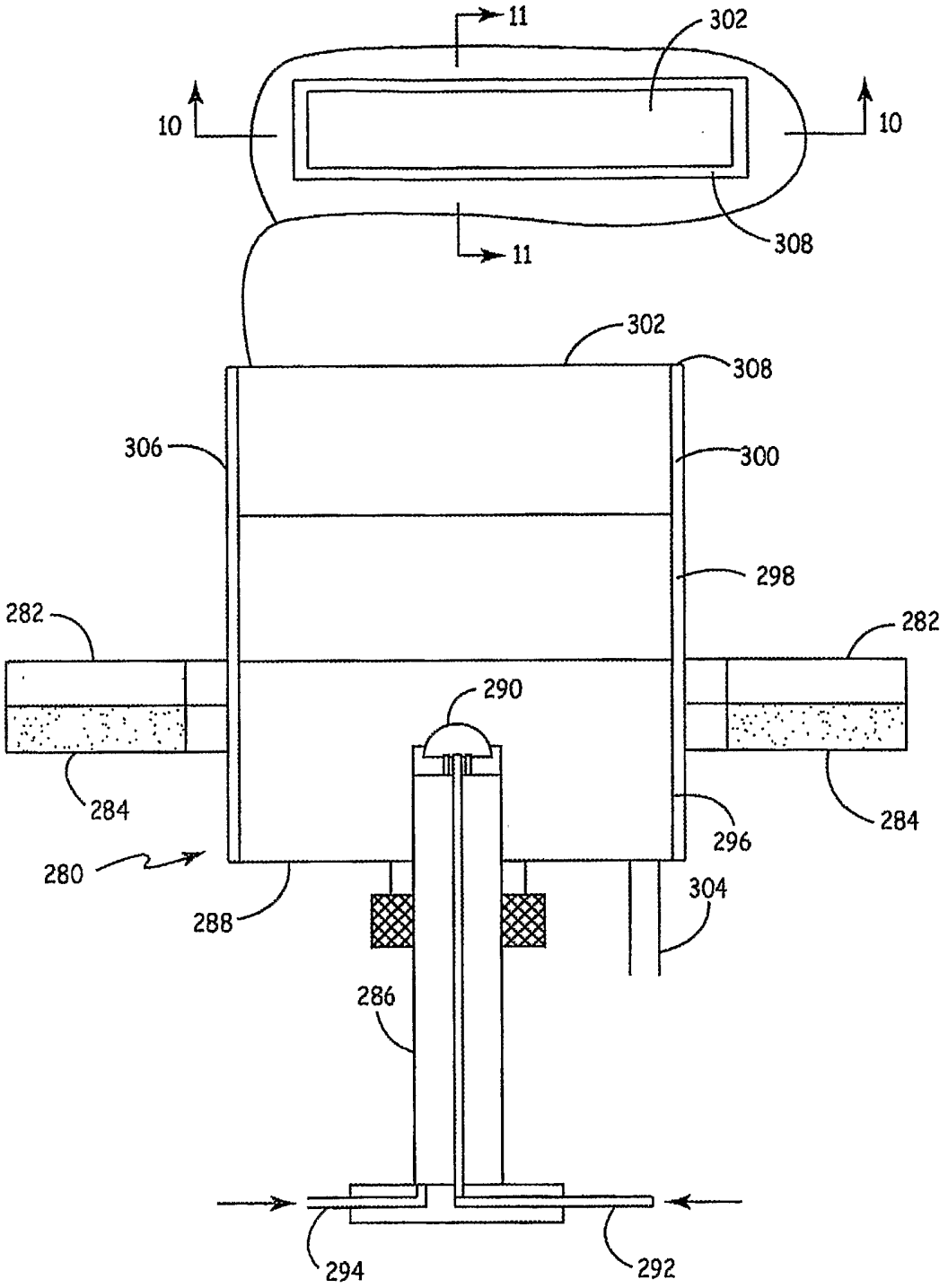

11
302
10
10
308
11
302
308
306
300
298
282
282
290
284
284
280
296
304
288
286
294
292

FIG. 10

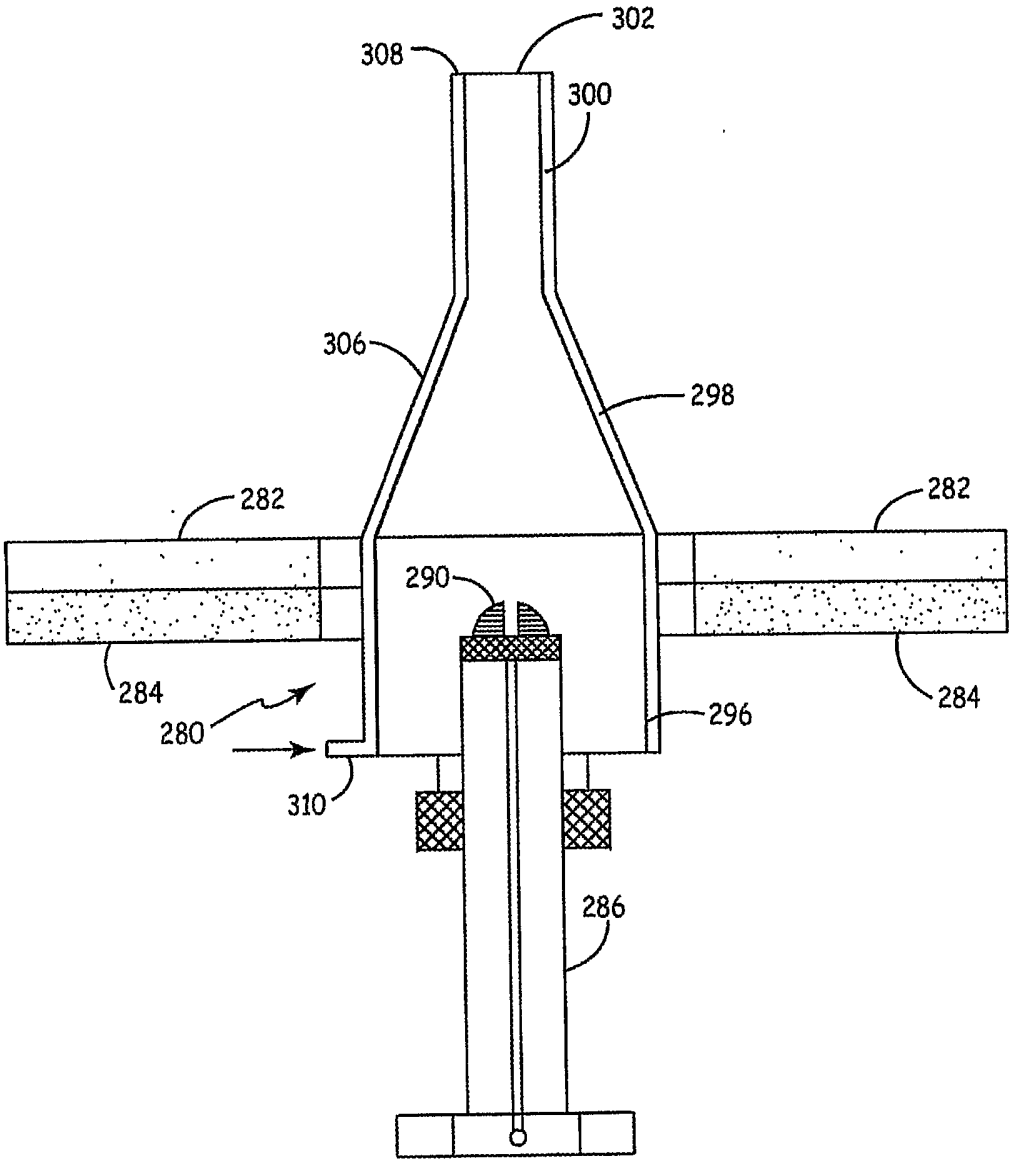
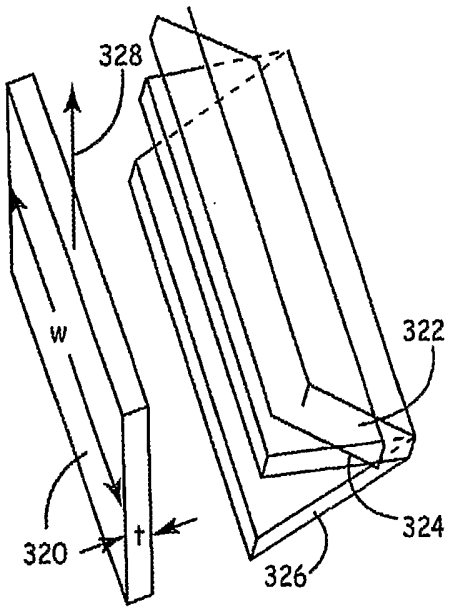


FIG. 11

FIG. 12


328
w
322
320
t
324
326

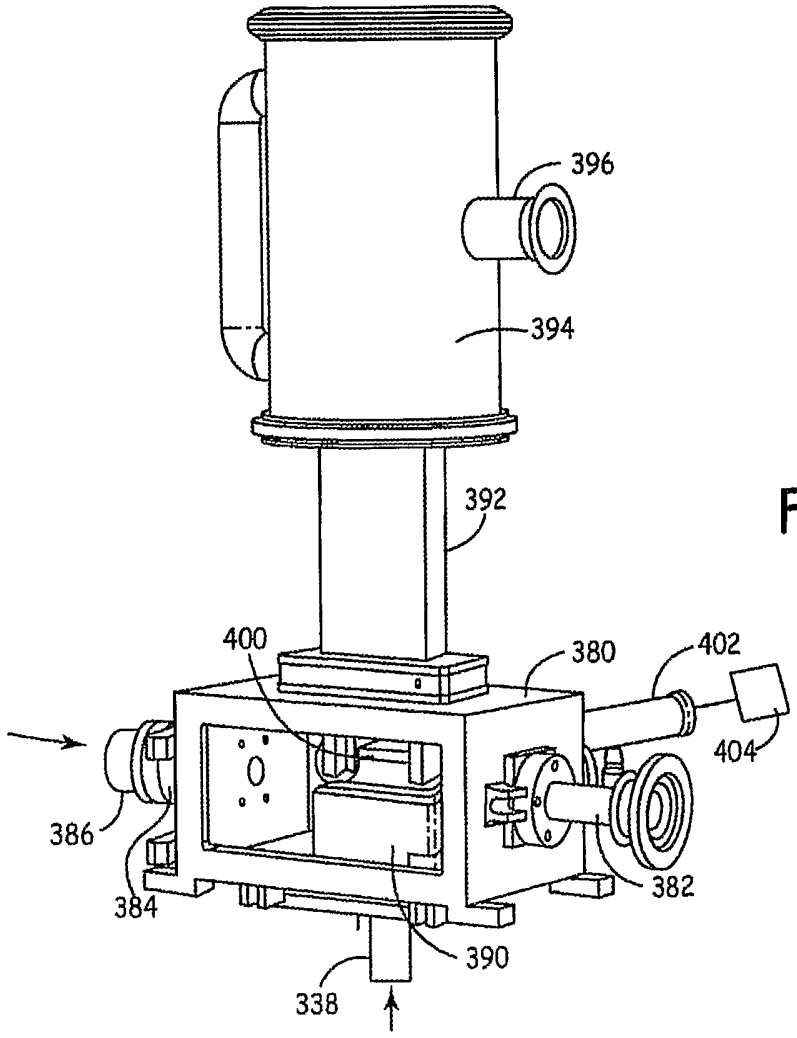

396
394
392
400
380
402
404
386
384
382
390
338

FIG. 17

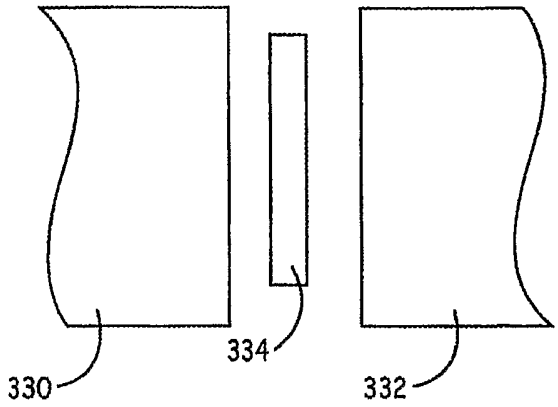


FIG. 13

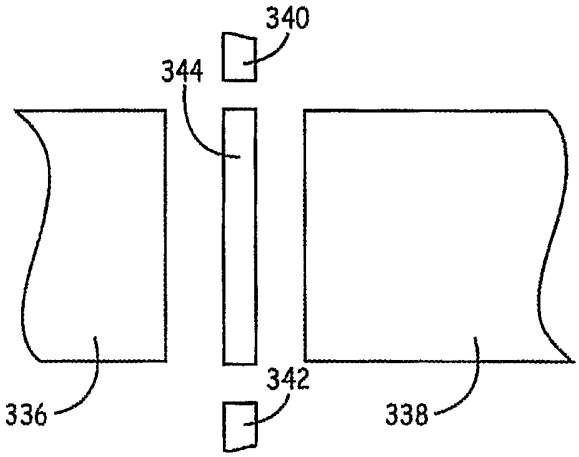


FIG. 14

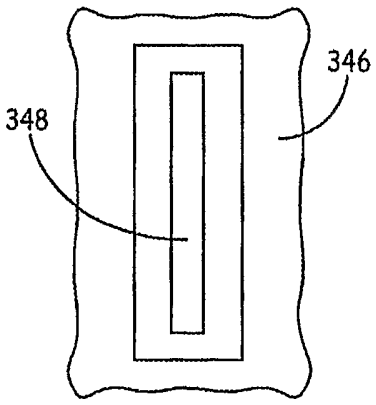


FIG. 15

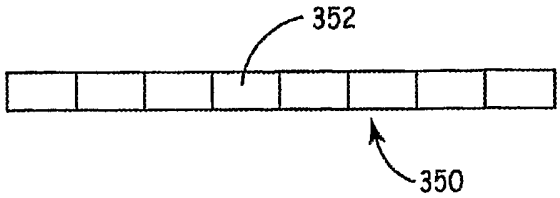


FIG. 16

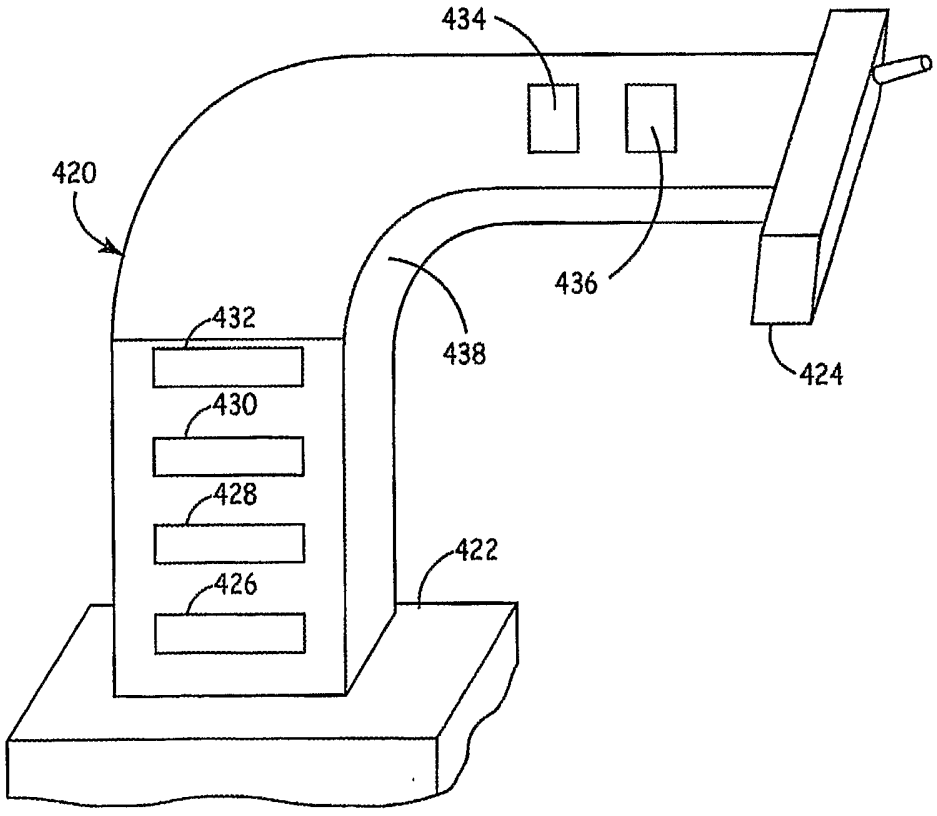


FIG. 18

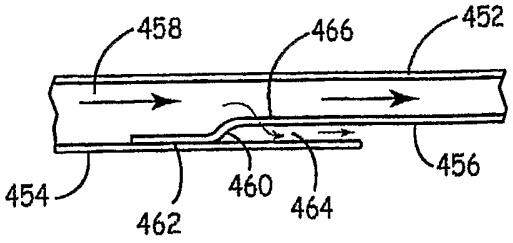


FIG. 19A

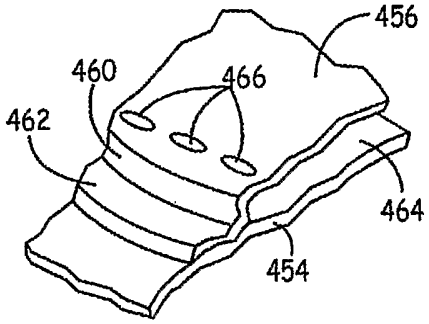


FIG. 19B

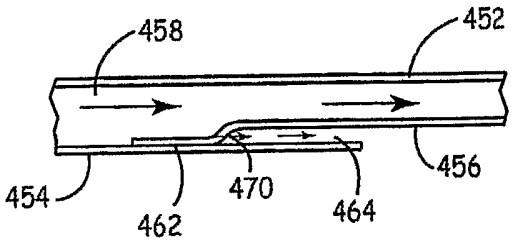


FIG. 20A

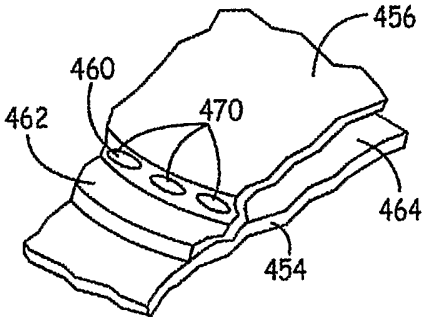


FIG. 20B

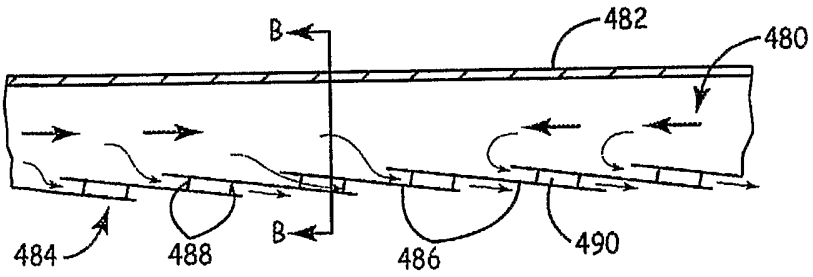


FIG. 21A

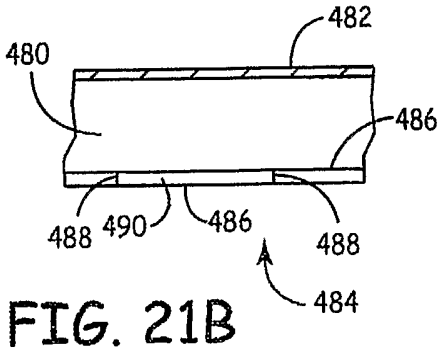


FIG. 21B

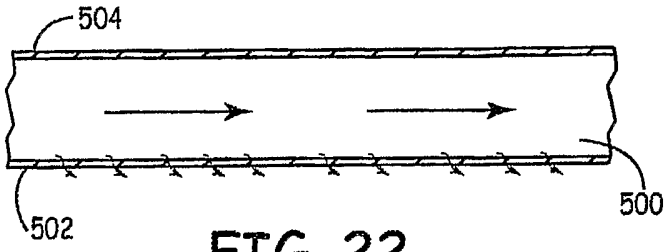


FIG. 22

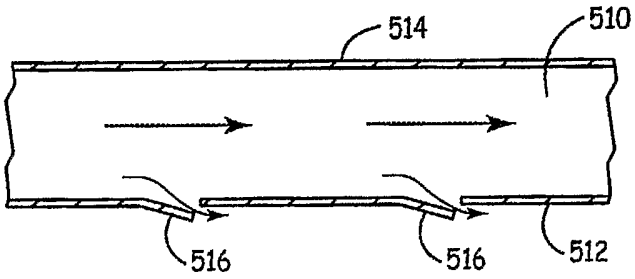


FIG. 23A

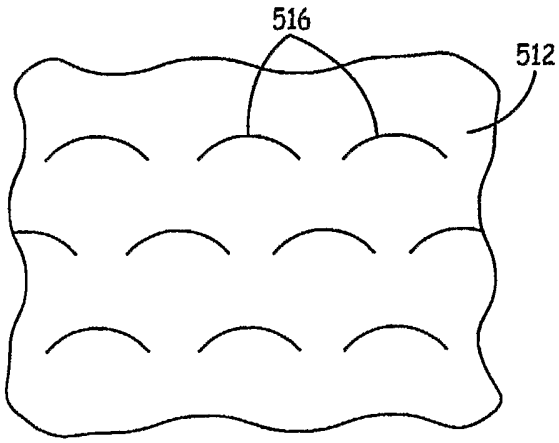


FIG. 23B

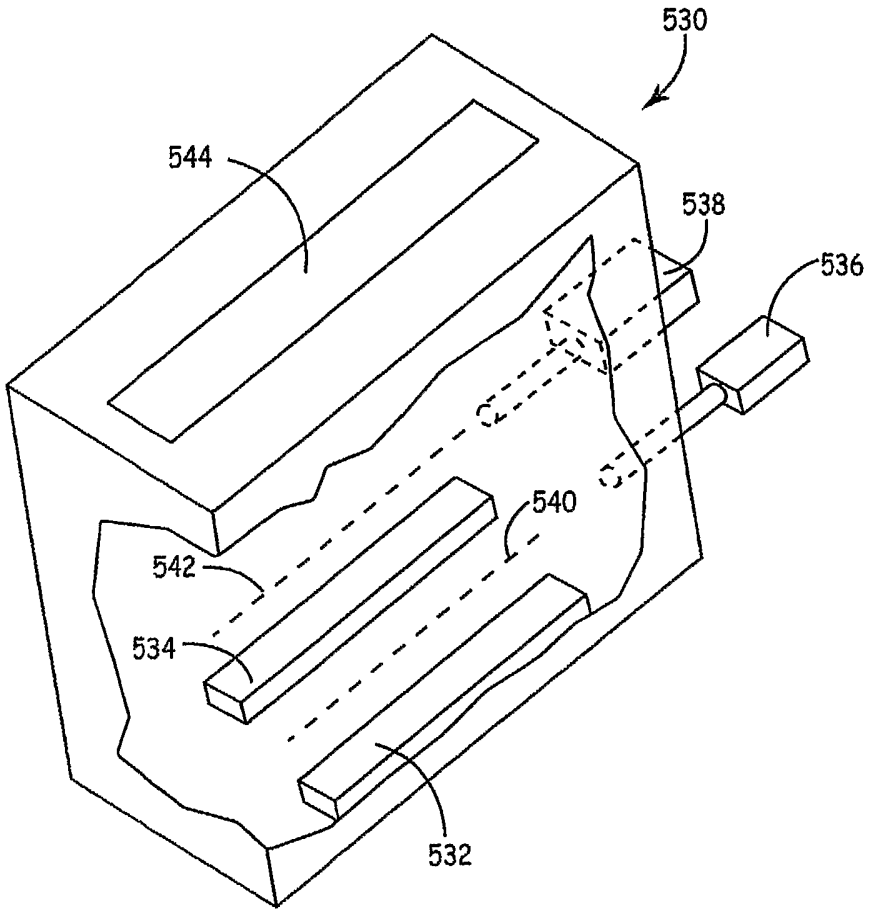


FIG. 24

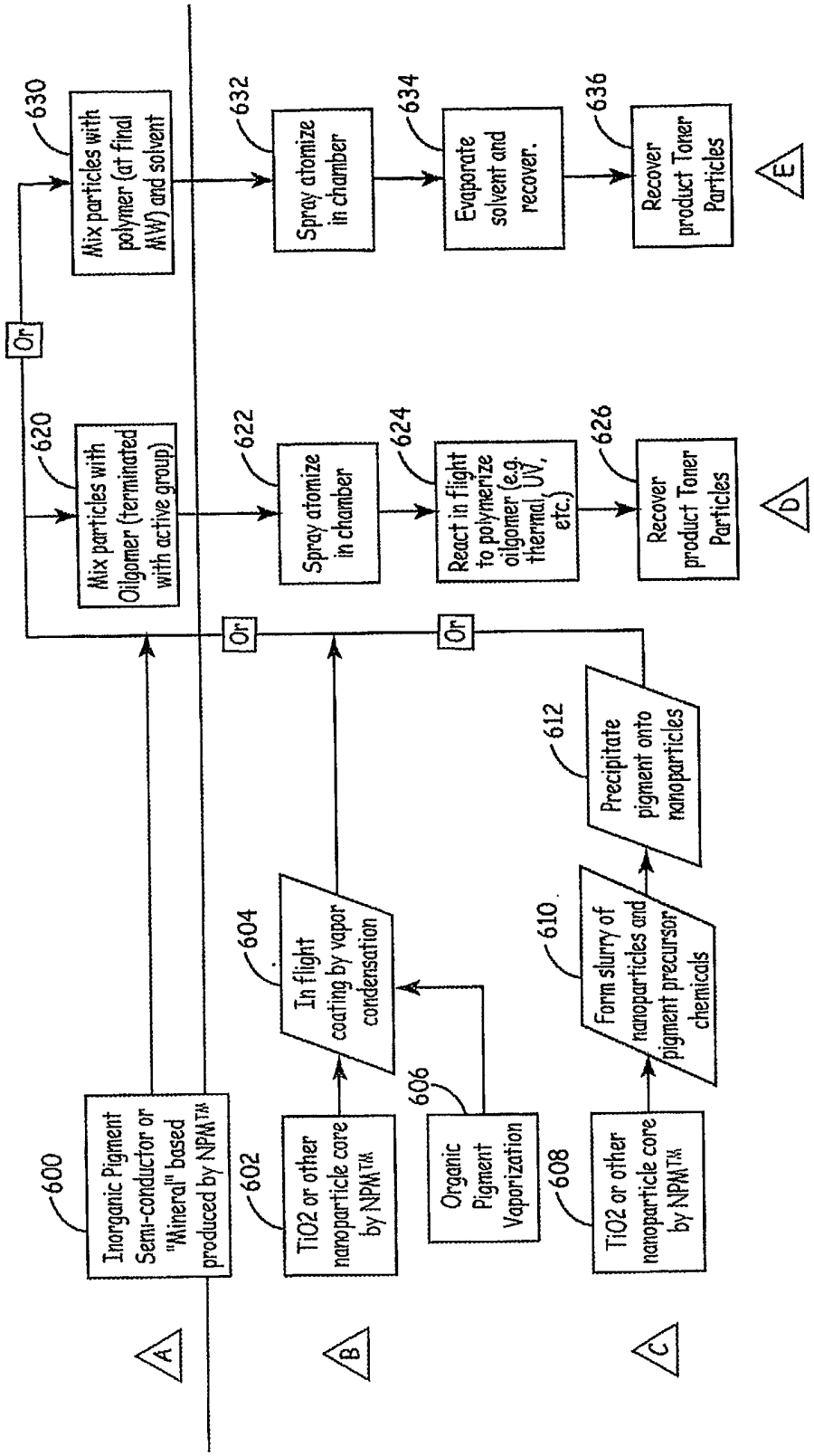

600
Inorganic Pigment Semi-conductor or "Mineral" based produced by NPM™
602
TiO2 or other nanoparticle core by NPM™
604
In flight coating by vapor condensation
606
Organic Pigment Vaporization
608
TiO2 or other nanoparticle core by NPM™
610
Form slurry of nanoparticles and pigment precursor chemicals
612
Precipitate pigment onto nanoparticles
620
Mix particles with Oligomer (terminated with active group)
622
Spray atomize in chamber
624
React in flight to polymerize oligomer (e.g. thermal, UV, etc.)
626
Recover product Toner Particles
630
Mix particles with polymer (at final MW) and solvent
632
Spray atomize in chamber
634
Evaporate solvent and recover.
636
Recover product Toner Particles
Or
Or
Or
A
B
C
D
E

FIG. 26

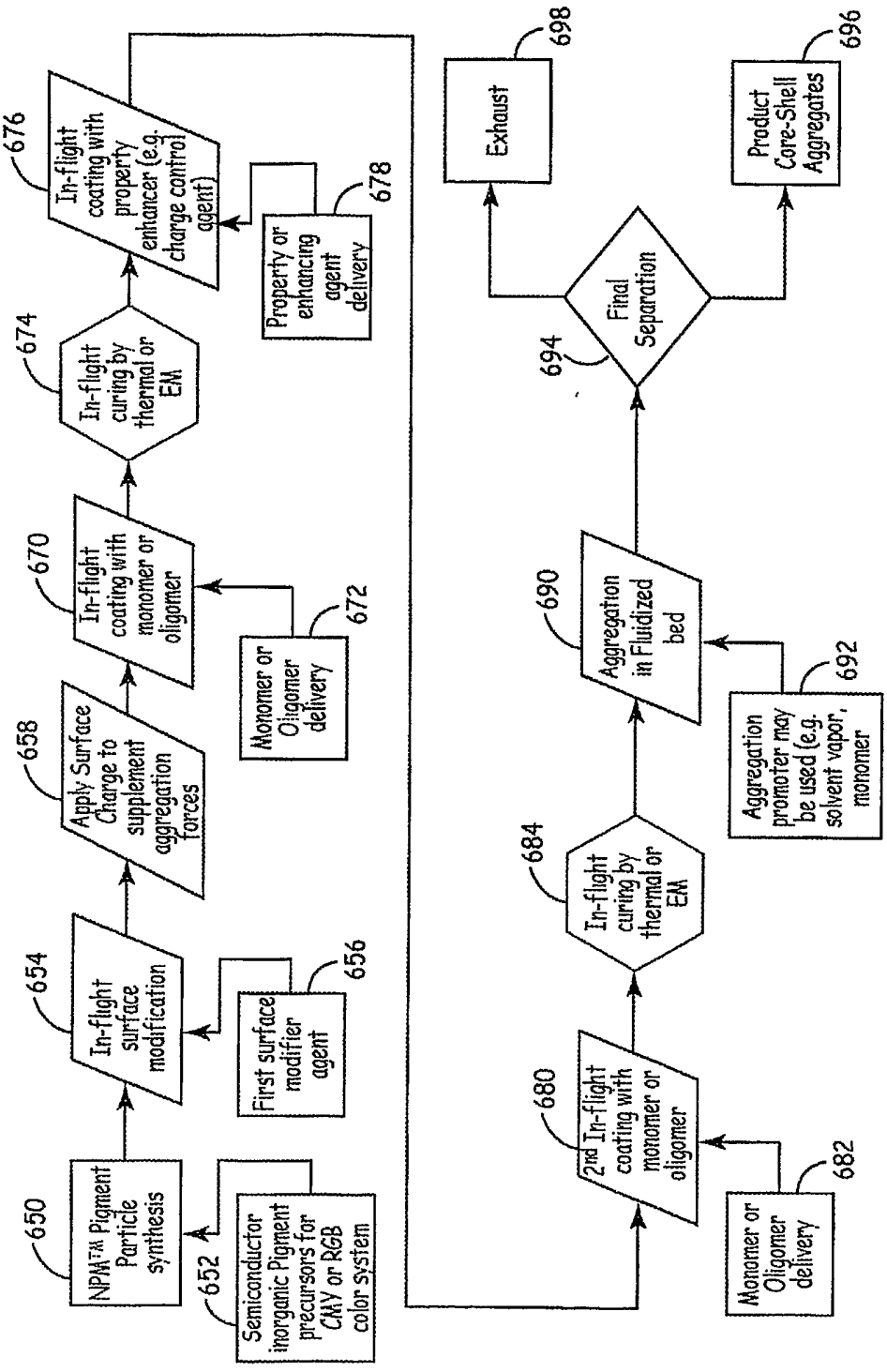

650
NPA™ Pigment Particle synthesis
652
Semiconductor inorganic Pigment precursors for CMY or RGB color system
654
In-flight surface modification
656
First surface modifier agent
658
Apply Surface Charge to supplement aggregation forces
670
In-flight coating with monomer or oligomer
672
Monomer or Oligomer delivery
674
In-flight curing by thermal or EM
676
In-flight coating with property enhancer (e.g. charge control agent)
678
Property or enhancing agent delivery
680
2nd In-flight coating with monomer or oligomer
682
Monomer or Oligomer delivery
684
In-flight curing by thermal or EM
690
Aggregation in Fluidized bed
692
Aggregation promoter may be used (e.g. solvent vapor, monomer
694
Final Separation
696
Product Core-Shell Aggregates
698
Exhaust

FIG. 27

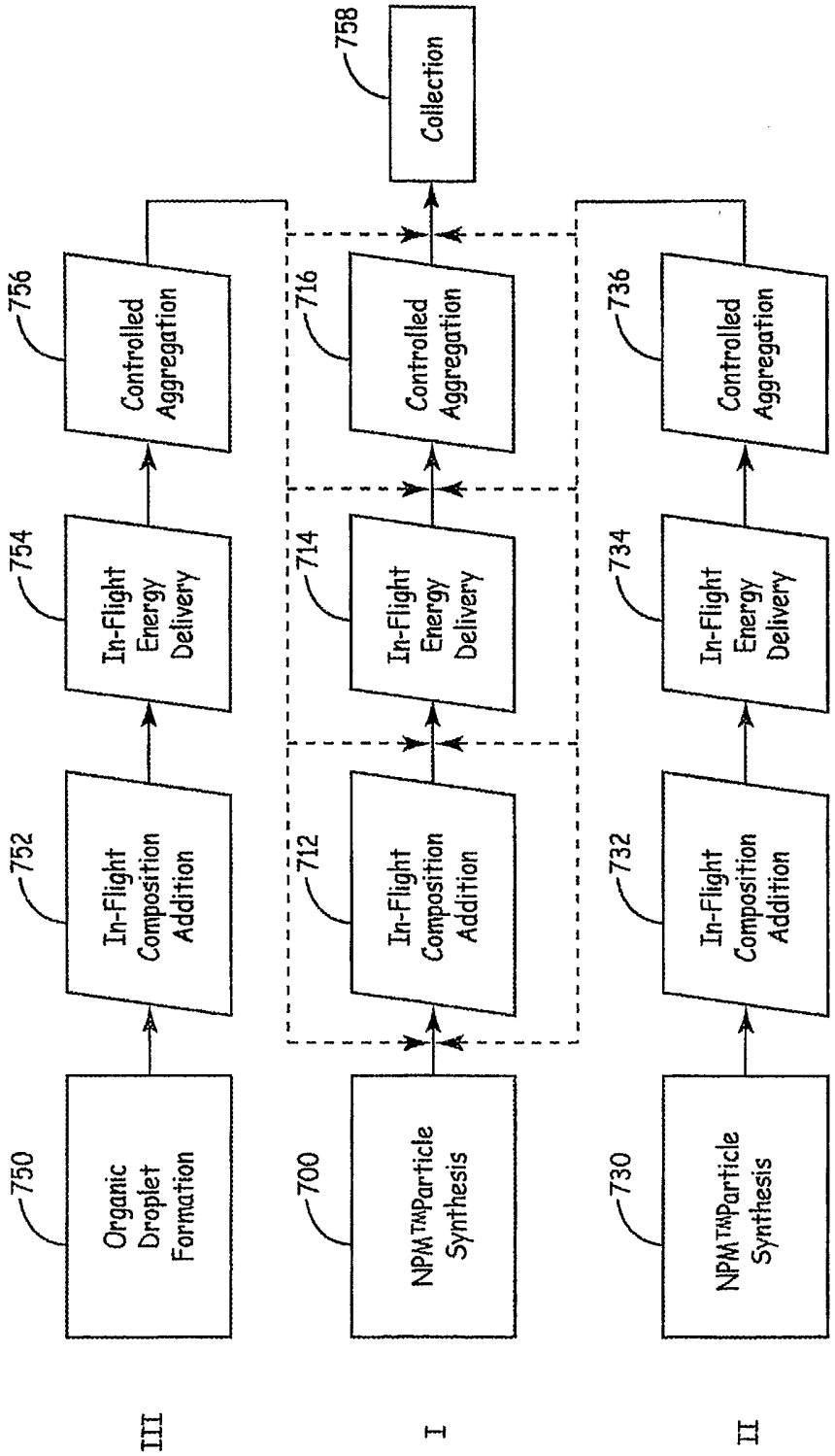

758
Collection
756
Controlled Aggregation
754
In-Flight Energy Delivery
752
In-Flight Composition Addition
750
Organic Droplet Formation
III
716
Controlled Aggregation
714
In-Flight Energy Delivery
712
In-Flight Composition Addition
700
NPM™Particle Synthesis
I
736
Controlled Aggregation
734
In-Flight Energy Delivery
732
In-Flight Composition Addition
730
NPM™Particle Synthesis
II

FIG. 28

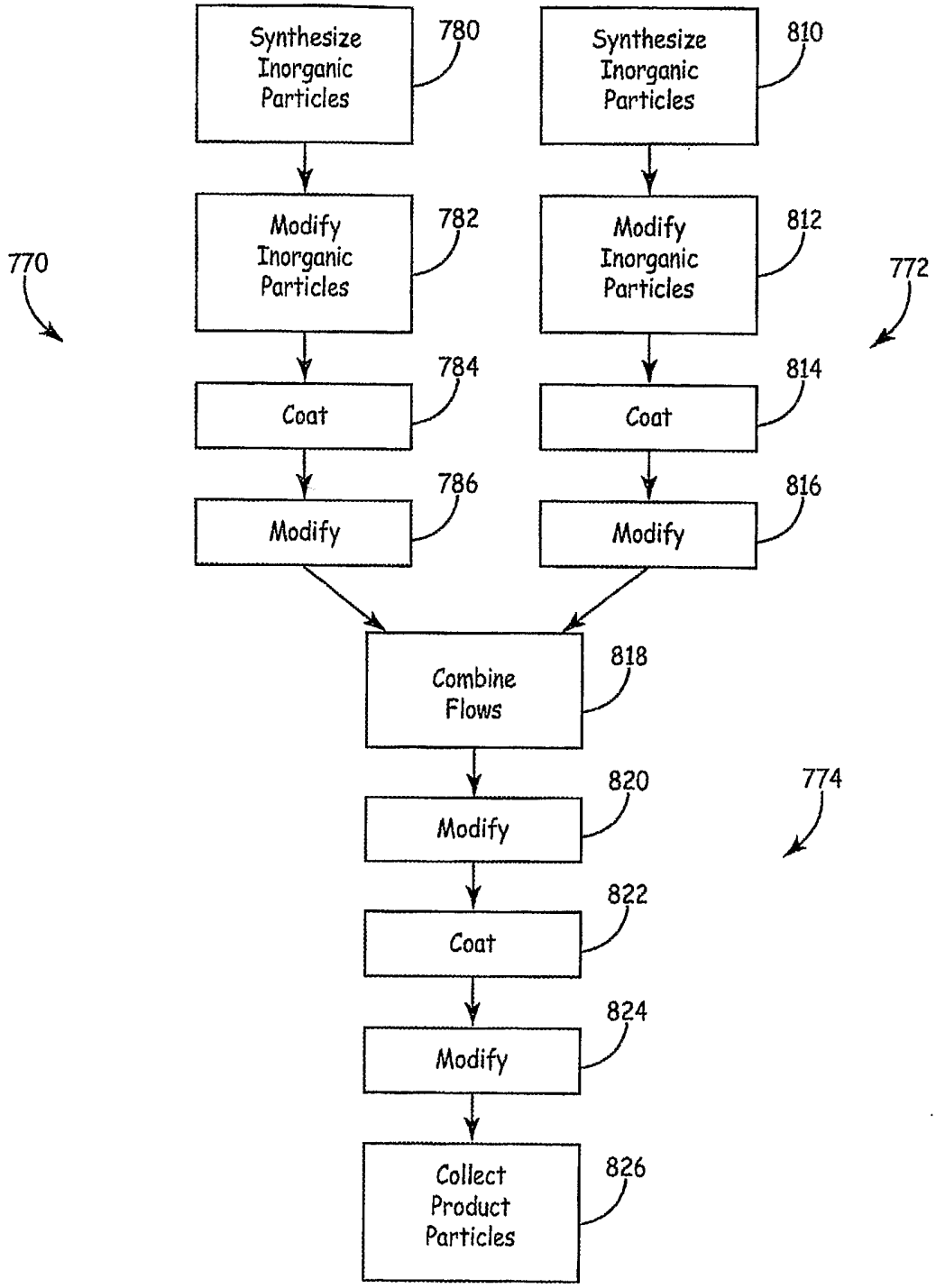

Synthesize Inorganic Particles
780
Modify Inorganic Particles
782
770
Coat
784
Modify
786
Synthesize Inorganic Particles
810
Modify Inorganic Particles
812
772
Coat
814
Modify
816
Combine Flows
818
Modify
820
774
Coat
822
Modify
824
Collect Product Particles
826

FIG. 29

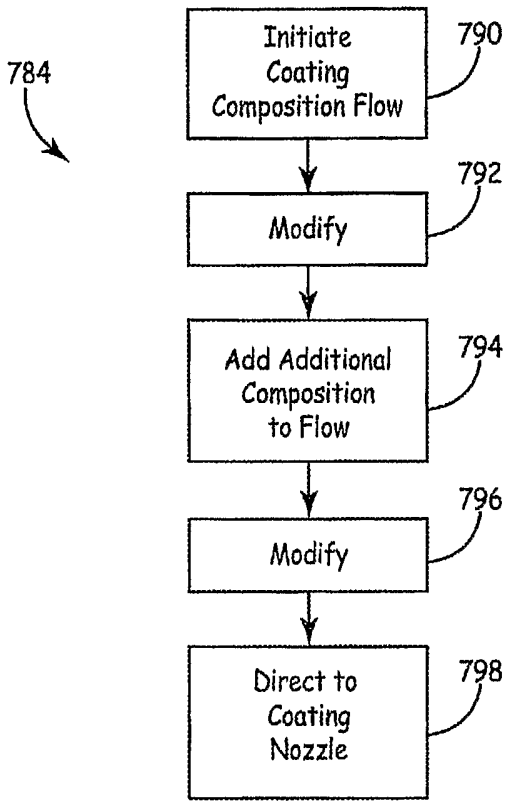

784
Initiate Coating Composition Flow
790
Modify
792
Add Additional Composition to Flow
794
Modify
796
Direct to Coating Nozzle
798

FIG. 30

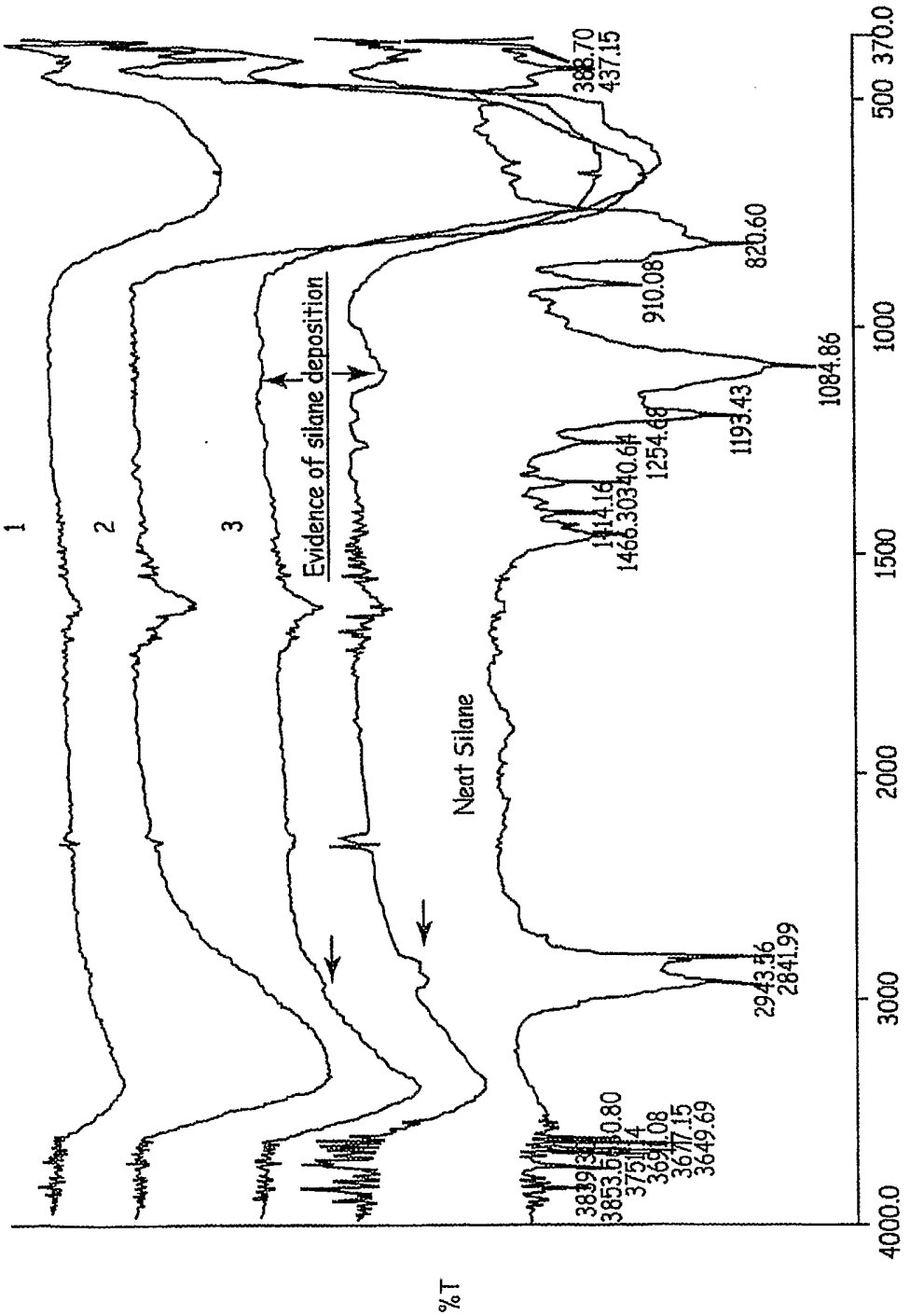

1
2
3
Evidence of silane deposition
Neat Silane
%T
cm-1
4000.0
3000
2000
1500
1000
500
370.0
3839.34
3853.04
3753.14
3691.08
3677.15
3649.69
2943.36
2841.99
1466.30
1414.16
1340.64
1254.48
1193.43
1084.86
910.08
820.60
437.15

FIG. 31

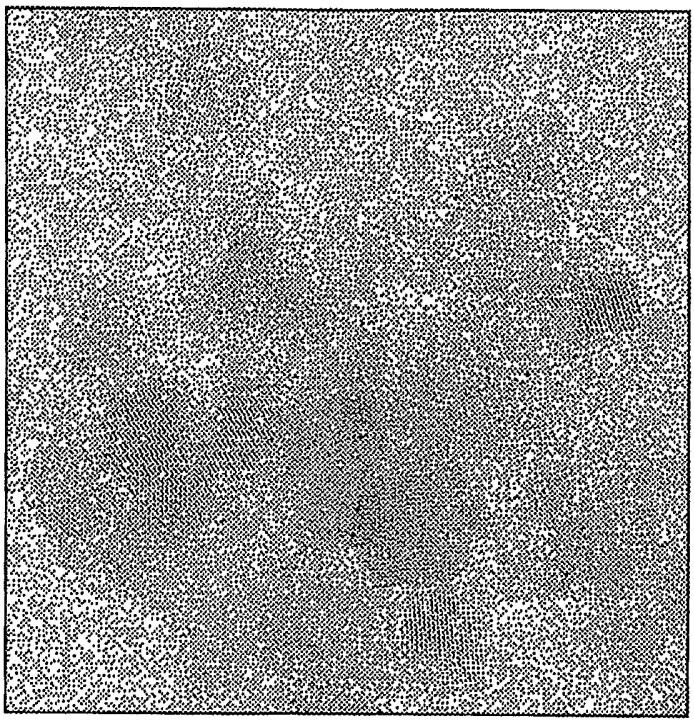


FIG. 32

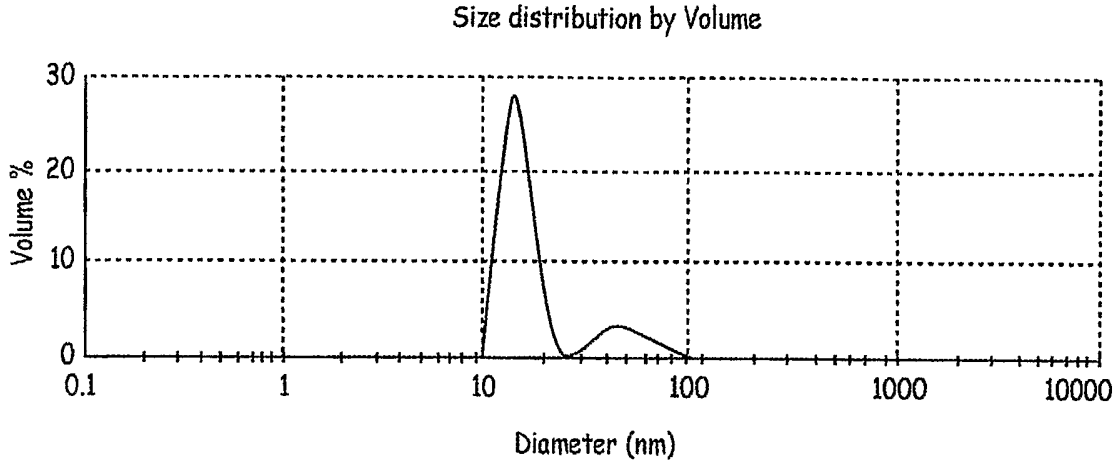


FIG. 33A

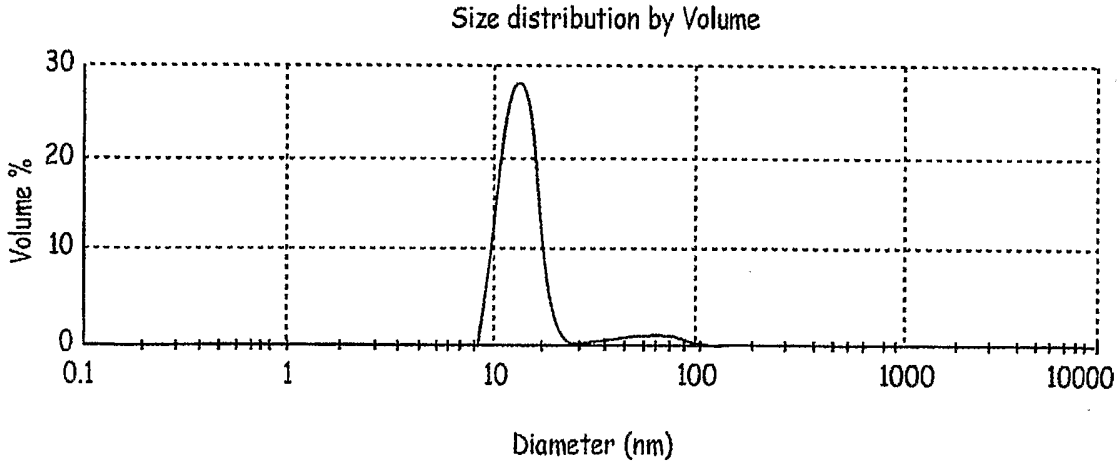


FIG. 33B