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(54) Title: COATING COMPOSITIONS COMPRISING HOLLOW CERAMIC MICROSPHERES AND FILMS THEREFROM

(57) Abstract: Described herein is a coating composition and films therefrom, wherein the coating composition comprises a plurality of hollow ceramic microspheres wherein the plurality of hollow ceramic microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering; and at least one film-forming polymer.

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COATING COMPOSITIONS COMPRISING HOLLOW CERAMIC MICROSPHERES AND FILMS THEREFROM

TECHNICAL FIELD

[0001] A coating composition comprising a film-forming polymer and a plurality of hollow ceramic microspheres is described along with films made therefrom.

SUMMARY

[0002] There is a desire to identify ways to balance performance characteristics (such as durability and appearance) of coating compositions and/or films. There is also a desire to decrease the cost of coating compositions and/or resulting films.

[0003] In one aspect, a coating composition is described comprising a plurality of hollow ceramic microspheres wherein the plurality of hollow ceramic microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering; and at least one film-forming polymer.

[0004] In another aspect, a film is described comprising a binder and a plurality of hollow ceramic microspheres, wherein the plurality of hollow ceramic microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering.

[0005] The above summary is not intended to describe each embodiment. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages will be apparent from the description and from the claims.

DETAILED DESCRIPTION

[0006] As used herein, the term

"a", "an", and "the" are used interchangeably and mean one or more; and

"and/or" is used to indicate one or both stated cases may occur, for example A and/or B includes, (A and B) and (A or B).

[0007] Also herein, recitation of ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 10 includes 1.4, 1.9, 2.33, 5.75, 9.98, etc.).

[0008] Also herein, recitation of "at least one" includes all numbers of one and greater (e.g., at least 2, at least 4, at least 6, at least 8, at least 10, at least 25, at least 50, at least 100, etc.).

[0009] Water-based architectural paints are comprised of many ingredients each having a specific effect on the paint prior to, during, and/or after application. Environmental regulations, material cost, and the properties of the paint can all factor into determining the final formulation. For example, environmental regulations have dictated decreasing levels of volatile organic compounds

(VOC's) in coatings. One of the main reasons for VOC's in coatings is to serve as coalescents, which plasticize the film-forming polymer allowing it to form a continuous film as the paint dries. With lower amounts of VOC's or even no VOC's, film-forming polymers with lower glass transition temperatures (Tg) that coalesce more easily have been used. These lower Tg polymers are more expensive and do not generate a hard film as compared to coatings comprising traditional film-forming polymers plasticized with VOC's.

[0010] Solid ceramic microspheres have found application in these new low-VOC paint formulations for their ability to maintain scrub and burnish properties at higher pigment volume concentration.

[0011] Hollow ceramic microspheres (e.g., hollow glass microspheres also commonly known as "glass microbubbles", "glass bubbles ", "hollow glass beads", or "glass balloons") having an average diameter of less than about 500 micrometers are widely used in industry, for example, as additives to polymeric compositions. In many industries, hollow glass microspheres are useful, for example, for lowering weight and improving processing, dimensional stability, and flow properties of a polymeric composition. Commercially available hollow glass microspheres do not have small enough size to be generally applicable in interior architectural paints. Large particles stick up out of the applied paint decreasing gloss. In addition, the paint properties of scrub and burnish with commercially available hollow glass microspheres are lower than with ceramic microspheres.

[0012] The present disclosure relates to the use of hollow ceramic microspheres in coating compositions. In the present disclosure, the use of a defined, narrow distribution of hollow ceramic microspheres along with a film-forming polymer in a coating composition can generate a film having improved performance characteristics over non-hollow ceramic microspheres such as improved tint strength and opacity, while also offering durability (e.g., scrub) in paint formulations. Additionally, or alternatively, the use of a defined, narrow distribution of hollow ceramic microspheres can be more cost effective in these coating compositions.

[0013] In one embodiment, the hollow ceramic microspheres of the present disclosure have an average apparent density in a range from at least 0.7, 0.8, 0.85, or even 0.9 grams per cubic centimeter (g/cc); and at most 1.2, 1.5, 1.75, 2, or even 2.5 g/cc, determined according to the method described below. The "average apparent density" of hollow ceramic microspheres is the quotient obtained by dividing the mass of a sample of hollow ceramic microspheres by the volume of that mass of hollow ceramic microspheres as measured by a gas pycnometer.

[0014] For the purposes of this disclosure, average apparent density is measured using a pycnometer following a similar method as disclosed in ASTM D2840- 69, "Average True Particle Density of Hollow Microspheres". The pycnometer may be obtained, for example, under the trade designation "ACCUPYC 1330 PYCNOMETER" from Micromeritics, Norcross, Georgia, or under

the trade designations "PENTAPYCNOMETER" or "ULTRAPYCNOMETER 1000" from Formanex, Inc., San Diego, CA. Average apparent density can typically be measured with an accuracy of 0.001 g/cc. Accordingly, each of the density values provided above can be ± five percent.

[0015] In one embodiment, the ceramic hollow microsphere has an average actual density which is less than 90%, 85%, 80%, or even 70% of the theoretical density of the microsphere assuming a solid core.

[0016] The hollow ceramic microspheres useful for practicing the present disclosure generally are those that are able to survive (i.e., not crushed) the grinding process and/or the capillary forces present during coalescence to form the film. A useful isostatic pressure at which ten percent (or less) by volume of hollow ceramic microspheres collapses is typically at least about 100, 150, 200, or even 250 MPa. For the purposes of the present disclosure, the collapse strength of the hollow ceramic microspheres is measured on a dispersion of the hollow ceramic microspheres in glycerol using ASTM D3102 -72 "Hydrostatic Collapse Strength of Hollow Glass Microspheres" with the exception that the sample size (in grams) is equal to 10 times the density of the ceramic microspheres. Collapse strength can typically be measured with an accuracy of ± about five percent. Accordingly, each of the collapse strength values provided above can be ± five percent. It should be understood by a person skilled in the art that not all hollow ceramic microspheres with the same density have the same collapse strength and that an increase in density does not always correlate with an increase in collapse strength.

[0017] In one embodiment, the hollow ceramic microspheres useful in the present disclosure may be transparent, or translucent (partially transparent).

[0018] The shape of the ceramic hollow microsphere can be determined using techniques known in the art. Such a procedure for determining the size and shape of particles is described in Handbook of Mineral Dressing, by A. F. Taggart, John Wiley & Sons, Inc., New York, 1945, chapter 19, pages 118-120. Many refinements of this basic method are known to those skilled in the art. For instance, one may analyze the magnified two-dimensional images of suitably prepared samples using image analysis software in conjunction with a microscope or a source that inputs data from digital images obtained from a light microscope or SEM (scanning electron microscope).

[0019] The hollow ceramic microspheres of the present disclosure are spherical in nature, meaning that ceramic microspheres have curved edges and or shapes. In one embodiment, the plurality of ceramic microspheres are substantially spherical, which means that the plurality of ceramic particles when magnified into a two-dimensional image appear at least substantially circular. A particle will be considered substantially spherical if its outline fits within the

intervening space between two, concentric, truly circular outlines differing in diameter from one another by up to about 10% of the diameter of the larger of these outlines.

[0020] The particle size of the hollow ceramic microspheres can be determined based on techniques known in the art, for example, microscopy, electrical impedance, or light scattering techniques. In the present disclosure, the plurality of hollow ceramic microspheres has a Dv50, when measured using a light scattering technique of at least 2, 5, or even 10 micrometers and at most 15, 18, or even 20 micrometers. The Dv50 measurement, or median, referred to herein as D50, is where 50 percent by volume of hollow ceramic microspheres in the distribution are smaller than the indicated size diameter. For the purposes of the present disclosure, the median size by volume is determined by laser light diffraction by dispersing the hollow ceramic microspheres in deaerated, deionized water. Laser light diffraction particle size analyzers are available, for example, a Model S3500 Particle Size Analyzer obtained from Nikkiso America, San Diego, CA.

[0021] The plurality of hollow ceramic microspheres of the present disclosure has a unimodal particle size distribution. However, in one embodiment, the plurality of hollow ceramic microspheres may have a bimodal distribution, wherein the particle size distribution curve comprises a small peak, making up less than 10 %, 8%, 5%, or even 1% of the volume of the distribution, at the low end of the distribution. Although not wanting to be limited by theory it is believed that these small diameter particles adhere, perhaps due to electrostatic forces, to larger diameter particles during the sorting (e.g., sieving) process and become unattached when added to a liquid for measuring the diameter using light scattering.

[0022] The plurality of hollow ceramic microspheres has a narrow particle size distribution. Dv90, referred to herein as D90, is the diameter on a particle size distribution curve, where 90 percent by volume of hollow ceramic microspheres fall below this diameter value. In the present disclosure, the plurality of hollow ceramic microspheres has a D50 to D90 ratio greater than 0.62, 0.65, 0.70, 0.75, or even 0.80. The D90 measurement can be used to identify the width of the particle size distribution, where a D50 to D90 ratio of 1.0 would mean that the D90 value is the same as the D50 value.

[0023] To achieve this narrow particle size distribution, typically, the hollow ceramic microspheres are sorted to remove the unwanted sizes, or special care is taken during the manufacture of the hollow ceramic microspheres resulting in a narrow size distribution.

[0024] In one embodiment of the present disclosure, the narrow particle size distribution can be obtained by sorting the plurality of hollow ceramic microspheres using techniques known in the art. For example, the hollow microspheres can be sorted via screen sieves or by an air classifier. With sieving, a screen with controlled sized openings is used and the microspheres passing through the openings are assumed to be equal to or smaller than that opening size. For

microspheres, this is true because the cross-sectional diameter of the microsphere is almost always the same no matter how it is oriented to a screen opening. The microspheres can be mechanically pushed through the screen or vibration can be used to sort the microspheres through the screen. In air classifiers, air is used to separate the material based on size, shape and/or density. The particle separate based on the forces applied (such as centrifugal force and/or gravity) and their drag. For example, commercially available hollow ceramic microspheres may be sorted (or classified) as described above, to achieve the particle size and distribution disclosed herein. Exemplary commercially available hollow ceramic microspheres include those from 3M Company, St. Paul, MN, available under the trade designation "3M GLASS BUBBLES"(e.g., grades K37, XLD-3000, S38, S38HS, S38XHS, K46, A16/500, A20/1000, D32/4500, H50/10000, S60, S60HS, iM30K, iM16K, S38HS, S38XHS, K42HS, K46, and H50/10000); from Potters Industries, Valley Forge, PA, (an affiliate of PQ Corporation) under the trade designations "SPHERICEL HOLLOW GLASS SPHERES" (e.g., grades 110P8 and 60P18) and "Q-CEL HOLLOW SPHERES" (e.g., grades 30, 6014, 6019, 6028, 6036, 6042, 6048, 5019, 5023, and 5028); from Silbrico Corp., Hodgkins, IL under the trade designation "SIL-CELL" (e.g., grades SIL 35/34, SIL-32, SIL-42, and SIL-43); and from Sinosteel Maanshan Inst. of Mining Research Co., Maanshan, China, under the trade designation “Y8000”.

[0025] In another embodiment, the narrow particle size distribution may be achieved by controlling the process in which the particles are made.

[0026] Hollow glass microspheres can be made by techniques known in the art (see, e.g., U. S. Pat. Nos. 2,978,340 (Veatch et al.); 3,030,215 (Veatch et al.); 3,129,086 (Veatch et al.); and 3,230,064 (Veatch et al.); 3,365,315 (Beck et al.); 4,391,646 (Howell); and 4,767,726 (Marshall); and U. S. Pat. Pub. No. 2006/0122049 (Marshall et. al). In one embodiment, a milled frit, commonly referred to as "feed", which contains mineral components of glass and a blowing agent (e.g., sulfur or a compound of oxygen and sulfur) is heated at high temperatures. Upon heating, the blowing agent causes expansion of the molten frit to form hollow glass microspheres. In one embodiment, the frit is sorted by size prior to making the hollow ceramic microspheres, which can result in a plurality of hollow ceramic microspheres having a controlled particle size distribution. Such a process is disclosed in U.S. Pat. No. 2006/0122049 (Marshall et al.).

[0027] When making hollow glass microspheres from frit, the frit and/or feed may have any composition that is capable of forming a glass, typically, on a total weight basis, the frit comprises from 50 to 90 percent of SiO_2, from 2 to 20 percent of alkali metal oxide, from 1 to 30 percent of B_2O_3, from 0.005-0.5 percent of sulfur (for example, as elemental sulfur, sulfate or sulfite), from 0 to 25 percent divalent metal oxides (for example, CaO, MgO, BaO, SrO, ZnO, or PbO), from 0

to 10 percent of tetravalent metal oxides other than SiO_2 (for example, TiO_2, MnO_2, or ZrO_2), from 0 to 20 percent of trivalent metal oxides (for example, Al_2O_3, Fe_2O_3, or Sb_2O_3), from 0 to 10 percent of oxides of pentavalent atoms (for example, P_2O_5 or V_2O_5), and from 0 to 5 percent fluorine (as fluoride) which may act as a fluxing agent to facilitate melting of the glass composition. Additional ingredients are useful in frit compositions and can be included in the frit, for example, to contribute particular properties or characteristics (for example, hardness or color) to the resultant hollow glass microspheres. In some embodiments, the hollow glass microspheres have a glass composition comprising more alkaline earth metal oxide than alkali metal oxide. In some of these embodiments, the weight ratio of alkaline earth metal oxide to alkali metal oxide is in a range from 1.2:1 to 3:1. In some embodiments, the hollow glass microspheres have a glass composition comprising B_2O_3 in a range from 2 percent to 6 percent based on the total weight of the hollow glass microspheres. In some embodiments, the hollow glass microspheres have a glass composition comprising up to 5 percent by weight Al_2O_3, based on the total weight of the hollow glass microspheres. In some embodiments, the glass composition is essentially free of Al_2O_3. "Essentially free of Al_2O_3" may mean up to 5, 4, 3, 2, 1, 0.75, 0.5, 0.25, or 0.1 percent by weight Al_2O_3. Glass compositions that are "essentially free of Al_2O_3" also include glass compositions having no Al_2O_3.

[0028] In some embodiments, hollow ceramic microspheres useful for practicing the present disclosure are surface treated. In some embodiments, the hollow ceramic microspheres are surface treated with a coupling agent such as a zirconate, silane, or titanate. Typical titanate and zirconate coupling agents are known to those skilled in the art and a detailed overview of the uses and selection criteria for these materials can be found in Monte, S.J., Kenrich Petrochemicals, Inc., "Ken-React® Reference Manual - Titanate, Zirconate and Aluminate Coupling Agents", Third Revised Edition, March, 1995. Suitable silanes are coupled to ceramic (e.g., glass) surfaces through condensation reactions to form siloxane linkages with the siliceous surfaces. The treatment renders the microspheres more wet-able or promotes the adhesion of materials to the microsphere surface. This provides a mechanism to bring about covalent, ionic or dipole bonding between hollow ceramic microspheres and organic matrices. Silane coupling agents may be chosen based on the particular functionality desired. Suitable silane coupling strategies are outlined in Silane Coupling Agents: Connecting Across Boundaries, by Barry Arkles, pg 165 – 189, Gelest Catalog 3000-A Silanes and Silicones: Gelest Inc. Morrisville, PA. In some embodiments, useful silane coupling agents have amino functional groups (e.g., N-2-(aminoethyl)-3-aminopropyltrimethoxysilane and (3-aminopropyl)trimethoxysilane). In compositions of the present disclosure, it may be useful to employ a combination of amino-functional silane and a

maleic anhydride modified polyolefin (e.g., polyethylene or polypropylene) in a polyolefin based composition to enhance the coupling between the hollow ceramic microspheres and the polyolefin base resin. In some embodiments, it may be useful to use a coupling agent that contains a polymerizable moiety, thus incorporating the material directly into the polymer backbone. Examples of polymerizable moieties are materials that contain olefinic functionality such as styrenic, vinyl (e.g., vinyltriethoxysilane, vinyltri(2-methoxyethoxy) silane), acrylic and methacrylic moieties (e.g., 3-metacrylroxypropyltrimethoxysilane). Other examples of useful silanes that may participate in crosslinking include 3-mercaptopropyltrimethoxysilane, bis(triethoxysilipropyl)tetrasulfane (e.g., available under the trade designation "SI-69" from Evonik Industries, Wesseling, Germany), and thiocyanatopropyltriethoxysilane. If used, coupling agents are commonly included in an amount of about 1 to 3% by weight, based on the total weight of the hollow ceramic microspheres.

[0029] In some embodiments, the hollow ceramic microspheres useful for practicing the present disclosure are provided with an organic acid or mineral acid coating as described in U.S. Pat. No. 3,061,495 (Alford). In some embodiments, the hollow ceramic microspheres are treated with an aqueous solution of sulfuric acid, hydrochloric acid, or nitric acid at a concentration and for a time sufficient to reduce the alkali metal concentration of hollow ceramic microspheres.

[0030] The coating composition of the present disclosure includes the plurality of hollow ceramic microspheres and a film-forming polymer.

[0031] Film-forming polymers include those known in the art, including both synthetic and natural resins. Exemplary film-forming polymers include: acrylic (which includes both acrylic and methacrylic such as poly(methyl methacrylate-co-ethyl acrylate) or poly(methyl acrylate-co-acrylic acid), acrylic copolymers (such as acrylic-styrene copolymers (e.g., poly(styrene-co-butyl acrylate) and n-butyl acrylate-acrylonitrile-styrene copolymers) or vinyl-acrylic copolymers (e.g., poly(vinyl acetate/methyl acrylate)), vinyl acetate (e.g., poly(vinylidene chloride/vinyl acetate), vinyl acetate/ethylene (VAE), modified VAE, styrene-butadiene copolymer, polyesters (e.g, polyethylene terephthalate, polyethylene terephthalate isophthalate, or polycaprolactone), polyurethanes (e.g., reaction products of aliphatic, cycloaliphatic or aromatic diisocyanates with polyester glycols or polyether glycols), melamine resins, epoxy, alkyds (commonly known but defined as oil modified polyesters), polyamides, (e.g., polyhexamethylene adipamide), polydienes, (e.g., poly(butadiene/styrene)), poly(vinylidene fluoride), urea resins, silicone, and mixtures thereof. Such film-forming polymers may be commercially available under the trade designations "EVOCAR" from Dow Chemical Co., Midland, MI and "ROVACE" from Rohm and Haas Co., a wholly owned subsidiary of Dow Chemical Co. and "ACRONAL PLUS 4130" available from BASF Corp., Florian Park, NJ.

[0032] In one embodiment, the glass transition temperature (Tg) of the film-forming polymer may be at most 20, 15, 10, 5, or ever 0°C. At ambient conditions, coating comprising film-forming polymers with a Tg such as those just described will have a viscosity that allows the polymer droplets in the latex to coalesce. In one embodiment, it is believed the addition of hollow ceramic microspheres can improve the mechanical properties of these film-forming polymers in the dry state.

[0033] Depending on the coating composition, a liquid carrier may be used along with the plurality of hollow ceramic microspheres and the film-forming polymer. The liquid carrier may be aqueous, organic, or a combination thereof.

[0034] In coating compositions not comprising a liquid carrier, the amount of film-forming polymer present may be at least 20, 25, or even 30 wt%; at most 50, 60, 80, or even 95 wt% relative to the coating composition.

[0035] In coating compositions comprising a liquid carrier, such as in paints, the amount of film-forming polymer present may be at least 5, 10, 15, or even 20 wt%; at most 25, 30, 35, or even 40 wt% relative to the coating composition.

[0036] In one embodiment, the coating composition comprises at least 20, 30, 40, or even 45% by weight and at most 70, 65, or even 60% by wt of water based on the total weight of the coating composition.

[0037] In one embodiment, the coating composition may comprise an additive to improve the performance or impart various properties to the coating composition, as are known in the art. Additives may be added to modify the color, surface tension, improve flow properties, improve the finished appearance, improve the stability, impart antifreeze properties, control foaming, control skinning, etc. of the coating composition.

[0038] Examples of types of additives that may be added to the coating composition of the present disclosure, include: a pigment, a coalescent, a dye, a dispersing agent, a surfactant, a filler, preservatives (such as biocides), a defoamer, a thickner, a humectant, and combinations thereof. Additional additives include, for example, anti-corrosive pigment enhancers, curing agents, wetting agents, thickeners, rheology modifiers, plasticizers, waxes, anti-oxidants, antifoaming agents, antisettling agents, antiskinning agents, corrosion inhibitors, de hydrators, antigassing agents, driers, antistatic additives, flash corrosion inhibitors, floating and flooding additives, in-can and in-film preservatives, insecticidal additives, optical whiteners, reodorants, flatteners, de-glossing agents, ultraviolet absorbers, and the like and combinations thereof.

[0039] A pigment is a particulate incorporated into the coating composition to provide opacity, color, and other optical or visual effects. Pigments are those which are known in the art. White pigments include: titanium dioxide, zinc oxide, lithopone, antimony oxide, and zinc sulfide. Non-

white pigments include cadmium yellow, yellow oxides, pyrazolone orange, perinone orange, cadmium red, red iron oxide, prussian blue, ultramarine, cobalt blue, chrome green, and chromium oxide.

[0040] The amount of pigment used in the coating composition of the present disclosure is determined by the pigment's intensity and tinctorial strength, the required opacity, the required gloss, and/or the resistance and durability desired. In a paint composition, pigments may be added at least 5, 7, 10, or even 12 wt (weight) %; and no more than 18, 20, 22, 25, 27, 30, 35, or even 40wt % of a pigment is used in the total paint composition. However, more or less primary pigment may be needed, depending on the composition and the size and type of primary pigment used.

[0041] A coalescing agent is a solvent that is used to aid in the coalescence of the film-forming polymers and will evaporate upon drying of the coating composition. Coalescing agents function to externally and temporarily plasticize the film-forming polymer for a time sufficient to develop film formation, but then diffuse out of the coalesced film after film formation, which permits film formation and subsequent development of the desired film hardness by the volatilization of the coalescent. Internal plasticization is based on coreaction of soft monomers with hard monomers to form a polymeric copolymer binder, such as 80/20 vinyl acetate/butyl acrylate, to obtain the desired film-forming characteristics. Exemplary coalescing solvents include: aliphatics, aromatics, alcohols (such as isopropanol, propylene glycol, ethylene glycol, and methanol), ketones (such as trichlorethyleneacetone, methyl ethyl ketone, and methyl isobutyl ketone), white spirit, petroleum distillate, esters (such as ethyl acetate and n-isobutyl acetates), glycol ethers, perchlorethylene, volatile low-molecular weight synthetic resins, and combinations thereof, for example, ester alcohols such as 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (an ester alcohol available from Eastman Chemical Company, Kingsport, TN, under the trade designation "TEXANOL"). Typically, the coalescing agent is present in a low concentration, typically less than 10, 5 or even 1 wt% based on the total coating composition.

[0042] A dispersing agent may be added to the coating composition for wetting and/or stabilization purposes. The dispersing agent can be a non-ionic or an anionic compound, typically a polymer, such polyvinyl pyrrolidone. Such dispersing agents are known in the art.

[0043] A surfactant may be added to the coating composition to reduce the surface tension and/or for stabilization purposes. The surfactant can be non-ionic, cationic, anionic, or a zwitterionic compound. Such surfactants are known in the art and include for example, those sold under the trade designation "TRITON" and "TERGITOL" by Dow Chemical Co., Midland, MI.

[0044] The proportion of dispersing agent and/or surfactant depends upon the dispersant or surfactant or combinations used and the particular coating composition. The amount added can be determined by routine experimentation.

[0045] Fillers are usually made of inexpensive and inert materials and are added to the coating composition for various purposes, such as to thicken the composition, support its structure and simply increase the volume of the composition. For example, in paints, the fillers have little or no effect on hue, although they may reduce the chroma (that is the intensity) of the hue. They may also enhance opacity, control surface sheen, and facilitate the ease of sanding for example.

[0046] Fillers for coating compositions are known in the art. The filler can be classified as either natural or synthetic types. Exemplary fillers include: diatomaceous earth, talc, lime, clay, fine quartz sand, various clays, blanc fix, calcium carbonate, mica, silicas, aluminum silicate, magnesium silicate, barium sulphate, silica, nepheline syenite, ceramics, and talcs. Exemplary synthetics fillers include engineered molecules or polymeric structures such as "ROPAQUE ULTRA" by Dow Chemical, Midland, MI; and the like.

[0047] Other known additives, such as metal flake and/or pearlescent pigments may be added to modify the visual characteristics of the coating composition and the resulting film.

[0048] In one embodiment, the coating composition of the present disclosure further comprises a preservative, a defoamer, a thickener, and/or a humectant. These additives are commercially available. Examples of preservatives include biocides, in particular Bronopol/(CIT/MIT). Examples of defoamers are polysiloxanes. Examples of humectants include: propylene glycol, ethylene glycol, polyethylene glycol, glycerol, sucrose, and combinations thereof. Examples of thickeners include both polymeric and inorganic and include are those sold under the trade designations "ATTAGEL" by BASF Corp., Florham Park, NJ; "ACRYSOL RM" by Rohm and Haas, a wholly owned subsidiary of Dow Chemical, Midland, MI; "NATROSOL PLUS" by Ashland Inc., Covington, KY.; and "LATTICE" by FMC BioPolymer, Philadelphia, PA.

[0049] In the present disclosure, the plurality of hollow ceramic microspheres and the film-forming polymer can be combined using techniques known in the art.

[0050] In one embodiment, the coating composition is a paint composition. For example, in one embodiment, the dry ingredients such as pigments and fillers are mixed with a suitable medium (such as a liquid) to form the millbase. This is the grind stage and is characterized by high shear rates. The millbase is then gradually diluted with the balance of the ingredients of the paint formulation (typically the vehicle and the film-forming polymer) and any final additives are then added to form the desired paint composition. This let down phase is characterized by lower shear rates than the grind stage.

[0051] The coating compositions of the disclosure are stable. For example, the coating compositions are stable dispersions that remain dispersed over useful time periods without substantial agitation or which are easily redispersed with minimal energy input (e.g., stirring or shaking).

[0052] As used herein, "separate" means that the solid particles in a liquid dispersion gradually settle or cream, forming distinct layers with very different concentrations of the solid particles and continuous liquid phase. For a dispersion with good dispersion stability, the particles remain approximately homogeneously distributed within the continuous phase. For a dispersion with poor dispersion stability, the particles do not remain approximately homogeneously distributed within the continuous phase and may separate. The amount of material that separates, if any, and its properties are indicative of the settling behavior of the dispersion.

[0053] In one embodiment, the coating compositions of the present disclosure have a low to zero volatile organic solvent contents (VOC). Generally speaking, such compositions will have a VOC of less than about 100 grams/liter. The VOC content may be measured, for example, by ASTM D3960-5 (2013) Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings. In many locations, VOCs are regulated and the regulations may differ from locale to locale. Therefore, what may be considered a non-VOC in one locale may be a VOC in another. According to 40 CFR (Code of Federal Regulations) §51.100(s): VOC means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides orcarbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions. 40 CFR §51.100(s) recites a list of organic compounds which are determined to have negligible photochemical reactivity and are thus, not considered VOCs. As of the date of filing, exemplary non-VOC solvents according to 40 CFR §51.100(s) include for example, acetone, and methyl acetate. See 40 CFR §51.100(s) for a complete list of non-VOC solvents.

[0054] In one embodiment, the coating compositions of the present invention have a viscosity allowing for ease of application. In other words, the coating composition is flowable. Depending on the coating composition, the viscosity can be measured using a Brookfield RVT viscometer using a 3, 4, 5, 6 or 7 spindle at greater than 5, 6, 8, or even 10 rpm (revolutions per minute). Preferably, the viscosity is less than about 100,000 centipoise (cP), 10000 cP, 5000 cP, 2500 cP, 2000 cP, 1500 cP, 1000cP or even 500 cP. In one embodiment, viscosities are measured with a Brookfield KU-2 Viscometer as described by ASTM method D562-10 "Standard Test Method for Consistency of Paints Measuring Krebs Unit Viscosity Using a Stormer-Type Viscometer".

[0055] The coating compositions of the present disclosure can be applied to a surface by various means including, but not limited to, brushing, rolling, spraying and the like. Generally a coating is applied to a surface and forms a wet film. Examples of surfaces to which the coating composition

can be applied include: wood, plastic, metal, cement, ceramic, paper, asphalt, plaster, plasterboard, previously primed or coated surfaces, and the like. The coating compositions of the present disclosure are applied such that the resulting film has a cross-sectional thickness of at least 25, 30, 40, or even 50 micrometers; and at most 80, or even 100 micrometers.

[0056] After coating, the film-forming polymer (also known as a binder) anneals (via coalescing, curing, or combinations thereof) to form a film.

[0057] In one embodiment, film formation of the coating composition occurs when the coating composition is applied to a substrate and the carrier liquid evaporates. During this process, the particles of binder (and optional pigment) come closer together. As the last vestiges of liquid evaporate, capillary action draws the binder particles together with great force, causing them to fuse into a continuous film in a process often referred to as coalescence. In coating applications such as paints, the film-forming polymer imparts adhesion, binds the pigments together, and strongly influences such properties as gloss potential, exterior durability, flexibility, and toughness.

[0058] In another embodiment, the coating composition comprises little to no liquid carrier and upon thermal or photo-initiation cures or crosslinks the binder forming a film.

[0059] In the present disclosure, it has been discovered that by using a plurality of hollow ceramic microspheres in a coating composition with the narrow particle size distribution disclosed herein, that films can be generated that have improved performance characteristics such as opacity and tint, while offering sufficient scrub resistance.

[0060] Although not wanting to be limited by theory, it is believed that the use of the particular particle size distribution of the plurality of hollow ceramic microspheres impacts the performance of the coating composition.

[0061] PVC (pigment volume concentration) is used to describe the volume ratio of all pigments (including for example primary pigment, secondary pigment, and fillers) in the coating composition to the total non-volatiles present. Typically, a lower PVC value results in better durability and higher gloss of the coating composition (e.g., a paint) and a higher PVC value has a better hiding. For most coating compositions (especially in paint applications) there is a critical PVC value, wherein there is just the right amount of binder present to fill the voids of the pigment particles. Additionally, pigments and binders are expensive components of paint. Thus, it would be desirable to not use as much binder to wet-out the fillers and pigments. It has been discovered that by using the particular hollow ceramic microspheres of the present disclosure that at the same PVC value, the coating compositions comprising the narrower particle size distribution have improved performance (such as scrub, washability, opacity, and tint strength) as compared to the

same coating composition using a broader distribution. In one embodiment, the PVC value of the resulting film is at least 20%, 25%, 30%, 35% or even 40%; and no more than 50%, 55%, 60%, 65%, or even 70%. In another embodiment, the PVC value is at least 8%, 10%, or even 12% and no more than 18%, 20% or even 25 %.

[0062] Exemplary coating compositions that may be improved by the addition of a narrow size distribution of hollow ceramic microspheres in a film-forming polymer include architectural paint (e.g., for indoor or outdoor applications), floor polishes and finishes, varnishes for a variety of substrates (e.g., wood floors), waterborne gels applied in the manufacture of photographic film, automotive or marine coatings (e.g., primers, base coats, or topcoats), sealers for porous substrates (e.g., wood, concrete, or natural stone), hard coats for plastic lenses, coatings for metallic substrates (e.g., cans, coils, electronic components, or signage), inks (e.g, for pens or gravure, screen, or thermal printing), and coatings used in the manufacture of electronic devices (e.g., photoresist inks).

[0063] Exemplary embodiments of the present disclosure include, but are not limited to, the following.

[0064] Embodiment 1. A coating composition comprising a plurality of hollow ceramic microspheres wherein the plurality of hollow ceramic microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering; and at least one film-forming polymer.

[0065] Embodiment 2. The coating composition of embodiment 1, wherein the hollow ceramic microspheres comprise silica and a boron trioxide.

[0066] Embodiment 3. The coating composition of any one of the previous embodiments, wherein the hollow ceramic microspheres have an average apparent density of at least 0.8 g/cc.

[0067] Embodiment 4. The coating composition of any one of the previous embodiments, further comprising a liquid carrier.

[0068] Embodiment 5. The coating composition of embodiment 4, wherein the liquid carrier is water.

[0069] Embodiment 6. The coating composition of embodiment 5, wherein the water comprises 30% to 70% wt of the coating composition.

[0070] Embodiment 7. The coating composition of any one of the previous embodiments, wherein the film-forming agent is selected from at least one of polyvinyl acetate, acrylic, styrene-butadiene copolymers, and combinations thereof.

[0071] Embodiment 8. The coating composition of any one of the previous embodiments, wherein the at least one film-forming polymer comprises 5% to 30% wt of the coating composition.

[0072] Embodiment 9. The coating composition of any one of the previous embodiments, wherein

the coating composition further comprises a dispersant, a surfactant, or combinations thereof.

[0073] Embodiment 10. The coating composition of any one of the previous embodiments, wherein the coating composition further comprises a pigment, a dye, or combination thereof.

[0074] Embodiment 11. The coating composition of any one of the previous embodiments, wherein the coating composition further comprises a coalescent.

[0075] Embodiment 12. The coating composition according to embodiment 11, wherein the coalescent is selected from the group consisting of: ester alcohols, alcohols, glycol ethers, and combinations thereof.

[0076] Embodiment 13. The coating composition of any one of the previous embodiments, wherein the coating composition further comprises a filler.

[0077] Embodiment 14. The coating composition according to embodiment 13, wherein the filler is selected from the group consisting of: calcium carbonate, clay, and combinations thereof.

[0078] Embodiment 15. A film comprising a binder and a plurality of hollow glass microspheres wherein the plurality of hollow glass microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering.

[0079] Embodiment 16. The film of embodiment 15, wherein the hollow ceramic microspheres comprise silica and a boron trioxide.

[0080] Embodiment 17. The film of any one of embodiments 15-16, wherein the hollow ceramic microspheres have an average apparent density of at least 0.8 g/cc.

[0081] Embodiment 18. The film of any one of embodiments 15-17, wherein the binder is selected from at least one of polyvinyl acetate, acrylic, styrene-butadiene copolymers, and combinations thereof.

[0082] Embodiment 19. The film of any one of embodiments 15-18, further comprising an additive, wherein the additive is selected from at least one of a filler, a pigment, a rheology modifier, and a surfactant.

[0083] Embodiment 20. The film of any one of embodiments 15-19, wherein the film has a cross-sectional thickness of 25 micrometers to 100 micrometers.

EXAMPLES

[0084] Advantages and embodiments of this disclosure are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In these examples, all percentages, proportions and ratios are by weight unless otherwise indicated.

[0085] All materials are commercially available, for example from Sigma-Aldrich Chemical Company; Milwaukee, WI, or known to those skilled in the art unless otherwise stated or apparent. These abbreviations are used in the following examples: g = gram, hr = hour, kg = kilograms, min = minutes, mol = mole; cm= centimeter, mm = millimeter, mL = milliliter, L = liter, MPa = megaPascals, and wt = weight.

Materials

Material Name/Designation	Description
KTPP	Potassium tripolyphosphate, obtained from Aldrich Chemical Company, Milwaukee, WI
VANTEX-T	A multifunctional neutralizing amine (a tertiary amine) additive with virtually no ammonia or amine-type odor, obtained from Eastman Chemical Company, Kingsport, TN under trade designation "EASTMAN VANTEX-T"
NATROSOL PLUS 330	Hydrophobically modified hydroxyethylcellulose, obtained from Ashland Specialty Chemical Company, Covington, KY under trade designation "NATROSOL PLUS 330"
FOAMSTAR ST-2438	100% active defoamer compound combining a hyper-branched Star polymer with high-end, organo-silicones, obtained from BASF Corporation, Florham Park, NJ under trade designation "FOAMSTAR ST-2438"
TAMOL 1124	A high performance hydrophilic copolymer pigment dispersant, commercially available from Dow Chemical, Midland, MI under the trade designation "TAMOL 1124"
TRITON CF-10	Low foam nonionic surfactant, commercially available from Dow Chemical, Midland, MI under the trade designation "TRITON CF-10"
TI-PURE R-706	Rutile titanium dioxide pigment, 2.4 g/cc true density with 1-24 micron size range, commercially available from The Chemours Co., Wilmington, DE available under the trade designation "TI-PURE R-06"
3M Additive W-410	Solid ceramic microspheres, available from 3M Co., St. Paul, MN under trade designation "3M CERAMIC MICROSPHERES W-410"

3M Additive iM30K	Hollow glass microspheres, available from 3M Co., St. Paul, MN under trade designation "3M GLASS BUBBLES iM30K"
3M Additive HGM	Hollow glass microspheres prepared as described below
MINEX 4	A micronized functional filler and/or extender produced from nepheline syenite; a naturally occurring, silica deficient, sodium-potassium alumina silicate, obtained from Unimin Corporation, New Canaan, CT under trade designation "MINEX 4"
DURAMITE	A coarse, unique, medium particle size marble, obtained from Imerys Carbonates, Roswell, GA under trade designation "DURAMITE"
ACRONAL 4130	All acrylic latex for less than 50 g/L VOC semi-gloss paints with outstanding block resistance and enhanced titanium dioxide efficiency, obtained from BASF Corporation, Florham Park, NJ under trade designation "ACRONAL 4130"
ACRYSOL TT-935	A nonionic urethane rheology modifier commercially available from Dow Chemical, Midland, MI, available under the trade designation "ACRYLSOL TT-935"

[0086] Preparation of 3M Additive HGM

[0087] The 3M Additive HGM was prepared using a glass frit prepared as described in U.S. Pat. No. 4767726 (Marshall). The frit was classified using the process as described in U.S. Pat. Publ. No. 2006/0122049 (Marchall et al.). The frit was classified with an air classifier (CFS 5-HD-S available from Erich NETZSCH GmbH & Co. Holding KG, Selb Germany) using an RPM of 7000 at a dosage rate of 70% and an air flow rate of 75 normal cubic meters per hour, which resulted in a fine fraction and a coarse fraction. Shown in Table 1 below is the equivalent spherical diameter of the particles in micrometers at D5, D50, and D95 as measured on a Coulter LS-13 320 (Beckman Colter Inc, Brea CA).

Table 1

	D5	D50	D95
Input Feed	2.34	7.29	13.8
Fine fraction	2.12	6.07	11.6
Coarse fraction	6.188	10.15	16.7

[0088] The classification resulted in 1270 g the fine fraction and 895 g of the coarse fraction. The coarse fraction of the frit was used to make the hollow ceramic microspheres as described below.

[0089] The frit composition was 70-80 % SiO_2, 8-15 wt % CaO, 3-8% Na_2O, 2-6%B_2O_3 and up to about 1.5 wt% of SO_3 (blowing agent). The coarse fraction of the frit was passed through a natural gas/air flame as described in the Examples 1-8 of U.S. Pat. No. 4,767,726 (Marshall) to make the hollow glass microspheres.

[0090] Particle Size

[0091] The particle size was determined by laser diffraction (using a Model S3500 Particle Size Analyzer obtained from Nikkiso America) operating in the wet mode with water as a medium. The mmicrospheres were placed in water and sonicated for 60 seconds at 25 % power prior to collecting the data. The data was analyzed using the laser diffraction software.

[0092] Density

[0093] The density of the microspheres was determined using a gas pycnometer (from Micromeritics, Norcross, Georgia under trade designation “ACCUPYC 1330 PYCNOMETER") according to ASTM D2840- 69, "Average True Particle Density of Hollow Microspheres”.

[0094] Strength and % Survival

[0095] The strength and % survival at strength of the microspheres was determined using a dispersion of the microspheres in glycerol using ASTM D3102 -72 "Hydrostatic Collapse Strength of Hollow Glass Microspheres" with the exception that the sample size (in grams) is equal to 10 times the density of the 3M Additive HGM.

[0096] The three different microspheres (3M Additive HGM, 3M Additive iM30K, and 3M Additive W-410) were each tested for particle size, density, strength, and % survival at strength using the methods described above. Show in Table 2 are the results.

Table 2

Sample	Density (g/cc)	D50 (micrometer)	D90 (micrometer)	D50/D90	Strength (MPa)	% Survival at Strength
3M Additive W-410	2.40	10.32	23.28	0.44	N/A	N/A
3M Additive iM30K	0.60	16.04	26.47	0.61	193.05	90
3M Additive HGM	1.02	13.10	19.87	0.66	206.84	95

N/A means the test was not run for this sample.

[0097] Preparation of Paint

[0098] The paint was prepared in a two stages.

[0099] The grind was prepared by mixing in an 800 mL beaker equipped with a 1.5 inch (38.1 mm) Cowles blade, predetermined amounts of water, KTPP and VANTEX-T at 600 rpm for 4 minutes. Then, a predetermined amount of NATROSOL PLUS 330 was added and allowed to dissolve until it was clear of seeds (which took about 20 minutes). Afterwards, predetermined amounts of FOAMSTAR ST-2438, TAMOL 1124 and TRITON CF-10 were added to the mixture which was further mixed for 5 minutes at 600 rpm. Separately, predetermined amounts of the dry components MINEX 4, DURAMITE, TI-PURE R-706 and 3M Additive were blended together using a wooden spatula and the blended dry components were added to above solution over a period of 6 minutes while mixing at 3500 rpm. The mixing was continued another 20 minutes.

[00100] The let-down was prepared by mixing predetermined amounts of water and ACRONAL 4130 in a 800 mL container equipped with a propeller blade at low speed with a vortex pulling about 1 inch (25.4 mm) into the liquid.

[00101] The grind from above was then added to the let-down and the resulting mixture was mixed for 10 minutes. Finally, ACRYSOL TT-935 thickener was added to bring the Krebs unit viscosity of the mixture to approximately 95 KU ($\pm$ 2 KU) to complete preparation of the paint. Kreb unit viscosity was measured using a Brookfield KU-2 Viscometer (commercially available form Brookfield AMETEK, Middleborough, MA) as described by ASTM method D562-10 "Standard Test Method for Consistency of Paints Measuring Krebs Unit Viscosity Using a Stormer-Type Viscometer".

[00102] The resulting paint formulation from above was coated on sealed Leneta 3B opacity charts with a 3 mil (75 micrometers) bird bar and Leneta scrub panels with a 7 mil (178 micrometers) draw down bar (available from Leneta Company, Mahwah, NJ) to prepare samples for testing. The coated paint samples were allowed to dry under ambient conditions for 7 days before testing using the test methods described below.

[00103] Opacity test

[00104] Opacity of the samples was measured using a colorimeter (available under the trade designation "COLORFLEX EZ" from Hunter Lab in Reston, VA) to measure the Y tristimulus value over white and black regions of the sealed 3B charts. Contrast ratio is the ratio of Y_{black} / Y_{white}.

[00105] Scrub test

[00106] The scrub test is a measure of the number of passes with abrasive media over a thin shim that a paint can withstand before breaking. The scrub test was performed similarly to the method described in ASTM 2486-06 (2012). The breaking point was determined by observation across the width of the shim. Two tests were run on at least three paths. The values were averaged

to obtain the reported values.

[00107] Washability test

[00108] The wash test was based on ASTM D3450-00 (2010) and used ASTM ST-1 soil as the soilant. The soilant was applied for 16 hours, blotted using a paper towel and a two pound roller, then washed with 5 mL of a 10% detergent solution (dish washing liquid available under the trade designation "DAWN" from Procter & Gamble, Cincinnati, OH) and 2.5 g of water for 25 passes with a sponge. The initial reflectance of the panels was measured at three points in each of two paths before the soiling and washing and the final reflectance was measured at three points in each of two paths after the washing. The ratio of the averages of these six numbers was taken to be the reflectance recovery as given in the following equation. A higher number is better and indicates more of the dark soiling was removed by washing.

$$Reflectance\ recovery = \frac{Reflectance_{final}}{Reflectance_{initial}}$$

[00109] Tint test

[00110] Tint strength is a measure of the effectiveness of a pigment to change the color of a coating. For this study, 1 g of BASF PureOptions B Lamp black pigment (obtained from BASF Corporation, Florham Park, NJ under trade designation "PUREOPTIONS B LAMP BLACK") was mixed into 50 g of each of the three paints described above using a Flacktek speed mixer (obtained from FlackTek, Inc, Landrum SC under trade designation "FLACKTEK SPEED MIXER") operating at 1500 rpm for 30 s. The now grey paints were drawn down on sealed 3B Leneta opacity charts and allowed to dry for 1 week. The Y tristimulus reflectance value was measured using a Colorite colorimeter. Tint strength was calculated according to the following equation:

TS =(T) [(1-Y)2/2Y]s/[(1-Y)2/2Y]u(T)

where:

TS = tinting strength of test pigment,

Y` = measured reflectance factor as Y tristimulus as a decimal,

T = assigned tinting strength of standard, usually 100 %,

and subscripts " u" and "s" refer to the pigment of interest and the standard pigment. For this study the standard pigment was 3M Additive W-410.

[00111] Example 1 and Comparative Examples A and B

[00112] Example 1 and Comparative Examples A and B paint mixtures were prepared according to the method for preparation of paint described above. The type of microsphere and the amount used (as a result of density differences among 3M Additives) was varied.

[00113] Table 3, below, summarizes the amounts of the various components used in

preparing the paint mixtures used in Example 1 and Comparative Examples A and B described below.

Table 3

Material	Amount (g)
Grind	
Water	134.23
KTPP	0.79
NATROSOL PLUS 330	2.60
VANTEX-T	1.95
FOAMSTAR ST-2438	1.32
TAMOL 1124	3.97
TRITON CF-10	1.32
TI-PURE R-706	96.56
3M Additive	See below for the type and amount of 3M Additive used for Example 1 and Comparative Examples A and B
MINEX 4	54.46
DURAMITE	59.06
Let-down	
ACRONAL 4130	328.25
Water	81.25
ACRYSOL TT-935	2.39
Pigment Volume Concentration (PVC)	40
Non-Volatiles Volume % (NVV)	39

[00114] For Example 1, the 3M Additive was 30.04 g of 3M Additive HGM prepared as described above.

[00115] For Comparative Example A, the 3M Additive was 69.38 g of 3M Additive W-410.

[00116] For Comparative Example B, the 3M Additive was 17.38 g of 3M Additive iM30K.

[00117] The resulting Example 1 and Comparative Examples A and B paint samples were tested according to the test methods described above. The test results are summarized in Table 4, below.

Table 4

		Example 1	Comparative Example A	Comparative Example B
Opacity	Average	95.58	95.44	95.58
	Standard deviation	0.19	0.09	0.06
Scrub	Average	783	911	619
	Standard deviation	31.43	18.04	27.06
Washability	R average	0.8183	0.7884	0.8064
	R st.dev	0.0460	0.0268	0.0459
Tint	Y tristimulus	0.3619	0.338	0.3637
	Tint strength relative to Comparative Example A	1.15	1	1.16

[00118] Foreseeable modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to the embodiments that are set forth in this application for illustrative purposes.

What is claimed is:

1. A coating composition comprising
   (a) a plurality of hollow ceramic microspheres wherein the plurality of hollow ceramic microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering; and
   (b) at least one film-forming polymer.

2. The coating composition of claim 1, wherein the hollow ceramic microspheres comprise silica and a boron trioxide.

3. The coating composition of any one of the previous claims, wherein the hollow ceramic microspheres have an average apparent density of at least 0.8 g/cc.

4. The coating composition of any one of the previous claims, further comprising a liquid carrier.

5. The coating composition of any one of the previous claims, wherein the film-forming agent is selected from at least one of polyvinyl acetate, acrylic, styrene-butadiene copolymers, and combinations thereof.

6. The coating composition of any one of the previous claims, wherein the at least one film-forming polymer comprises 5% to 30% wt of the coating composition.

7. The coating composition of any one of the previous claims, wherein the coating composition further comprises a coalescent.

8. A film comprising
   (a) a binder; and
   (b) a plurality of hollow glass microspheres wherein the plurality of hollow glass microspheres has a D50 diameter of 2 to 20 microns and a D50 to D90 ratio greater than 0.62 as measured by light scattering.

9. The film of claim 8, wherein the hollow ceramic microspheres comprise silica and a boron trioxide.

10. The film of any one of claims 8-9, wherein the hollow ceramic microspheres have an average apparent density of at least 0.8 g/cc.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/013699

A. CLASSIFICATION OF SUBJECT MATTER

C09D 7/00 (2018.01) ***C03C 11/00 (2006.01)*** *C08K 7/24 (2006.01)*

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D, C08K, B01J 13/00

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)

Databases: EPODOC, WPI, TXTE and FAMPAT
Search terms: coating, hollow, microspheres, D50, D90, size distribution and other related terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6531222 B1 (TANAKA, M. ET AL.) 11 March 2003 lines 24-25 and 40, column 2; lines 30-31 and 65, column 3; lines 50-51, column 7; lines 16-20, column 9; lines 40-41, column 15; and example 1	1, 2, 3-9
X	US 2010/0222487 A1 (NISHI. Y. ET AL.) 2 September 2010 abstract; paras [0008]-[0010], [0014], [0033], [0039] and [0042]; examples 1-7; and table 1	1-10
A	US 2005/0137088 A1 (HAYAKAWA, K. ET AL.) 23 June 2005 whole document, in particular para [0210]; table 1; and examples 1	
A	JP H07-179533 A (TOYO BOSEKI) 18 July 1995 whole document, in particular examples 1-4 and table 3 of the machine translation	

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

*Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search	Date of mailing of the international search report
20/04/2018 *(day/month/year)*	18/05/2018 *(day/month/year)*

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2018/013699

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2345541 B1 (RICOH COMPANY LTD) 29 August 2012 whole document, in particular paras [0042], [0055], [0149] and [0153]	
A	JP 2006-256895 A (TOKAI KOGYO CO LTD) 28 September 2006 whole document, in particular para [0009] of the machine translation	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2018/013699

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6531222 B1	11/03/2003	EP 1172341 A1 WO 01/02314 A1	16/01/2002 11/01/2001
US 2010/0222487 A1	02/09/2010	KR 20080091850 A WO 2007/102569 A1	14/10/2008 13/09/2007
US 2005/0137088 A1	23/06/2005	EP 1543985 A2 AT 409593 T JP 2009279943 A CN 1796151 A	22/06/2005 15/10/2008 03/12/2009 05/07/2006
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