



- (51) International Patent Classification:
C09C 1/40 (2006.01) C09C 1/00 (2006.01)
- (21) International Application Number:
PCT/US2013/073716
- (22) International Filing Date:
6 December 2013 (06.12.2013)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
13/708,810 7 December 2012 (07.12.2012) US
- (71) Applicant: BUNGE AMORPHIC SOLUTIONS LLC
[US/US]; 50 Main Street, White Plains, New York 10606
(US).
- (72) Inventors: LEWARCHIK, Ronald James; 2154 Pine
Hollow Trail, Brighton, Michigan 48114 (US). FO-
SCANTE, Raymond E.; 20547 Manzanita Avenue, Yorba
Linda, California 92886 (US).
- (74) Agents: LANGTON, Grant T. et al.; Novak Druce Con-
nolly Bove + Quigg LLP, P.O. Box 2207, Wilmington,
Delaware 19899 (US).

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

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ALUMINUM PHOSPHATE COMPOSITE MATERIALS AND COMPOSITIONS

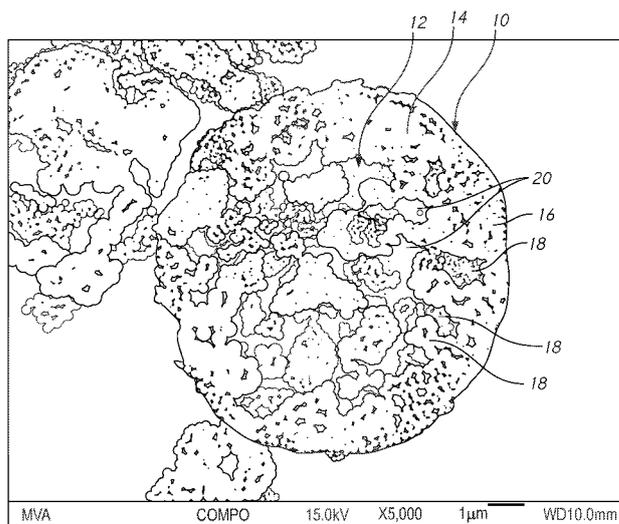


FIG. 1

(57) Abstract: AIP composite materials comprise an AIP aggregate core, and a shell disposed partially or entirely over the core and formed from a pigment material, e.g., TiO₂, having an index of refraction greater than the core, providing an overall index of refraction greater than the core and suited for use as a pigment replacement or extender. The AIP core comprises amorphous AIP, crystalline AIP, or a combination thereof, and can have an average particle size of less than about 30 microns. The TiO₂ can have an average grain size less than about 10 microns. The shell can have a layer thickness that is at least about 0.0001 microns. The shell is bonded to the core by a reaction between functional groups of the shell and core. The AIP composite material can be engineered to provide properties in addition to brightness for use as a pigment such as anticorrosion and/or antimicrobial protection.



ALUMINUM PHOSPHATE COMPOSITE MATERIALS AND COMPOSITIONS

FIELD

[0001] Aluminum phosphate composite materials and compositions comprising the same are disclosed herein that are engineered to provide properties making them useful as a pigment replacement and/or pigment extender, e.g., for use in place of conventional pigments such as TiO_2 and the like, and that can provide additional properties not otherwise present with such conventional pigments

BACKGROUND

[0002] The use of conventional pigments such as TiO_2 and the like in coating formulations is well known. TiO_2 pigments are the widest used pigments in the coatings industry, as they are used in virtually all white or pastel coating compositions because of its brightness and very high refractive index (having an index of refraction of about 2.61). While such conventional TiO_2 pigments are useful for providing a desired level of brightness and high refractive index in coating formulations, the raw material cost of conventional TiO_2 has increased over the years, reducing the profit margin obtainable for chemical formulations or coating products containing the same if the raw material cost increase cannot be passed onto the product consumer.

[0003] Also, while TiO_2 is useful for providing a desired degree of brightness, it alone is not useful for introducing one or more other performance properties that may be desired into a particular chemical or coating formulation. Accordingly, chemical or coating formulations calling for performance properties in addition to brightness conventionally rely on additives or agents in addition to TiO_2 , thereby adding further to the cost and/or complexity of formulating the chemical composition or coating.

[0004] It is, therefore, desired that a composite material be developed in a manner that provides pigment performance characteristics, e.g., brightness and high refractive index, that are the same as or similar to that of conventional pigments such as TiO_2 , e.g., to serve as a primary pigment replacement or as a pigment extender, and that is more cost efficient when compared to conventional TiO_2 from either a raw material and/or a formulated coating cost per unit volume solids. It is also desired that the composite material be one that is capable of providing one or more performance properties in addition to brightness to enable making chemical or coating formulations calling for

such additional performance properties without having to rely on additional additives or agents.

SUMMARY

[0005] Aluminum phosphate composite materials as disclosed herein comprise a core and shell structure, wherein the shell is formed from a material having an index of refraction that is higher than the core to provide the composite material with an overall index of refraction that is greater than the core, and wherein the core is formed from a material having a reduced material cost when compared to the shell. In an example, the core comprises an aggregate of joined-together primary aluminum phosphate grains or powder, and the aggregate is hereby referred to as an AIP particle. The AIP particle can comprise amorphous AIP, crystalline AIP, or a combination thereof. The AIP particle can have an average particle size of less than about 30 microns, in the range of from about 3 to 20 microns, and preferably in the range of from about 5 to 10 microns. The AIP can be made by precipitation, binary condensation, and sol gel methods of making.

[0006] In such example, the shell is provided in the form of a layer of pigment material disposed over an outside surface of the core. A preferred pigment material is TiO₂. The TiO₂ can have an average grain or powder size that is less than about 10 microns, in the range of from about 0.1 to 5 microns, and preferably in the range of from about 0.3 to 1 microns. The shell has a layer thickness that is at least about 0.0001 microns, and between about 0.001 to 2 microns, and preferably in the range of from about 0.01 to 1 microns. Generally, the shell layer thickness can comprise as little as a single grain, or can comprise several grains that are bonded or otherwise combined together on the core surface.

[0007] The shell may cover all or only a portion of the AIP core. In an example, the shell covers at least 20 percent of the total outside surface of the core, in the range of from about 30 to 100 percent of the total outside surface of the core, and preferably 20 percent of the core outside surface, and preferably in the range of from about 50 to 75 percent of the core outside surface. In an example, the TiO₂ is treated with or otherwise comprises a material that reacts with pendant POH groups from the AIP core to form a reaction product therebetween that operates to bond the shell to the core.

[0008] If desired, the AIP composite material can be engineered to provide properties in addition to being a pigment and/or pigment extender. In an example, the AIP composite can produce a controlled release of phosphate anion when placed into contact with moisture to provide a desired degree of anticorrosion protection. Additionally, the AIP composite material can be engineered to produce a controlled release of one or more other elements or compounds useful for providing anticorrosion, and/or for providing other properties such as antimicrobial and/or antifouling protection.

[0009] AIP composite materials as disclosed herein can be used as the sole pigment in a chemical or coating composition, e.g., comprising a binding polymer. In an example, the AIP can be used to replace about 100 percent of conventional pigment material. In another example, AIP composite materials as disclosed herein can be used in conjunction with conventional pigments to offset the amount, and thereby the cost, of such other conventional pigment that is used, and can comprise at least about 5 percent by weight of the total pigment used in a formulation, in the range of from about 10 to 80 percent by weight of the total pigment used, and in the range of from about 20 to 60 percent by weight of the total pigment used in a chemical or coating formulation. AIP composite materials as disclosed herein present a more cost-effective option than conventional pigment materials such as TiO_2 from either a raw material and/or a formulated coating cost per unit volume solids. Additionally, such AIP composite material are capable of being engineered to introduce one or more other performance property, in addition to brightness, to enable making chemical or coating formulations calling for such additional performance properties without having to rely on additional additives or agents.

DESCRIPTION OF THE DRAWING

[0010] These and other features and advantages of aluminum phosphate composite materials and compositions and methods for making the same as disclosed herein will be appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with figure 1, which is a photomicrograph showing a cross-sectional view of an example aluminum phosphate composite material as disclosed herein.

DETAILED DESCRIPTION

[0011] Aluminum phosphate composite materials and compositions comprising the same as disclosed herein generally comprise a two-component structure made up of a centrally oriented core, and a shell disposed around or over all or part of the core. In an example, the core is formed from a non-TiO₂ material such as aluminum phosphate that provides a cost advantage when compared to a core formed entirely from TiO₂. In an example, the shell that is disposed over the core is comprised of one or more layers of a conventional pigment material, i.e., a material having a high index of refraction such as TiO₂. Thus, an advantage of such composite material is that it has a desired high index of refraction (approaching that of conventional solid TiO₂), provided by the TiO₂ shell, and provides such desired property at a reduced cost (when compared to conventional solid TiO₂), by using a different core material that is relatively less costly than TiO₂. Additionally, aluminum phosphate composite materials as disclosed herein can be engineered to provide one or more additional performance properties. For example, aluminum phosphate composite materials can be engineered to additionally provide a desired degree of corrosion resistance and/or to provide a desired degree of antimicrobial protection depending on the particular end-use coating or formulation application. This is in addition to serving as a conventional pigment replacement and/or pigment extender.

[0012] An example core material useful for forming composite materials as disclosed herein is solid aluminum phosphate (AIP), which may be used in amorphous form, crystalline form, or a combination thereof. The AIP can be formed having a desired particle size during the chemical synthesis process, or can be sized after a chemical synthesis process by conventional sizing techniques. In an example, the AIP particle has an average particle size of less than about 30 microns, in the range of from about 3 to 20 microns, and preferably in the range of from about 5 to 10 microns. Ultimately, the end-use application will influence the particular size of the AIP particle and/or AIP particle distribution that is used for the core. Generally, the majority of coatings are medium and low gloss, and an average pigment particle size much over about 10 microns may end-use applications to those where a low degree of gloss is desired.

[0013] The term "particle" as used herein with respect to the AIP core is understood to mean an aggregate of a number of smaller AIP primary grains or powder that have

joined or aggregated together during the process of synthesizing the AIP. The exact number of smaller AIP primary grains or powder that combine to form each ALP particle or aggregate useful for forming the core can and will vary. Accordingly, it is to be understood that the core component of the composite material comprises an AIP aggregate formed from a plurality of primary AIP grains or powder as described above.

[0014] The AIP core material is preferably substantially irregular in shape, but can have a shape that is spherical, flat, or needle like if called for by a particular end-use application. For example, it may be desirable in certain applications to have composite material that has a high aspect ratio, or that is flat like a flake or the like. Accordingly, it is to be understood that the core material as disclosed herein can be engineered having a variety of different shapes as called for by a particular end-use application.

[0015] An example shell material useful for forming composite materials as disclosed herein is one having an index of refraction that is greater than that of the core material (e.g., AIP has an index of refraction of less than about 1.55), so as to make the resulting composite material suitable to serve as a replacement and/or extender of conventional pigment. In an example, it is desired that the shell material have an index of refraction that is greater than about 1.55, greater than about 1.7, and preferably greater than about 2. In a preferred embodiment, the shell material is formed from TiO_2 , which has an index of refraction of about 2.6. In a particularly preferred embodiment, the TiO_2 is one that has been surface treated with alumina, and/or silica or a combination of alumina and silica, or the like, e.g., rutile grade TiO_2 , to enhance both light stability and pigment dispersibility. Alternatively, the TiO_2 can be treated with any other material that may be reactive with pendant POH groups of the AIP core to thereby adhere to and form a shell with the AIP core.

[0016] TiO_2 useful for forming the shell of the composite material has an average grain or powder size that is less than about 10 microns, in the range of from about 0.1 to 5 microns, and preferably in the range of from about 0.3 to 1 microns. In certain end-use applications a desired TiO_2 particle size for opacity is about 0.3 microns. Thus, using a TiO_2 particle size greater or less than 0.3 microns may not provide a level or degree of opacity for certain end-use applications.

[0017] In an example embodiment, the TiO_2 is placed into contact with the AIP particles or cores, and is attached to the surface of the AIP cores to by reaction between

the core and the TiO₂ as better described below. Thus, in an example embodiment, AIP composite materials as disclosed herein comprise a reaction product interposed between the core and the shell that operates to bond the shell to the core. In an example, the TiO₂ shell can have an average thickness of at least 0.0001 microns, in the range of from about 0.001 to 2 microns, and preferably in the range of from about 0.01 to 1 microns. Generally, the TiO₂ shell or layer is formed having a thickness sufficient to provide a desired degree of brightness or index of refraction for a particular end-use application without using excess TiO₂ material that would unnecessarily add to the raw material cost of the composite material. The TiO₂ shell may have a thickness that may or may not be uniform along the core. Thus, the shell thicknesses provided above are representative of an average taken along different portions of the core surface.

[0018] The TiO₂ shell can cover the entire outside surface of the core material, i.e., it can encapsulate the core, or can cover a partial region or portion of the core outside surface. The extent of shell coverage over the core surface depends on such factors as whether the composite material is being used as the primary formulation pigment, whether it is being used as an extender pigment in conjunction with another pigment material, the desired degree of brightness desired for the particular end-use application, the particular material used to form the core, and particular material selected to use the shell, and the like.

[0019] In an example, where the core is AIP and the shell is TiO₂, it is desired that the TiO₂ shell cover a portion of the core surface sufficient to provide a degree of brightness or index of refraction sufficient to act as a primary or extender pigment. In such example, the TiO₂ shell covers at least about 20 percent of the core outside surface, in the range of from about 30 to 100 percent, and preferably in the range of from about 50 to 75 percent of the core outside surface. The exact degree of TiO₂ shell coverage as noted above can and will vary depending on the particular end-use application. Additionally, the amount of shell coverage can vary depending on the particular shell material that is used, e.g., if the shell material is a material other than TiO₂. For example, for shell materials having an index of refraction that is less than TiO₂, a higher degree of coverage may be useful to obtain a degree of brightness for the composite material than that achieved using TiO₂.

[0020] Figure 1 is a photomicrograph of an aluminum phosphate composite material as disclosed herein. Specifically, this figure illustrates a cross-section of an aluminum

phosphate composite 10 comprising a AIP core 12 in the form of an AIP particle or aggregate 14, and a TiO₂ shell 16 disposed over an outside surface 16 of the AIP core 12. As illustrated, the shell 16 may comprise a single TiO₂ particle or may comprise a number of TiO₂ particles that are combined with one another. In the example, the shell has a thickness that varies along the core surface. As illustrated, the AIP core comprises an aggregate of a number of smaller primary AIP particles 18 that are bonded with one another. The particle or aggregate 14 may include a plurality of open interstitial regions 20 that exist between the primary AIP particles. These interstitial regions can be empty or may include one or more desired materials disposed therein. In the example illustrated in figure 1, some of the interstitial regions are shown to include TiO₂ disposed therein.

[0021] The TiO₂ can be introduced into the AIP particle during the process of combining the AIP cores with the TiO₂ material. Alternatively, the TiO₂ may be introduced into the interstitial regions when the AIP composite material is sized, which operation may cause some of the cores to be opened up and thereby exposing the interstitial regions to any free TiO₂ that may be present. Besides or in addition to TiO₂, the AIP core can be treated to include one or more other materials disposed within the interstitial regions as called for or desired by the particular end-use application, wherein such other material can operate to introduce a particular performance property or characteristic.

[0022] For end-use applications calling for a certain degree of corrosion resistance, it may be desired to leave a portion of the underlying AIP core exposed. AIP as disclosed herein is a corrosion inhibiting material, capable of releasing passivating phosphate anion when placed into contact with moisture that operates to inhibit corrosion of metallic substrates. AIPs useful in this regard include those made in accordance with the references disclosed below and incorporated herein. Thus, a feature of AIPs as used herein as the core is that they can provide a controlled delivery of phosphate anions, of about 50 to 1,500 ppm, when contacted with moisture.

[0023] In addition to the corrosion inhibition mechanism of controlled phosphate anion release, such AIPs used as the core are capable of absorbing up to about 25 percent by weight moisture that they come into contact with. Thus, when present for example in the form of a cured film, such AIP core materials function as a sort of sponge to absorb and thus contain moisture entering the film, and thereby operate to prevent such

moisture from traveling further through the film to an underlying metallic substrate where it can cause the substrate to corrode. This is in addition to the AIP forming a corrosion inhibiting passivating film on the metallic substrate by reaction of the released phosphate anion and the metallic substrate. Further, in addition to phosphate anion release, AIPs as disclosed herein can be engineered to include one or more other materials useful for providing anticorrosion resistance, examples of which include and are not limited to zinc, calcium, strontium, chromate, borate, barium, magnesium, molybdenum, and combinations thereof.

[0024] The AIP core material can be formed according to a variety of different processes and methods, including those disclosed in US Patent Application Publication Nos. 2006/0045831, 2009/0217481, 2010/0203318, 2012/0091397, 2012/0094128, 2012/0094130, and US Patent Nos. 7,763,359 and 7,951,309, each of which is incorporated herein by reference in its entirety. Additionally, AIP core materials formed according to the references disclosed above can have the same properties of those AIP disclosed in the same references, as again incorporated herein by reference.

[0025] AIP core materials are generally formed by combining an aluminum source with a phosphate source, in desired proportions, under desired pH conditions, and under desired conditions of temperature, to result in the formation comprising solid AIP particles. As disclosed in the references disclosed and incorporated herein above, the AIP particles can be formed by precipitation methods, binary condensation, and sol gel methods.

[0026] Generally, the precipitation method of making AIP involves combining a suitable aluminum source such as aluminum sulfate or sodium aluminate with a suitable phosphate source such as phosphoric acid using desired aluminum and phosphate ratios, and using desired pH and/or temperature conditions to form AIP. The binary condensation method of making AIP involves combining a suitable aluminum source such as aluminum hydroxide with a suitable phosphate source such as phosphoric acid using desired aluminum and phosphate ratios, adding acid to base or base to acid, wherein acidic aluminum phosphate may be formed as an intermediate, and using desired pH and/or temperature conditions to form AIP. The sol gel method of making AIP involves combining an aluminum salt such as aluminum nitrate with phosphoric acid and adding to the mixture sufficient ammonium hydroxide sufficient to form an

aggregate of colloidal AIP forming a gel having a three-dimensional structure of linked amorphous aluminum phosphate particles.

[0027] Still further, AIP materials useful as the core of the composite material as disclosed herein can be engineered to incorporate one or more ingredients other than phosphate therein for controlled release to provide certain desired chemical composition or coating performance. For example, AIP materials useful as the core can be synthesized to incorporate one or more active material therein, such as Ag, Cu, Zn, Ca, Ni, Sr, and combinations thereof that may be useful to provide such performance features as antimicrobial protection, to provide conductivity and/or antifouling resistance or the like.

[0028] AIP materials as used herein may also comprise organic materials (volatile or nonvolatile, fugitive or nonfugitive) for a variety of reasons. For example, the inclusion of volatile materials may be incorporated to control pore volume, pore size, structure etc., (these materials could be volatilized with heat or vacuum as part of the manufacturing process). Fugitive active organic materials may be used to enhance antimicrobial resistance, enhance conductivity or antifouling properties, act as an antioxidant, and/or provide light stabilization or enhanced UV light stability for example. Nonfugitive organic moieties may be employed to provide functionality for additional modification with other reactive ingredients.

[0029] In an example, where antimicrobial protection is desired, the AIP material can be formed by one or more of the same methods described above, in the references incorporated herein, by either combining the desired active material with the AIP after the AIP has been formed, or by combining the desired active material at the time of synthesizing the AIP, to thereby form an AIP complex comprising the active material incorporated into the AIP material. In an example, where the active material is Ag, the resulting AIP material or complex that is formed has a controlled Ag release when in a cured film of about 5 to 1,000 ppm, which is sufficient to provide a desired level or antimicrobial protection on the surface of the film.

[0030] For end-use applications calling for one or more of such additional performance features, it is desired that some portion of the underlying AIP core remain exposed and not covered by the shell to thereby enable the AIP core to function in the manner disclosed above to provide desired release of one or more of its constituents, and/or to

provide for moisture absorption. Thus, in such applications wherein the AIP core is engineered to provide multiple functions (as a core for the shell and as a carrier for constituent release) in the formulation, the degree of AIP core coverage by the shell represents a compromise between the amount useful to provide a desired level of pigment performance as a replacement or extender and the amount useful to provide a desired release of an AIP constituent content. It is, therefore, to be understood that such shell coverage amounts can vary depending on such factors as the particular end-use application, the type of active ingredient contained in the AIP core, the type of material used to form the shell, and the like.

[0031] Composite materials and methods of making the same as disclosed herein may be better understood with reference to the following particular example.

Example – Formation of Composite Material

[0032] An example composite material is prepared by combining an aluminum source with a phosphate source in a water-borne system (to form a slurry comprising AIP particles with pendent POH groups) and adding TiO₂ (so the POH groups can be reacted with alumina surface treatment of the TiO₂) to the slurry to form a shell over the AIP particles. In an example, the aluminum source is aluminum trihydroxide (ATH) and the phosphate source is orthophosphoric acid.

Dispersions of ATH and TiO₂

[0033] ATH was dispersed in deionized water in a container comprising a high speed dispenser with a cowles blade. In an example, an ATH particle size of less than about 5 microns was desired. The high speed dispenser was used to achieve a 7.5+ Hegman gauge value, which occurred in about 90 to 120 minutes depending on the solid content and total batch size. The average solid content of the ATH dispersion as determined according to ASTM D-2369 was from about 25 to 30 percent. A dispersion of TiO₂ was formed by combining TiO₂ with deionized water and using a high speed dispenser with cowles blade until a 7.5+ Hegman value was achieved, which was within about 90 to 120 minutes. The solid content of the TiO₂ dispersion as determined according to ASTM D-2369 was from about 55 to 65 percent.

Synthesis of AIP

[0034] On solid base, one mole of the ATH solution prepared above was added into a reaction kettle along with an amount of deionized water. The reaction kettle included a mechanical stirrer, a heating mantle, a temperature controller, a thermocouple, a condenser, and an addition funnel containing one mole orthophosphoric acid on solid base (ATH to acid mole ratio set at approximately 1:1). The ATH and water solution was initially stirred at about 700 to 1,000 RPM, or in a way that splashing of solution did not occur within the reaction kettle. An initial reaction temperature was set at approximately 42°C, and at this temperature addition of the orthophosphoric acid was started. The addition time for the acid was between about 19 to 21 minutes. After the acid was completely added the stirring speed was increased to a maximum point and the reaction temperature was increased to approximately 92°C. At this condition, reaction was continued for a further 3 hours forming AIP particles. The pH was monitored every hour. Normally, the pH stabilizes within about 3 hours. In general, the pH achieved within this time (initial/stabilized pH) was about 3 to 3.8. The solids content of AIP particles in the batch at this stage was approximately 20.26 percent. The AIP particles in the batch comprised pendent POH groups.

Synthesis of Core-Shell Structure

[0035] Once the initial pH was achieved, an amount of the TiO₂ solution prepared above was added to the reaction kettle, and stirring was continued for a further 90 minutes. The pH stabilized within this 90 minute time, and was in the range of about 3.5 to 4.6. During this time, the pendent POH groups from the AIP particles reacted with the alumina surface treatment on the TiO₂ causing the TiO₂ to be strongly attached to the outer surface of the AIP particles, thereby forming a TiO₂ shell around each AIP particle or core. At this stage the solids content of the batch was approximately 22.196 percent.

Reacting with Imidazole

[0036] An amount of imidazole was added to the reaction kettle. The amount of the imidazole used depended on the total solids combined above, i.e., the ATH, orthophosphoric acid, and TiO₂. Depending on the pH achieved after the TiO₂ solution was added to the AIP, the amount of imidazole used in the system can vary between about 0.2325 percent to 2 percent to achieve a 5+ final product pH. The imidazole is

used to react with any residual POH groups to increase pH, and to improve wet adhesion to ease dispersion of the resulting AIP composite material into the coating formulation.

Filtration, Washing and Drying.

[0037] The final product was filtered using a Buckner funnel, and the filtered product was washed with deionized water. The deionized water amount was approximately 3.6 times the weight of the total solids of the batch. The washed product was dried at 110°C under 26 in.,Hg vacuum for a period of approximately 24 hours. The final product was stored in a metal container and consisted of the AIP composite material as disclosed herein, and had a d50 particle diameter of approximately 10 microns.

[0038] AIP composite materials as disclosed herein are specifically engineered to provide a high index of refraction that is greater than that of the core and relatively closer to that of the shell material, e.g., TiO₂, for the purpose of entirely or partially replacing the amount of conventional pigment material used in chemical or coating formulation, and provide such features at a cost that is less than conventional solid TiO₂. Accordingly, the use of AIP composite materials as disclosed herein operate to provide desired level of brightness at a reduced price, which price reduction depends on the amount of the AIP composite used to replace conventional solid TiO₂.

[0039] In certain end-use applications, AIP composite materials as discussed herein can be used to replace up to about 100 percent of conventional pigment material. In example embodiments, AIP composite materials as disclosed herein can be used in conjunction with conventional pigments to offset the amount, and thereby the cost, of such other conventional pigment that is used, and can comprise at least about 5 percent by weight of the total pigment used in a formulation, in the range of from about 10 to 80 percent by weight of the total pigment used, and in the range of from about 20 to 60 percent by weight of the total pigment used in a chemical or coating formulation.

[0040] For example a 50/50 blend of conventional solid TiO₂ with the AIP composite material as disclosed herein that comprises 15 percent TiO₂ present as the shell component of the composite provides a coating composition having a contrast ratio, whiteness and opacity that is comparable to that of a coating composition containing 100 percent conventional solid TiO₂. This example 50/50 blend provides a 35 percent

reduction in the amount of total TiO₂, thereby providing an associated savings in raw material price.

[0041] AIP composite materials as disclosed herein can be used in conjunction with both solvent and water-based coating systems, e.g., comprising solvent and/or water-based binding polymers, to provide a desired level of conventional pigment reduction. Examples of such binding polymers include polyurethanes, polyesters, solvent-based epoxies, solventless epoxies, water-borne epoxies, epoxy copolymers, acrylics, acrylic copolymers, silicones, silicone copolymers, polysiloxanes, polysiloxane copolymers, alkyds and combinations thereof.

[0042] Additionally, AIP composite materials as disclosed herein can be used for purposes other than as a pigment, e.g., they can be used as flatteners in coating compositions, this in addition to the additional uses disclosed above, e.g., to provide anticorrosion and/or antimicrobial resistance. Further, the pendent reactive POH groups of the AIP core can be used to attach other elements, ingredients, compounds, inorganic or organic moieties (in addition to or in place of the pigment material) that can provide certain other desired properties to the composite.

[0043] AIP composite materials as disclosed above provide a novel pigment replacement and/or pigment extender that may provide additional properties. While such AIP composite materials have been the invention has been described with respect to a limited number of embodiments, the specific features of one embodiment should not be attributed to other embodiments of AIP composite materials as disclosed herein. No single embodiment is representative of all aspects of AIP composite materials as disclosed herein. Variations and modifications from the AIP composite materials described herein exist. The method of making AIP composite materials is described as comprising a number of acts or steps by reference or otherwise. These steps or acts may be practiced in any sequence or order unless otherwise indicated. Finally, any number disclosed herein should be construed to mean approximate, regardless of whether the word "about" or "approximately" is used in describing the number. The appended claims intend to cover all those modifications and variations as falling within the scope of AIP composite materials as disclosed herein.

What is claimed is:

1. An aluminum phosphate composite material comprising:
an aluminum phosphate particle forming a core of the composite material; and
a layer of pigment material disposed over an outside surface of aluminum phosphate particle and forming a shell over the core.
2. The composite material as recited in claim 1 wherein the aluminum phosphate material is amorphous aluminum phosphate.
3. The composite material as recited in claim 1 wherein the aluminum phosphate material is crystalline aluminum phosphate.
4. The composite material as recited in claim 1 wherein the pigment material has an index of refraction that is greater than the core.
5. The composite material as recited in claim 4 wherein the pigment material is TiO_2 .
6. The composite material as recited in claim 1 wherein the pigment material has a layer thickness of at least about 0.01 microns.
7. The composite material as recited in claim 1 wherein the pigment material has a layer thickness of from about 0.001 to 2 microns.
8. The composite material as recited in claim 1 wherein the shell covers at least 20 percent of the total outside surface of the core.
9. The composite material as recited in claim 1 wherein the shell covers in the range of from about 30 to 100 percent of the total outside surface of the core.
10. The composite material as recited in claim 1 wherein the shell is formed from TiO_2 , and wherein the shell is attached to the core by a reaction product between pendant POH groups from the core and a material on the TiO_2 .

11. The composite material as recited in claim 1 having an index of refraction that is greater than the core, and the core provides a controlled release of phosphate anion when placed into contact with moisture to provide a degree of anticorrosion protection.
12. The composite material as recited in claim 11 wherein the core absorbs up to 25 percent by weight water.
13. The composite material as recited in claim 11 wherein the core comprises a constituent incorporated therein, and wherein the constituent is released over time when the composite material is present as a component in a cured composition.
14. A chemical composition comprising the composite material as recited in claim 1 dispersed in a binding polymer.
15. The chemical composition as recited in claim 14 comprising a further pigment material in addition to the composite material.
16. A chemical composition comprising;
an aluminum phosphate composite material comprising:
a plurality of cores formed from aluminum phosphate; and
a shell disposed at least partially over an outside surface of respective cores, the shells being formed from TiO_2 ; and
a binding polymer, wherein the aluminum phosphate composite material is dispersed in the binding polymer.
17. The composition as recited in claim 16 further comprising a pigment material.
18. The composition as recited in claim 16 wherein the aluminum phosphate comprises amorphous or crystalline aluminum phosphate.
19. The composition as recited in claim 16 wherein the shell covers at least about 20 percent of the surface area of a respective core.

20. The composition as recited in claim 19 wherein the shell covers about 30 to 100 percent of the surface area of a respective core.
21. The composition as recited in claim 16 wherein the core has an average particle size of less than about 30 microns.
22. The composition as recited in claim 16 wherein the core has an average particle size of between about 3 and 20 microns.
23. The composition as recited in claim 16 wherein the core provides a controlled release of phosphate anion of between about 50 to 1,500 ppm when exposed to moisture.
24. The composition as recited in claim 23 wherein the core absorbs up to about 25 percent by weight water when exposed to moisture.
25. The composition as recited in claim 16 wherein the core comprises a constituent material incorporated therein that is released in a controlled manner.
26. The composition as recited in claim 25 wherein the constituent material is a bioactive material.
27. The composition as recited in claim 26 wherein the constituent material is selected from the group consisting of Ag, Cu, Zn, Ca, Ni, Sr, and combinations thereof.
28. The composition as recited in claim 16 wherein the aluminum composite material comprises a reaction product between the core and shell a result of POH groups from the core reacting with a material on the shell.
29. The composition as recited in claim 16 wherein the composite material has a thickness in the range of from about 0.001 to 2 microns.
30. A coating composition comprising:
a binder polymer material; and

an aluminum phosphate composite material dispersed in the binder polymer material, wherein the aluminum phosphate composite material comprises:

a plurality of cores comprising amorphous aluminum phosphate; and
a shell disposed at least partially over an outside surface of a respective core, the shell being formed from a material having an index of refraction greater than the core.

31. The coating composition as recited in claim 30 further comprising a pigment material.
32. The coating composition as recited in claim 31 wherein the aluminum phosphate composite material comprises at least 5 percent by weight of the total weight of the aluminum phosphate composite material and the pigment.
33. The coating composition as recited in claim 30 wherein the shell has an index of refraction that is greater than 2.
34. The coating composition as recited in claim 33 wherein the shell is formed from TiO_2 .
35. The coating composition as recited in claim 30 wherein the aluminum phosphate composite material comprises a reaction product formed between pendant POH groups of the aluminum phosphate and a material from the TiO_2 .
36. The coating composition as recited in claim 30 wherein the shell has a thickness in the range of from about 0.001 to 2 microns.
37. The coating composition as recited in claim 30 wherein the shell covers at least 20 percent of the total outside surface of a respective shell.
38. A method for making an aluminum phosphate composite material comprising the steps of:
forming a dispersion of aluminum phosphate particles; and

combining aluminum phosphate particles with a pigment material having an index of refraction greater than the aluminum phosphate particles so that the pigment material at least partially covers the aluminum phosphate particles to form the aluminum phosphate composite material.

39. The method as recited in claim 38 wherein during the step of combining, the pigment material is TiO_2 .

40. The method as recited in claim 38 further comprising after the step of combining, adding imidazole to the aluminum phosphate composite material.

41. The method as recited in claim 38 comprising reacting the aluminum phosphate particles with the pigment material to form a reaction product there between.

42. The method as recited in claim 41 wherein the pigment material is TiO_2 .

43. The method as recited in claim 41 wherein during the step of reacting, POH groups from the aluminum phosphate particles react with a constituent of the pigment material.

44. The method as recited in claim 38 wherein during the step of forming, aluminum trihydroxide is combined with phosphoric acid.

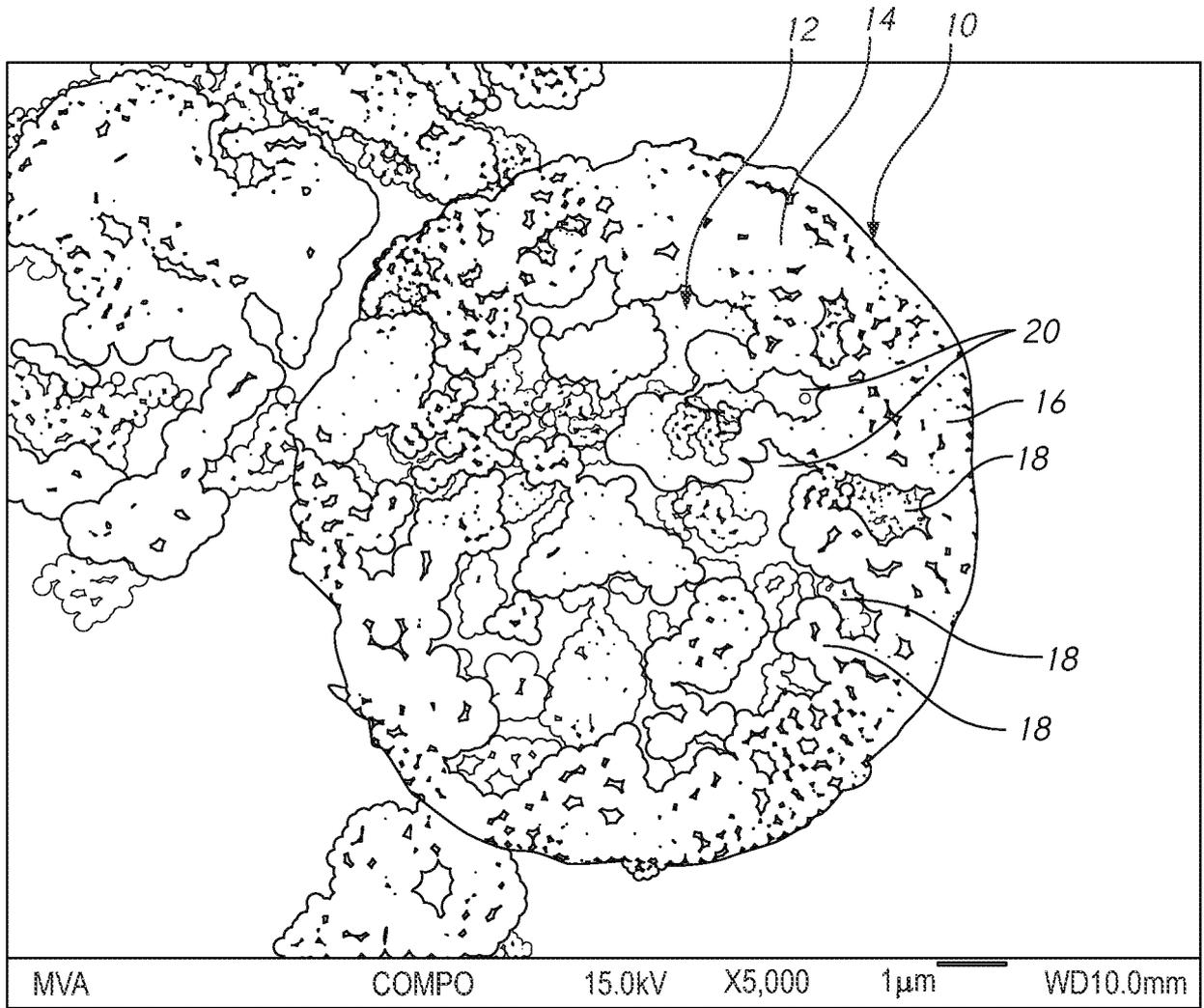


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/073716

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/40 C09C1/00
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)
C09C
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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7 264 672 B1 (TRABZUNI FADI MOHAMMED SAEED [SA] ET AL) 4 September 2007 (2007-09-04) column 6, line 45 - column 14, line 56; example 1	1-44
A	WO 2008/017135 A1 (BUNGE FERTILIZANTES SA [BR]; UNICAMP [BR]; DE BRITO JOAO [BR]; GALEMBE) 14 February 2008 (2008-02-14) page 2, line 48 - page 4, line 22 page 24, line 2 - page 25, line 26	1-44
A	US 2007/175363 A1 (BLUMEL SIEGFRIED [DE] ET AL BLUEMEL SIEGFRIED [DE] ET AL) 2 August 2007 (2007-08-02) paragraphs [0017] - [0041]; examples 1-5	1-44
	-/--	

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
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "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

"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

"&" document member of the same patent family

Date of the actual completion of the international search 13 February 2014	Date of mailing of the international search report 20/02/2014
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 Corrias, M

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/073716

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/091397 A1 (FOSCANTE RAYMOND E [US]) 19 April 2012 (2012-04-19) cited in the application paragraphs [0008] - [0070] -----	1-44

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/US2013/073716

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 7264672	B1	04-09-2007	AU 2007350976 A1	23-10-2008
			AU 2012203265 A1	21-06-2012
			GB 2456725 A	29-07-2009
			US 7264672 B1	04-09-2007
			WO 2008125904 A2	23-10-2008

WO 2008017135	A1	14-02-2008	AR 062313 A1	29-10-2008
			AU 2007283472 A1	14-02-2008
			BR PI0715813 A2	23-07-2013
			CA 2660564 A1	14-02-2008
			CL 23422007 A1	14-03-2008
			CO 6160215 A2	20-05-2010
			EA 200970191 A1	28-08-2009
			EP 2066585 A1	10-06-2009
			JP 2010500266 A	07-01-2010
			KR 20090037935 A	16-04-2009
			US 2008038556 A1	14-02-2008
			US 2011301272 A1	08-12-2011
			UY 30532 A1	31-03-2008
WO 2008017135 A1	14-02-2008			

US 2007175363	A1	02-08-2007	NONE	

US 2012091397	A1	19-04-2012	AU 2011315912 A1	30-05-2013
			CA 2814692 A1	19-04-2012
			CN 103237850 A	07-08-2013
			EA 201390562 A1	30-09-2013
			EP 2627717 A1	21-08-2013
			JP 2013545833 A	26-12-2013
			SG 189903 A1	28-06-2013
			US 2012091397 A1	19-04-2012
			UY 33673 A	31-05-2012
WO 2012051580 A1	19-04-2012			
