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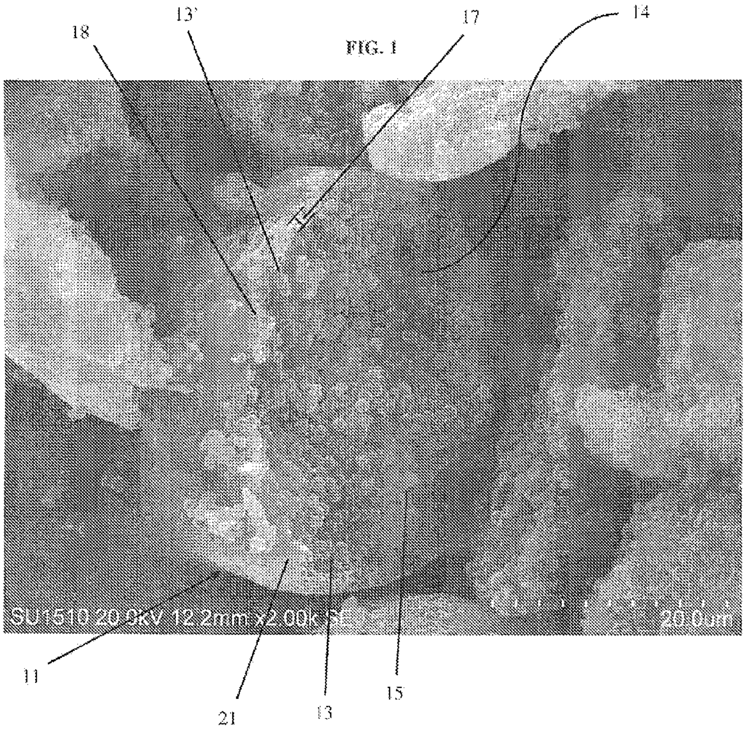
(54) **Title**: SUPRAPARTICLES INCLUDING HOLLOW POLYMERIC PARTICLES

(57) **Abstract**: A supraparticles comprising an assemblage of hollow polymeric particles encapsulated by a polymeric binder layer.

FIG. 1



WO 2015/051364 A1

SUPRAPARTICLES INCLUDING HOLLOW POLYMERIC PARTICLES

FIELD OF THE INVENTION

[0001] Embodiments of the invention are directed toward supraparticles including hollow polymeric particles.

BACKGROUND OF THE INVENTION

[0002] Hollow polymeric particles are known. These particles generally include spheres of thermoplastic resin, such as polystyrene, that are formed by polymerizing the thermoplastic resin on an acid or ester-containing core. Removal of the core provides the thermoplastic sphere.

SUMMARY OF THE INVENTION

[0003] Embodiments of the invention are directed toward a method for forming a supraparticle, the method comprising combining a plurality of hollow polymeric particles with a binder polymer to form a blend; and spray drying the blend to produce a supraparticle.

[0004] Other embodiments of the invention are directed toward a supraparticle comprising a core including a plurality of hollow polymeric particles and a binder layer surrounding the core.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Fig. 1 is a scanning electron micrograph (SEM) image of a supraparticle that has been severed to reveal its interior.

[0006] Fig. 2 is an SEM image of a plurality of supraparticles.

[0007] Fig. 3 is an SEM image of a supraparticle that has been severed to reveal its interior.

[0008] Fig. 4 is an SEM image of the core of a supraparticles that includes TiO2 particles.

[0009] Fig. 5 is a severed cross-sectional SEM image of supraparticle that includes TiO2 particles.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0010] Embodiments of the invention are based, at least in part, on the discovery of supraparticles including hollow polymeric particles. In one or more embodiments, these supraparticles include a core of individual hollow polymeric particles enclosed in an outer shell or layer including binder. It has unexpectedly been discovered that these supraparticles self-assemble upon spray drying a blend of binder latex and hollow polymeric particles. It has also unexpectedly been discovered that these supraparticles are dispersible in water and yet remain appreciably intact. As a result, the resulting supraparticles demonstrate technologically useful porosity and are advantageously light weight. Moreover, these supraparticles can be prepared in the presence of organic and/or inorganic materials that, upon self-assembling of the supraparticles, encapsulate the organic and inorganic particles within the supraparticle. It is contemplated that these supraparticles can be used in personal care compositions, waste-water treatment and purification, and geotechnical applications.

SUPRAPARTICLE CONSTRUCTION

[0011] The supraparticles of one or more embodiments of the invention can be described with reference to the Figures. For example, Fig. 1 shows supraparticle 11 including a plurality of hollow polymeric particles 13 within a core 14 of supraparticle 11. Interstitial voids 15 exist between adjacent hollow polymeric particles 13 within core 14. The individual hollow polymeric particles 13 are encapsulated or enclosed within a binder layer 17. In other words, binder layer 17 surrounds core 14. In one or more embodiments, binder layer 17 includes binder polymer 18 and optionally hollow polymeric particles 13’ located in binder layer 17. In one or more embodiments, an exterior layer of binder polymer 18 may form an outermost layer or skin 21 of binder layer 17. As will be described in greater detail below, binder polymer 18 includes coalesced polymer. In one or more embodiments, binder polymer 18 forms a matrix around hollow polymeric particles 13' within binder layer 17.

[0012] Fig. 2 shows that supraparticles 11 are generally spherical, although, as shown, the supraparticles can have other three-dimensional shapes such as supraparticles that are generally ovoidal in shape or generally torodial in shape. Inasmuch as the supraparticles of the present invention often take on a spherical shape, reference may be made throughout this specification to spherically-shaped supraparticles, although it should be understood that supraparticles 11 are not necessarily limited thereto unless specifically stated. As best shown in Fig. 3, hollow polymeric particles 13 include internal voids 19.

[0013] Figs. 1 and 3 best show that binder polymer 18 is predominately, and in certain embodiments exclusively (to the extent appreciable), on the outer perimeter of supraparticles 11. Also, hollow polymeric particles 13 within core 14 of supraparticles 11 are not bound (i.e. they are loose) or appreciably not bound to one another. Instead, in one or more embodiments, hollow polymeric particles are encapsulated by binder layer 17. Stated another way, core 14 is appreciably free of binder polymer 18. In one or more embodiments, the amount, if any, of binder polymer 18 located within core 14 may be quantitatively described with respect to the total weight of binder polymer within supraparticle 11. In one or more embodiments, less than 20 wt%, in other embodiments less than 10 wt%, in other embodiments less than 5 wt %, in other embodiments less than 2 wt%, and in other embodiments less than 1 wt% of the total binder within supraparticle 11 is located within core 14. Stated another way, binder layer 17 includes that portion or region of supraparticle 11 where at least 70 wt%, in other embodiments 80 wt%, in other embodiments 90 wt%, in other embodiments 95 wt%, in other embodiments 98 wt%, and in other embodiments 99 wt% of binder polymer resides within supraparticle 11.

[0014] As suggested above, supraparticles 11 may include organic and/or inorganic materials besides the hollow polymeric particles and the binder. For example, organic and/or inorganic materials, such as those in the form of particles, may be distributed throughout the supraparticles. For example, as shown in Figs. 4 and 5, inorganic particles 25 are located in interstitial voids 15 of supraparticles 11. As best shown in Fig. 5, inorganic particles 25 are generally distributed randomly, or in other embodiments statistically, throughout supraparticle 11.

[0015] In one or more embodiments, the size of the supraparticles, which includes a distribution of sizes, can be described with respect to the particles sizes within a percentile of the whole population of a given sample. For example, the particle sizes can be described with respect to the 90th percentile (i.e. d90), 50th percentile (i.e. d50), and 10th percentile (i.e. d10) of a given population. While several analytical techniques may be used, one useful technique employed in measuring the particles described herein is the use of a laser defractor-based particles size analyzer, which ultimately provides spherical diameters for the particles measured.

[0016] In one or more embodiments, the supraparticles may have a d90 diameter (i.e. 90 % of the particles have a diameter) of at least 5 μm, in other embodiments at least 10 μm, and in other embodiments at least 15 μm. In these or other embodiments, the supraparticles may have d90 diameter of at most 120 μm, in other embodiments at most 100 μm, and in other embodiments at most 80 μm. In one or more embodiments, the supraparticles may have d90 diameter of from about 5 to about 120 μm, in other embodiments from about 10 to about 100 μm, and in other embodiments from about 15 to about 80 μm.

[0017] In these or other embodiments, the supraparticles may have a d50 diameter (i.e. 50 % of the particles have a diameter) of at least 5 μm, in other embodiments at least 10 μm, and in other embodiments at least 15 μm. In these or other embodiments, the supraparticles may have d50 diameter of at most 80 μm, in other embodiments at most 70 μm, and in other embodiments at most 60 μm. In one or more embodiments, the supraparticles may have d50 diameter of from about 5 to about 80 μm, in other embodiments from about 10 to about 70 μm, and in other embodiments from about 15 to about 60 μm.

[0018] In these or other embodiments, the supraparticles may have a d10 diameter (i.e. 10 % of the particles have a diameter) of at least 5 μm, in other embodiments at least 10 μm, and in other embodiments at least 15 μm. In these or other embodiments, the supraparticles may have d10 diameter of at most 60 μm, in other embodiments at most 50 μm, and in other embodiments at most 40 μm. In one or more embodiments, the supraparticles may have d10 diameter of from about 5 to about 60 μm, in other embodiments from about 10 to about 50 μm, and in other embodiments from about 15 to about 40 μm.

[0019] In one or more embodiments, binder layer 17 may have thickness of at least 5 nm, in other embodiments at least 50 nm, and in other embodiments at least 100 nm. In these or other embodiments, the thickness of binder layer 17 may be at most 7 μm, in other embodiments at most 5 μm, in other embodiments at most 3 μm, in other embodiments at most 2 μm, in other embodiments at most 1 μm, and in other embodiments at most 0.5 μm. In one or more embodiments, the thickness of the exterior binder layer may be from about 5 nm to about 2 μm, in other embodiments from about 5 nm to about 7 μm, in other embodiments from about 50 nm to about 5 μm, in other embodiments from about 50 nm to about 3 μm, in other embodiments from about 50 nm to about 1 μm, and in other embodiments from about 100 nm to about 0.5 μm.

HOLLOW POLYMERIC PARTICLES

[0020] As suggested above, the individual hollow polymeric particles are hollow spheres formed from a thermoplastic resin. In one or more embodiments, the hollow polymeric particles include a porous outer shell, which may include a sphere wherein surface pores traverse the outer surface of the sphere and connect to the interior hollow void of the hollow polymeric particles.

[0021] In one or more embodiments, the thermoplastic resin of the shell has a glass transition temperature (Tg) of at least 80 °C, in other embodiments at least 90 °C, and in other embodiments at least 100 °C.

[0022] In one or more embodiments, the hollow spheres, which may also be referred to as polymeric shells, may include, in polymerized form, at least one of styrene; methyl methacrylate; methacrylic acid; acrylic acid, allyl methacrylate, divinyl benzene; and combinations of two or more thereof. In particular embodiments, the hollow sphere includes polystyrene or copolymers of styrene and comonomer. In one or more embodiments, the hollow sphere may include, based on 100 parts by weight of the total monomers used to form the shell, from about 75 to about 100 parts styrene; from about 0 to about 25 parts methyl methacrylate; from about 0 to about 3 parts methacrylic acid; from about 0 to about 3 parts acrylic acid; and from about 0 to about 5 parts allyl methacrylate and/or divinyl benzene.

[0023] In one or more embodiments, the size of the individual hollow polymeric particles within the supraparticles may have an average particle size (i.e. particle diameter) of at least 0.5 μm, in other embodiments at least 0.7 μm, and in other embodiments at least 0.9 μm. In these or other embodiments, the individual hollow polymeric particles may have an average particle size of at most 1.5 μm, in other embodiments at most 1.3 μm, and in other embodiments at most 1.1 μm. In one or more embodiments, the individual hollow polymeric particles may have an average particle size of from about 0.5 to about 1.5 μm, in other embodiments from about 0.7 to about 1.3 μm, and in other embodiments from about 0.9 to about 1.1 μm.

[0024] In one or more embodiments, the internal void volume of the individual hollow spheres within the supraparticles may be at least 45 %, in other embodiments at least 55 %, and in other embodiments at least 65 % of the total volume of the hollow spheres. In these or other embodiments, the internal void volume may be at most 95 %, in other embodiments at most 85 %, and in other embodiments at most 75 % of the total volume of the hollow spheres. In one or more embodiments, the internal void volume may be from about 45 to about 95 %, in other embodiments from about 55 to about 85 %, and in other embodiments from about 55 to about 75 % of the total volume of the hollow spheres.

PREPARATION OF HOLLOW POLYMERIC PARTICLES

[0025] In one or more embodiments, the hollow polymeric particles can include, but are not limited to, those produced through an acid core process and/or those produced through an ester core process. Examples of hollow polymeric particles produced using an acid core process can be found in U.S. Pat. No. 4,468,498 to Kowalski, which is incorporated herein by reference in its entirety. Examples of hollow polymeric particles produced using an ester core process can be found in U.S. Pat. Nos. 5,157,084 to Lee, 5,521,253 to Lee, and US Pat. Pub. 2010/0317753 all of which are incorporated herein by reference in their entirety.

[0026] In one or more embodiments, the creation of pores in the porous outer shell may be inherent in the production of the hollow polymeric pigments. In these or other embodiments, the porosity of the outer shell may be increased by including a hydrolysable monomer in the shell formation stage of the production of the hollow polymeric pigment. An example of hollow polymeric pigments produced with the inclusion of hydrolyzable monomers in the shell formation can be seen in WO 2010/120344 which is incorporated herein by reference.

BINDER

[0027] In one or more embodiments, useful binder resins include film-forming binder resins. As the skilled person understands, film-forming binders coalesce to form a film. In one or more embodiments, the film-forming binder resins are characterized by a minimum film formation temperature (MFFT), which is the minimum temperature required to coalesce the binder when laid on a substrate as a film, of less than 100 °C, in other embodiments less than 90 °C, and in other embodiments less than 80 °C. In one or more embodiments, the film-forming binder has a minimum film formation temperature from about 50 °C to about 100 °C, and in other embodiments from about 60 °C to about

90 °C, and in other embodiments from about 70°C to about 80 °C. As the skilled person understands, MFFT may be determined according to ASTM D2354.

[0028] In one or more embodiments, useful film-forming binders may be characterized by a glass transition temperature (Tg) of at least 40 °C, in other embodiments at least 50 °C, and in other embodiments at least 60 °C. In these or other embodiments, the Tg of the film-forming binder may be at most 90 °C, in other embodiments at most 80 °C, and in other embodiments at most 70 °C. In one or more embodiments, the Tg of the film-forming binder may be from about 40 °C to about 90 °C, in other embodiments from about 50 °C to about 80 °C, and in other embodiments from about 60 °C to about 80 °C.

[0029] In one or more embodiments, the glass transition temperature of the film-forming binder may be described relative to the glass transition temperature of the hollow polymeric particle. In one or more embodiments, the glass transition temperature of the film-forming resin is at least 15 °C, in other embodiments at least 10 °C, in and in other embodiments at least 5 °C lower than the glass transition temperature of the hollow polymeric sphere.

[0030] In one or more embodiments, the film-forming binder may be characterized by a gel content of at of at least 40 %, in other embodiments at least 50 %, and in other embodiments at least 60 %. In these or other embodiments, the gel content of the film-forming binder may be at most 90 %, in other embodiments at most 80 %, and in other embodiments at most 70 %. In one or more embodiments, the gel content of the film-forming binder may be from about 40 to about 90 %, in other embodiments from about 50 % to about 80 %, and in other embodiments from about 60 % to about 80 %.

[0031] In one or more embodiments, the film-forming binder may include copolymers that derive from copolymerization of alkenyl aromatic monomer together with one or more of aliphatic conjugated diene monomer, ethylenically unsaturated nitrile monomer, ethylenically unsaturated acid monomer, ethylenically unsaturated functional monomer, ethylenically unsaturated non-functional ester monomer, and other monomer copolymerizable therewith. In particular embodiments, the film-forming binder includes a copolymer including (in polymerized form) alkenyl aromatic monomer, aliphatic conjugated diene monomer, ethyleneically unsaturated nitrile monomer, and at least one functional monomer. In one or more embodiments, the film-forming binder is a latex polymer, and therefore reference may be made to polymeric particles.

[0032] Examples of alkenyl aromatic monomer include styrene, alpha-methyl styrene, p-tertiary butyl styrene, methyl vinyl toluene, p-vinyl toluene, divinyl benzene, and 3-ethyl styrene, or mixtures thereof.

[0033] Examples of diene monomers include piperylene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene,1,3-butadiene, or mixtures thereof.

[0034] Examples of nitriles of ethylenically unsaturated carboxylic acid include acrylonitrile and methacrylonitrile. Inasmuch as acrylonitrile is the most popular nitrile of ethylenically unsaturated carboxylic acids, reference may be simply made to acrylonitrile, but unless otherwise specified, is not intended to limit beyond nitriles of ethylenically unsaturated carboxylic acid.

[0035] Examples of acid-bearing monomers include ethylenically unsaturated carboxylic acid monomers such as acrylic acid, methacrylic acid, fumaric acid, crotonic acid, maleic acid, itaconic acid, 2-carboxyethylacrylate, 2-acrylamido-2-methylbutanoic acid, and the like, and combinations of two or more such acids.

[0036] In one or more embodiments, functional monomer includes monomer that will provide electronic stabilization to the particles in latex. In one or more embodiments, functional monomers include hydroxyl and/or amide functionality or groups. In one or more embodiments, the simple presence of a carboxyl group, such as may be present in an ester group or moiety, is not considered a functional group. In one or more embodiments, functional monomer may include various organic salts, for example sodium styrene sulfonate, sodium methallyl sulfonate, the alkali, ammonium, and amine salts of 2-acrylamido-2-methylpropanesulfonate, and the 3-sulfopropyl(meth)acrylate salt of sodium or potassium. With respect to these functional monomer, which may be referred to as AMPS or Na-AMPS, reference can be made to U.S. Pat. No. 6,184,287, which is incorporated herein by reference.

[0037] Examples of amides of ethylenically unsaturated carboxylic acid include various unsaturated amides or derivatives thereof having a total of from about 3 to about 12 carbon atoms. Examples of unsaturated amides or derivatives thereof include acrylamide, methacrylamide, N,N-methylenebisacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-ethyoxymethylacrylamide, N-butoxymethylacrylamide, N-isobutoxymethylacrylamide, N,N-dimethylacrylamide, derivatives thereof, and mixtures thereof.

[0038] In one or more embodiments, hydroxyl-containing monomers include hydroxyl derivatives of acrylates and methacrylates. In one or more embodiments, the alkyl portion of these compounds includes from 1 to 10, optionally from 1 to 4, carbon atoms. Examples of ester derivatives include hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, 4-hydroxybutyl acrylate, and ethylene oxide extended derivatives of ethyleneglycol methacrylate.

[0039] In one or more embodiments, non-functional esters of ethylenically unsaturated carboxylic acid include alkyl (meth)acrylates. These monomers are devoid of acid, hydroxyl, and amide groups. Examples include methylacrylate, methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, iso-decylacrylate, propyl acrylate, ethyl acrylate, ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, diethyleneglycol diacrylate, diethyleneglycol dimethacrylate, triethyleneglycol diacrylate, and triethyleneglycol dimethacrylate.

[0040] In one or more embodiments, the film-forming binder includes copolymers that include (in polymerized form) at least 45 weight %, in other embodiments at least 50 weight %, in other embodiments at least 55 weight %, and in other embodiments at least 60 weight % *mer* units deriving from the polymerization of alkenyl aromatic (e.g. styrene), based on the total weight of the *mer* units within the particles. In these or other embodiments, the film-forming binder includes copolymers that include less than

95 weight %, in other embodiments less than 90 weight %, in other embodiments less than 85 weight %, and in other embodiments less than 80 weight % *mer* units deriving from the polymerization of alkenyl aromatic (e.g. styrene), based on the total weight of the *mer* units within the particles.

[0041] In one or more embodiments, the film-forming binder includes copolymers that include at least 10 weight %, in other embodiments at least 15 weight %, in other embodiments at least 20 weight %, and in other embodiments at least 25 weight % *mer* units deriving from the polymerization of conjugated diene monomer (e.g. 1,3-butadiene) based on the total weight of the *mer* units within the particles. In these or other embodiments, the film-forming binder includes copolymers that include less than 50 weight %, in other embodiments less than 45 weight %, in other embodiments less than 40 weight %, and in other embodiments less than 35 weight % *mer* units deriving from the polymerization of conjugated diene (e.g. 1,3-butadiene), based on the total weight of the *mer* units within the particles.

[0042] In one or more embodiments, the film-forming binder includes copolymers that include at least 5 weight %, in other embodiments at least 8 weight %, in other embodiments at least 10 weight %, and in other embodiments at least 12 weight % *mer* units deriving from the polymerization of acrylonitrile, based on the total weight of the *mer* units within the particles. In these or other embodiments, the film-forming binder includes copolymers that include less than 30 weight %, in other embodiments less than 25 weight %, in other embodiments less than 20 weight %, and in other embodiments less than 15 weight % *mer* units deriving from the polymerization of acrylonitrile, based on the total weight of the *mer* units within the particles.

[0043] In one or more embodiments, the film-forming binder includes copolymers may include at least 0.2 weight %, in other embodiments at least 0.5 weight %, in other embodiments at least 1 weight %, and in other embodiments at least 2.0 weight % *mer* units deriving from the polymerization of acid monomer (e.g. itaconic acid), based on the total weight of the *mer* units within the particles. In these or other embodiments, the copolymers may include less than 8 weight %, in other embodiments less than 7 weight %, in other embodiments less than 5 weight %, and in other embodiments less than 3 weight % *mer* units deriving from the polymerization of acid monomer (e.g. itaconic acid), based on the total weight of the *mer* units within the particles. In particular embodiments, the copolymers are devoid or substantially devoid of acid-bearing monomer.

[0044] In one or more embodiments, the film-forming binder includes copolymers that may include at least 0.1 weight %, in other embodiments at least 0.2 weight %, in other embodiments at least 0.3 weight %, and in other embodiments at least 0.4 weight % *mer* units deriving from the polymerization of functional monomer (e.g. Na-AMPS), based on the total weight of the *mer* units within the particles. In these or other embodiments, the film-forming binder includes copolymers that include less than 3 weight %, in other embodiments less than 2 weight %, in other embodiments less than 1.5 weight %, and in other embodiments less than 1.0 weight % *mer* units deriving from the polymerization of functional monomer (e.g. Na-AMPS), based on the total weight of the *mer* units within the particles. In particular embodiments, the copolymers are devoid or substantially devoid of functional monomer.

[0045] In one or more embodiments, the film-forming binder includes copolymers that may include at least 0.2 weight %, in other embodiments at least 0.5 weight %, in other embodiments at least 0.8 weight %, and in other embodiments at least 1.2 weight % *mer* units deriving from the polymerization of amide monomer, based on the total weight of the *mer* units within the particles. In these or other embodiments, the copolymers may include less than 5 weight %, in other embodiments less than 4 weight %, in other embodiments less than 3 weight %, and in other embodiments less than 2 weight % *mer* units deriving from the polymerization of amide monomer, based on the total weight of the *mer* units within the particles. In particular embodiments, the copolymers are devoid or substantially devoid of amide monomer.

[0046] In one or more embodiments, the film-forming binder includes copolymer that may include at least 0.2 weight %, in other embodiments at least 0.5 weight %, in other embodiments at least 0.8 weight %, and in other embodiments at least 1.2 weight % *mer* units deriving from the polymerization of hydroxyl monomer, based on the total weight of the *mer* units within the particles. In these or other embodiments, the copolymers may include less than 5 weight %, in other embodiments less than 4 weight %, in other embodiments less than 3 weight %, and in other embodiments less than 2 weight % *mer* units deriving from the polymerization of hydroxyl monomer, based on the total weight of the *mer* units within the particles. In particular embodiments, the copolymers are devoid or substantially devoid of hydroxyl monomer.

[0047] In one or more embodiments, the film-forming binder includes copolymers that may include at least 0.2 weight %, in other embodiments at least 0.5 weight %, in other embodiments at least 1 weight %, and in other embodiments at least 2 weight % *mer* units deriving from the polymerization of non-functional ester monomer, based on the total weight of the *mer* units within the particles. In these or other embodiments, the copolymers may include less than 5 weight %, in other embodiments less than 3 weight %, in other embodiments less than 2 weight %, in other embodiments less than 1 weight %, in other embodiments less than 0.5 weight %, and in other embodiments less than 0.1 weight % *mer* units deriving from the polymerization of non-functional ester monomer, based on the total weight of the *mer* units within the particles. In particular embodiments, the copolymers are devoid or substantially devoid of non-functional monomer.

INORGANIC PARTICLES

[0048] In one or more embodiments, useful inorganic particles include one or more mineral fillers or pigments. In particular embodiments, the mineral fillers are heavy or highly dense mineral fillers. In other embodiments, the inorganic particles may include synthetic materials.

[0049] In one or more embodiments, the inorganic particles may be characterized by an average particle size of less than 2 μm, in other embodiments less than 1.0 μm, and in other embodiments less than 0.7 μm. In these or other embodiments, the inorganic particles may have an average particle size of from about 5 nm to about 2 μm, in other embodiments from about 25 nm to about 1.0 μm, and in other embodiments from about 50 nm to about 0.7 μm.

[0050] In one or more embodiments, the inorganic particles may include dense minerals such as barite, hematite, and magnesium oxide.

[0051] In other embodiments, the inorganic particles may include titanium oxide, calcium oxide, zinc oxide, and magnesium oxide.

[0052] In other embodiments, the inorganic particles include clays. Useful clays include mineral clays, which may also be referred to as hydrous aluminum silicates. These clays include kaolin (i.e. kaolinite) clays and smectite clays. Examples of smectite clays include, montmorillonite, hectorite, nontrite, beidellite, volkonskoite, saponite, sauconite, sobockite, sterensite, and sinfordite clays.

[0053] In particular embodiments, the clays are layered clays, which may include a plurality of stacked platelets that may include or be modified to include cationically exchangeable ions between the platelets. Exemplary smectite clays of this nature are known in the art as described in U.S. Patent Nos 5,552,469, 6,818,693, and 7,019,063, which are incorporated herein by reference.

PREPARATION OF SUPRAPARTICLES

[0054] In one or more embodiments, the supraparticles may be prepared by combining hollow polymeric particles with a binder to form a blend, and then spray drying the blend to produce the supraparticles. During the spray drying process, the hollow polymeric particles self-assemble into the supraparticles. Accordingly, reference may be made to self-assembled particles or self-assembled supraparticles.

[0055] In one or more embodiments, the blend is in the form of a latex wherein the solids portion of the latex includes the hollow polymeric particles and the binder. The latex may also include optional inorganic particles, as well as other constituents that may facilitate formation of the blend or spray drying of the same. Exemplary additional ingredients include partitioning agents. Exemplary portioning agents include various aliphatic waxes.

[0056] In particular embodiments, the blend, which may also be referred to as the sprayable latex or emulsion, includes at least 10, in other embodiments at least 20, and in other embodiments at least 30 percent by weight solids based on the total weight of the latex. In these or other embodiments, the sprayable latex includes at most 70, in other embodiments at most 60, and in other embodiments at most 50 percent by weight solids based on the total weight of the latex. In one or more embodiments, the latex includes from about 10 to about 70, in other embodiments from about 20 to about 60, and in other embodiments from about 30 to about 50 percent by weight solids based on the total weight of the latex.

[0057] In one or more embodiments, the solids portion of the sprayable latex includes at least 40, in other embodiments at least 50, and in other embodiments at least 60 percent by weight hollow polymeric particles based on the total weight of the solids. In these or other embodiments, the solids portion of the sprayable latex includes at most 90, in other embodiments at most 80, and in other embodiments at most 70 percent by weight hollow polymeric particles based on the total weight of the solids. In one or more embodiments, the solids portion of the latex includes from about 40 to about 90, in other embodiments from about 50 to about 80, and in other embodiments from about 60 to about 70 percent by weight hollow polymeric particles based on the total weight of the solids.

[0058] In one or more embodiments, the solids portion of the sprayable latex includes at least 10, in other embodiments at least 15, and in other embodiments at least 20 percent by weight binder resin based on the total weight of the solids. In these or other embodiments, the solids portion of the sprayable latex includes at most 40, in other embodiments at most 30, and in other embodiments at most 25 percent by weight binder resin based on the total weight of the solids. In one or more embodiments, the solids portion of the latex includes from about 10 to about 40, in other embodiments from about 15 to about 30, and in other embodiments from about 20 to about 25 percent by weight binder resin based on the total weight of the solids.

[0059] In one or more embodiments, the solids portion of the sprayable latex includes at least 10, in other embodiments at least 15, and in other embodiments at least 20 percent by weight inorganic particles based on the total weight of the solids. In these or other embodiments, the solids portion of the sprayable latex includes at most 40, in other embodiments at most 30, and in other embodiments at most 25 percent by weight inorganic particles based on the total weight of the solids. In one or more embodiments, the solids portion of the latex includes from about 10 to about 40, in other embodiments from about 15 to about 30, and in other embodiments from about 20 to about 25 percent by weight inorganic particles based on the total weight of the solids.

[0060] In one or more embodiments, the solids portion of the sprayable latex includes at least 0.5, in other embodiments at least 1, and in other embodiments at least 2 percent by weight partitioning agent based on the total weight of the solids. In these or other embodiments, the solids portion of the sprayable latex includes at most 10, in other embodiments at most 8, and in other embodiments at most 5 percent by weight partitioning agent based on the total weight of the solids. In one or more embodiments, the solids portion of the latex includes from about 0.5 to about 10, in other embodiments from about 1 to about 8, and in other embodiments from about 2 to about 5 percent by weight partitioning agent based on the total weight of the solids.

[0061] In one or more embodiments, the sprayable latex is spray dried using conventional atomization techniques. Exemplary spray drying processes that may be used include those disclosed in U.S. Pat. No. 6,013,594, which is incorporated herein by reference.

PHYSICAL PROPERTIES OF SUPRAPARTICLES

[0062] In one or more embodiments, the supraparticles are, on a macro scale, dry powders. In particular embodiments, the supraparticles are free-flowing powders. In these or other embodiments, the dry powder lacks the visible appearance of moisture. In one or more embodiments, dry powder contains a moisture content of less than about 5 wt %, in other embodiments less than 3 wt %, and in other embodiments less than 1 wt % water.

[0063] In one or more embodiments, the supraparticles may be characterized by a specific surface area that is at least 2 m^2/g, in other embodiments at least 3 m^2/g, and in other embodiments at least 4 m^2/g. In these or other embodiments, the supraparticles may be characterized by a specific surface area that is at most 10 m^2/g, in other embodiments at most 8 m^2/g, and in other embodiments at most 7 m^2/g. In certain embodiments the supraparticles may be characterized by a specific surface area that is from about 2 to about 10 m^2/g, in other embodiments from about 3 to about 8 m^2/g, and in other embodiments from about 4 to about 7 m^2/g. specific surface area can be determined by using a BET surfanalyzer.

[0064] In one or more embodiments, the supraparticles may be characterized by a bulk density that is at least 0.05 g/cc, in other embodiments at least 0.15 g/cc, and in other embodiments at least 0.20 g/cc. In these or other embodiments, the supraparticles may be characterized by a bulk density that is at most 0.50 g/cc, in other embodiments at most 0.40 g/cc, and in other embodiments at most 0.30 g/cc. In certain embodiments the supraparticles may be characterized by a bulk density that is from about 0.05 g/cc to about 0.50 g/cc, in other embodiments from about 0.15 g/cc to about 0.40 g/cc, and in other embodiments from about 0.20 g/cc to about 0.30 g/cc.

[0065] In one or more embodiments, the supraparticles may be characterized by an apparent density that is at least 0.07, in other embodiments at least 0.15, and in other embodiments at least 0.25 g/cc. In these or other embodiments, the supraparticles may be characterized by an apparent density that is at most 1.0, in other embodiments at most 0.8, and in other embodiments at most 0.7 g/cc. In certain embodiments the supraparticles may be characterized by an apparent density that is from about 0.07 to about 1.0 g/cc, in other embodiments from about 0.15 to about 0.8 g/cc, and in other embodiments from about 0.25 to about 0.7 g/cc.

[0066] In one or more embodiments, the supraparticles may be characterized by a total pore area that is at least 50 m^2/g, in other embodiments at least 70 m^2/g, and in other embodiments at least 90 m^2/g. Total pore area can be determined by using mercury porosimetry.

[0067] In one or more embodiments, the supraparticles may be characterized by a pore median diameter that is at least 0.03 μm, in other embodiments at least 0.05 μm, and in other embodiments at least 0.15 μm. In these or other embodiments, the supraparticles may be characterized by a pore median diameter that is at most 0.2 μm, in other embodiments at most 0.15 μm, and in other embodiments at most 0.10 μm. In certain embodiments, the supraparticles may be characterized by a pore median diameter that is from about 0.03 μm to about 0.2 μm, in other embodiments from about 0.05 μm to about 0.15 μm, and in other embodiments from about 0.07 μm to about 0.10 μm. Total pore median diameter can be determined using mercury porosimetry

[0068] In one or more embodiments, the supraparticles may be characterized by a percent porosity that is at least 20 %, in other embodiments at least 25 %, and in other embodiments at least 30 %. In these or other embodiments, the supraparticles may be characterized by a percent porosity that is at most 60 %, in other embodiments at most 55 %, and in other embodiments at most 50 %. In certain embodiments, the supraparticles may be characterized by a percent porosity that is from about 20 to about 60 %, in other embodiments from about 25 to about 55 %, and in other embodiments from about 30 to about 50 %.

[0069] In one or more embodiments, the supraparticles may be characterized by a jojoba oil absorption that is at least 100, in other embodiments at least 120, and in other embodiments at least 130 grams oil per 100 grams of powder. In these or other embodiments, the supraparticles may be characterized by a jojoba oil absorption that is at most 300, in other embodiments at most 250, and in other embodiments at most 200 grams oil per 100 grams of powder. In certain embodiments the supraparticles may be characterized by a jojoba oil absorption that is from about 100 to about 300, in other embodiments from about 120 to about 250, and in other embodiments from about 130 to about 200 grams oil per 100 grams of powder.

INDUSTRIAL APPLICABILITY

[0070] In one or more embodiments, the supraparticles of this invention may be used in personal care compositions. For example, the supraparticles can be used as base materials in cosmetics. It has been advantageously discovered that the supraparticles of the present invention have high oil absorbency, softness, and refract light, which makes them very advantageous for use in cosmetics.

[0071] In other embodiments, especially where the supraparticles carry light-reflective minerals such as titanium dioxide and/or zinc oxide, the supraparticles can be used in sunscreens. It has advantageously been discovered that the supraparticles of the present invention can serve as carriers for reflective pigments such as titianium oxide and zinc oxide, wherein the pigments are well dispersed, which makes them very advantageous for use as sunscreens.

[0072] In one or more embodiments, the supraparticles may be used as proppants in geotechnical applications such as hydraulic fracturing (i.e. “fracking”). It has advantageously been discovered that the supraparticles of the present invention exhibit high strength and crush resistance when dispersed in fluids, which makes them very advantageous for use as proppants.

[0073] In other embodiments, the supraparticles may be used in drilling fluids such as drilling muds, drilling cements, and fracking fluids for oil and gas drilling operations.

It has advantageously been discovered that the supraparticles of the present invention are light weight and exhibit high buoyancy, which makes them very advantageous for use in drilling fluids, such as carriers for heavy materials.

[0074] In yet other embodiments, the supraparticles can be used in water purification including the treatment of wastewater and in the purification of drinking water. It has advantageously been discovered that the supraparticles of the present invention are highly absorbent, which makes them very advantageous for use as filter media.

[0075] Various modifications and alterations that do not depart from the scope and spirit of this invention will become apparent to those skilled in the art. This invention is not to be duly limited to the illustrative embodiments set forth herein.

CLAIMS

What is claimed is:

1. A method for forming a supraparticle, the method comprising:

   combining a plurality of hollow polymeric particles with a binder polymer to form a blend; and

   spray drying the blend to produce a supraparticle.

2. The method of the preceding claim, where the blend further includes an inorganic particle.

3. The method of any one or more of the preceding claims, where the binder polymer is a film-forming polymer.

4. The method of any one or more of the preceding claims where the binder polymer has a minimum film forming temperature of less than 100 °C.

5. The method of any one or more of the preceding claims where the binder polymer has a minimum film forming temperature of less than 80 °C.

6. The method of any one or more of the preceding claims where the binder polymer has a glass transition temperature of at least 40 °C.

7. The method of any one or more of the preceding claims where the binder polymer has a glass transition temperature of at least 60 °C.

8. The method of any one or more of the preceding claims where the glass transition temperature of the binder polymer is at least 15 °C lower than the glass transition temperature of the hollow polymeric particles.

9. The method of any one or more of the preceding claims where the hollow polymeric particles have a glass transition temperature of at least 80 °C.

10. The method of any one or more of the preceding claims where the hollow polymeric particles include styrene in polymerized form.

11. A supraparticle comprising:

a core including a plurality of hollow polymeric particles and a binder layer surrounding the core.

12. The supraparticle of any one or more of the preceding claims, where the core further includes inorganic particles encapsulated by the binder layer.

13. The supraparticle of any one or more of the preceding claims, where the binder layer includes binder polymer.

14. The supraparticle of any one or more of the preceding claims, where the binder layer further includes hollow polymeric particles within a matrix of binder polymer.

15. The supraparticle of any one or more of the preceding claims, where at least 70 wt % of the binder within the entire supraparticle is located in the binder layer.

16. The supraparticle of any one or more of the preceding claims, where the binder polymer is a film-forming polymer.

17. The supraparticle of any one or more of the preceding claims, where the supraparticle has a d50 of from about 5 to about 80 µm.

18. The supraparticle of any one or more of the preceding claims, where the average particle size of the hollow polymeric particles is from about 0.5 to about 1.5 µm.

19. The supraparticle of any one or more of the preceding claims, where the glass transition temperature of the binder polymer is at least 15 °C lower than the glass transition temperature of the hollow polymeric particles.

20. The supraparticle of any one or more of the preceding claims, where the hollow polymeric particles include styrene in polymerized form.

FIG. 1

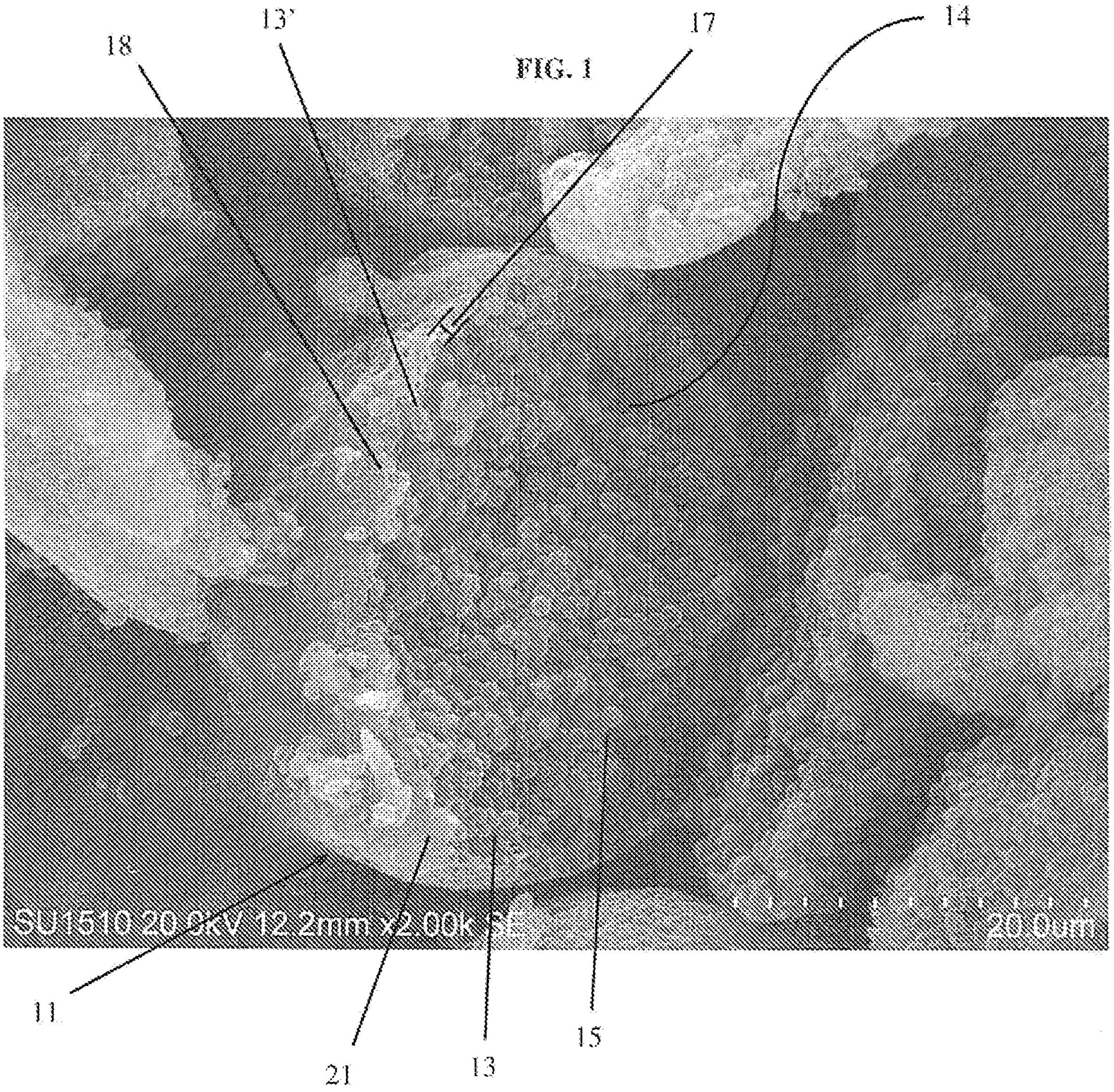


FIG. 2

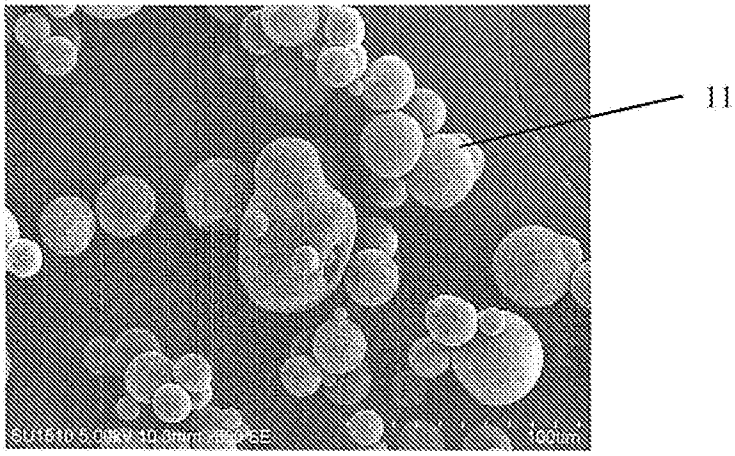


FIG 3

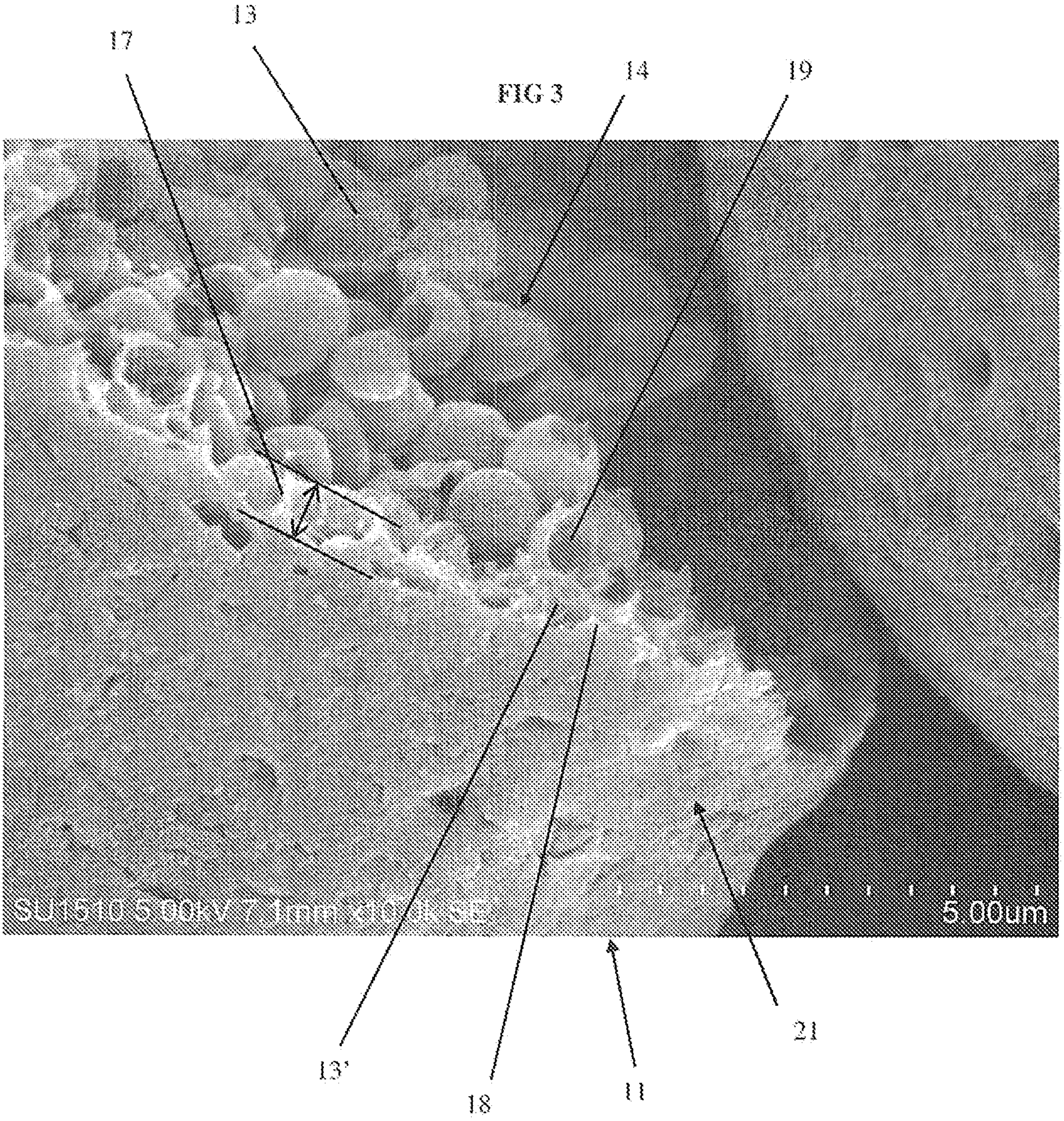


FIG. 4

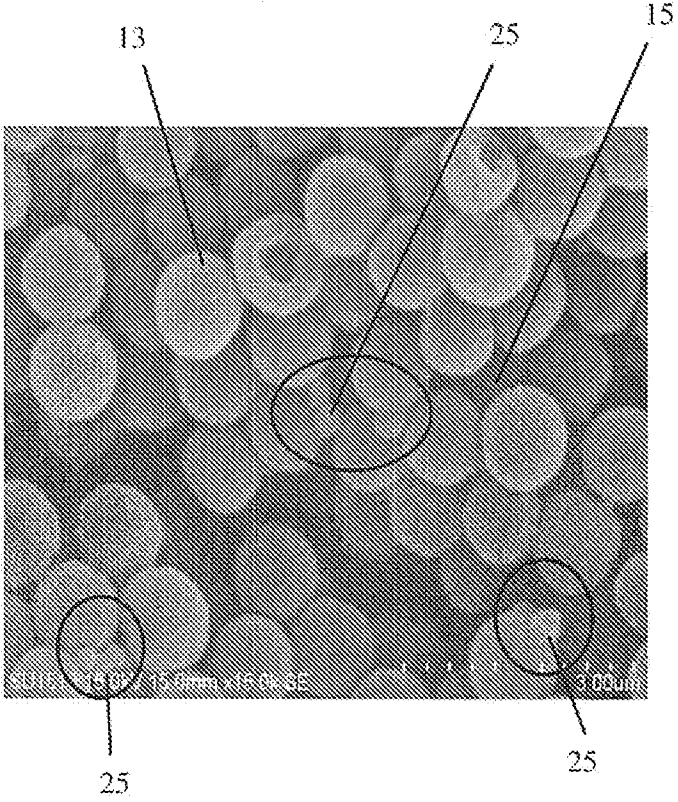
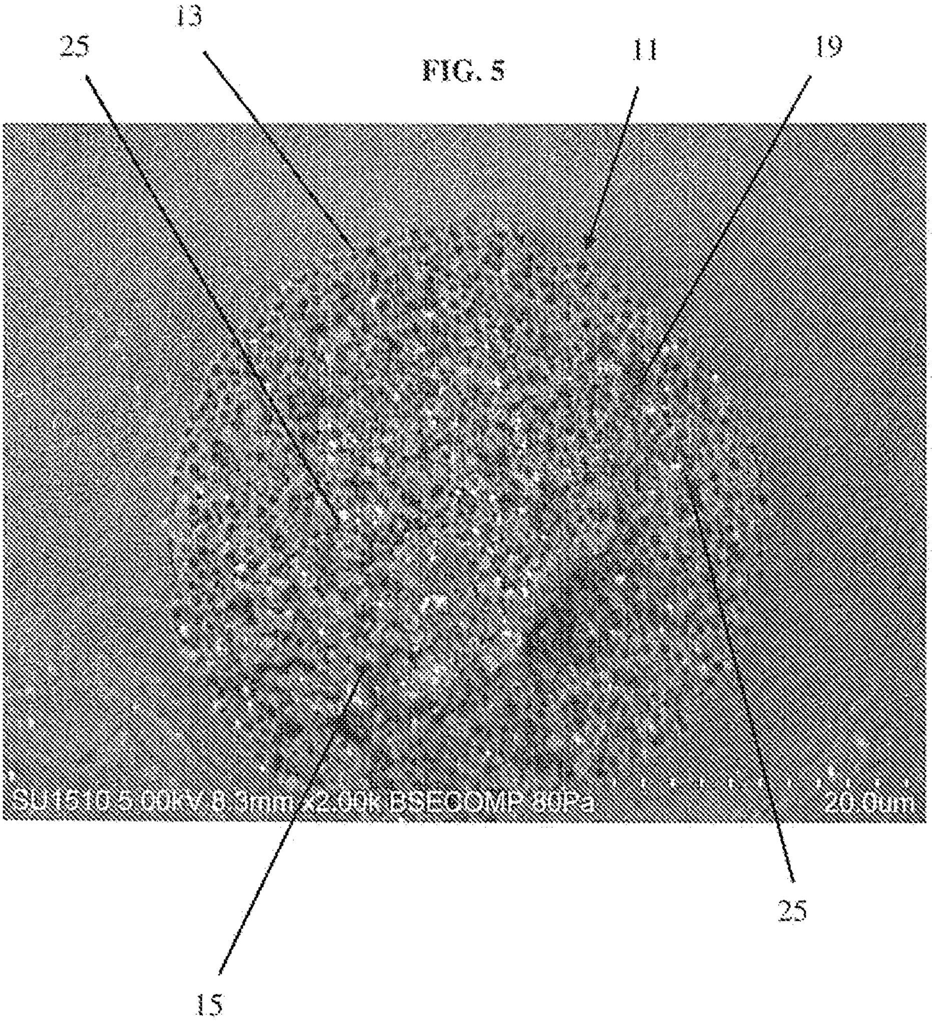


FIG. 5



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/059291

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J3/12 C08K7/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 3 371 053 A (LOU RASKIN BETTY) 27 February 1968 (1968-02-27) page 7; claim 4 -----	11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search 2 December 2014	Date of mailing of the international search report 10/12/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Schweissguth, Martin

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

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