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(54) Title: COMPOSITE PIGMENTS HAVING ENHANCED LIGHT SCATTERING ABILITY

(57) Abstract

Composite pigment materials that are endowed with enhanced light scattering and opacity properties, which are useful as an active paper pigment, filler or coating pigment. There also is a unique method for making the composite pigment materials in which the pH of a reaction bath containing seed particles and high refractive index particles is reduced effective that the surface potential of the high refractive index particle is reversed to cationic so as to make them attachable to a seed particle surface under aqueous conditions.

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DESCRTIPTION

COMPOSITE PIGMENTS HAVING ENHANCED LIGHT SCATTERING ABILITY

Field of the Invention

The present invention relates to composite white pigment particles and manufacturing techniques for their preparation.

Background Art

It is well known in the art to use various types of mineral particles as coating and filler pigments. In particular, aluminosilicates are well known as paper fillers, as are various forms of clay such as kaolin. It is also known in the art to modify mineral particles by application of surface coatings of various inorganic compositions.

For instance, U.S. Pat. Nos. 5,262,239, 5,219,660, 5,312,485, 5,352,287, all by S. Wason and M. Withiam, relate to composite mineral products useful as a paper pigment and as a filler which involve substantially inert mineral nuclei each having coated thereon a substantially continuous uniform coating consisting of discrete active paper pigment particles of a silicate reaction product or equivalent thereof. The discrete active paper pigment particles are described in the above-identified four patents as being selected from among synthetic alkali metal silicates, alkali metal aluminosilicates, alkaline earth metal alumino-silicates, alkaline earth metal silicates, alkaline earth aluminocarbonates, amorphous silicas and mixtures thereof, with substantially all the active paper pigment particles having a diameter less than one micron. The processing protocol taught in the above-identified four patents generally involves producing the pigment product by preforming some of the active paper pigment coating to form a slurry of coating pigment under alkaline conditions, then adding a slurry of the mineral nuclei to the alkaline pigment slurry, followed by continuing formation of the coating pigment in the presence of the mineral nuclei, with the reaction mixture always maintained under alkaline conditions.

U.S. Pat. 4,537,636 describes mica platelets coated with metal oxides involving uniform co-precipitation thereon of titanium dioxide hydrate, silicon dioxide, and aluminum hydroxide.

U.S. Pat. 5,078,793 describes a method for preparing kaolin for use as a pigment extender of titanium dioxide pigments in plastic formulations in which a sprayable slurry is prepared comprising an aqueous hydrocolloid suspension of calcined anionic particles in admixture with a cationic polymeric reagent capable of binding to kaolin particles and making them cationic. Then, the slurry is spray dried by atomizing droplets of a pressurized mixture of the slurry with gas addition to promote droplet fluffing and fragmentation, and the frangible spray dried material thereafter is collected and dry blended with anionic surface-charged titanium dioxide which binds thereto.

U.S. Pat. 5,152,835 describes composite titania-calcined kaolin opacifying pigments formed of particles of titania pigment and calcined kaolin particles co-flocculated and bound together in the form of coherent aggregates by an organic cationic electrolyte.

U.S. Pat. 5,456,749 describes anti-discoloring pearly luster pigment comprising mica particles coated with titanium dioxide and/or titanium oxide hydrate further sequentially coated with silicon oxide and/or silicon oxide hydrate, then aluminum oxide and/or aluminum oxide hydrate, and then zinc oxide and/or zinc oxide hydrate. The '749 patent also describes a process in which the various coatings are sequentially formed by dropwise addition of a metal salt providing the appropriate cations for the desired metal oxide coating with pH maintained at constant value.

U.S. Pat. 5,540,769 describes platelet-like colored pigments comprising platelet-shaped substrate coated with a coating layer consisting of titanium dioxide and at least one suboxide thereof, and also silica, with concentration gradients such that the titanium oxide content decreases towards the outer surface while the silica content increases towards the outer surface.

U.S. Pat. 5,702,519 describes a pearlescent pigment, among other things, involving a core of flaky aluminum oxide, identified therein as corundum (i.e., Al_2O_3), that contains a small amount of titanium dioxide, and the core is surface-coated with titanium oxide. The titanium oxide surface coating is accomplished by hydrolysis of a metal salt by heating or alkali treatment, which deposits hydrated titanium oxide on the cores, followed by calcination of the coated cores at high temperatures.

Other prior art teachings on pigments, fillers, or particulates involving use of a high refractive index component, include, for example, U.S. Pat. Nos. 3,669,896, 3,212,911 3,418,147, 3,545,994, and 4,405,376.

It is an object of the present invention to provide a composite pigment having enhanced optical properties which is useful as a paper pigment, coating pigment, and filler. It is another object to provide a composite pigment that is compatible with food grade processing equipment. It is also an object of this present invention to provide a useful manufacturing technique to provide such pigment materials. The above and other objects, benefits, and advantages are achieved by the present invention as will become apparent as the description thereof proceeds below.

SUMMARY OF THE INVENTION

The present invention provides for unique composite pigment materials that are endowed with enhanced light scattering and opacity properties, which are useful as an active paper pigment, filler or coating pigment.

In one embodiment of the present invention, there is a composite product in which a seed particle has an exterior surface having an anionic surface potential to which is attached a plurality of smaller sized high refractive index pigment particles having an opposite surface potential to that of the exterior surface.

In one preferred embodiment, the high refractive index pigment particles used in this invention can be any white inorganic pigment having a cationic surface charge created thereon while the exterior surface of the seed particle is anionic. Preferably, the high refractive index particles have a refractive index above at least about 1.6 and are present in the composite pigment product in an amount of 0.1 to 30%, by dry weight. The high refractive index materials can include, without limitation, TiO_2, ZnO, BaO, ZrO, $BaSO_4$, Al_2O_3, MgO, and mixtures thereof. Also, in one preferred embodiment, the inventive composite product is produced essentially free of any organic constituents. For purposes of this invention, the terminology "organic" encompasses carbon containing compounds other than alkali or alkaline earth carbonates. Also, while the discussion herein occasionally refers to attaching a plurality of high refractive index particles to a single seed particle to simplify the illustration, it is understood from a practical standpoint that a plurality of seed particles will be concurrently processed in the same way in actually practicing this invention.

The remarkably enhanced brightness and opacity properties displayed by the inventive composite pigment products create improved light scattering capabilities, which, in turn, translate into significantly increased cost performance of paper products incorporating the inventive pigment material. Namely, the inventive composite material is especially well-suited as a filler pigment for lightweight grades of paper. The inventive composite pigment also can be used as a coating pigment and/or filler for other applications, such as for pigmenting rubbers, plastics, paints, lacquers, printing inks, bodycare agents and cosmetics, and so forth.

In another embodiment, there is a method for making the composite product in which a slurry is provided containing a seed particle that has an anionically-charged exterior surface, to which is sequentially added a pH reducing agent and a plurality of high refractive index particles such that an ample pH reduction is effected in the reaction medium whereby the high refractive index pigment particles attach under aqueous conditions to the exterior surface of the seed particle. While not desiring to be bound to any particular theory at this time, it nonetheless is thought that the pH reduction brought about in the reaction medium converts the surface potential of the high refractive index particles from anionic to cationic while the seed particle retains its anionic charge such that a cationic-anionic bonding interaction occurs between the high refractive index particles and the seed particle.

In a preferred embodiment, the pH reducing agent is an inorganic reagent, such as alum, which is added to the slurry of seed particles in an amount effective to reduce the pH of said resulting slurry to a pH value of 7 or less, preferably a pH ranging from 3 to 6, and more preferably a pH ranging from 4.0 to 5.5.

Additionally, because the inventive methodology provides for mixing of the seed particles with the surface-potential modified, high refractive index pigment particles under aqueous conditions, as opposed to dry blending, the high refractive index pigment particles are well-dispersed and have improved opportunities to disperse through the aqueous media among the seed particles to provide a high quality uniform pigment coating thereon without experiencing clumping, flocculation or agglomeration problems.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 shows scattering coefficient properties of several inventive composite product formulations versus a comparison particle.

FIG. 2 shows hand sheet opacity % properties of several inventive composite product formulations versus a comparison particle.

FIG. 3 shows hand sheet brightness properties of several inventive composite product formulations versus a comparison particle.

FIG. 4 shows hand sheet strike through properties of several inventive composite product formulations versus a comparison particle.

FIG. 5 shows a process flow diagram for preparation of a composite pigment product according to an embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

The seed particle that is to be coated with the high refractive index pigment particles according to this invention are solid particles, including conventional paper pigments and fillers. Preferably, the seed particles are formed of inorganic mineral material or inorganic amorphous material that intrinsically having an anionic surface potential. These inorganic particle materials can be, for example, kaolins, calcined kaolins, kaolinites, sodium aluminosilicates, acid leached clays (e.g., bauxite), talcs, micas, serpentinite, montmorillonites, hydrated alumina, precipitated calcium carbonate (PCC), magnesium carbonate, ground limestone, ultrafine ground limestone (UFGL), diatomaceous earth, amorphous silicas, aluminosilicates and mixtures thereof. Other equivalent materials and mixtures of these materials may also be used in the invention. For paper pigment, coating pigment and filler applications, the seed particles used in this invention generally should have an average particle size ranging from approximately 1 to 10 microns.

In a preferred embodiment of this invention, the seed particles can be unmodified aluminosilicate particles, such as those described in any one of U.S. patents 3,915,734, 3,798,046, and Reissued Patent No. 30,568, which are incorporated herein by reference for all purposes. A commercially available example of this type of seed particle is an amorphous aluminosilicate product manufactured by J.M. Huber Corporation, Havre de Grace, MD, U.S.A and sold under the trademark HYDREX®.

Other useful types of seed particles include, for example, seed particles that are pre-modified particles themselves, such as those having prior surface treatments for performance enhancement other than that additionally done in the present invention. In this respect, another suitable class of seed particles for use as the seed pigment particles of this invention are the composite pigment particles described in U.S. Pat. Nos. 5,262,239, 5,219,660, 5,312,485, 5,352,287, which are incorporated herein by reference for all purposes. Among other things, in these four identified patents, a substantially inert nucleus particle is coated with a substantially continuous uniform coating formed of discrete particles of less than one micron in size preferably selected from the group consisting of synthetic alkali metal silicates, synthetic alkali metal aluminosilicates, synthetic alkaline earth metal aluminosilicates, synthetic alkaline earth metal silicates, alkaline earth aluminocarbonates, precipitated silicas, and mixtures thereof. The inert nucleus particle used includes kaolins, talcs, micas, serpertine, montmorillonites, hydrated alumina, precipitated calcium carbonate (PCC), ultrafine ground limestone (UFGL), diatomaceous earths, and so forth. A commercially available coated pigment product of the type described in the four identified patents is sold under the Hysnap® trademark by J.M. Huber Corporation, Havre de Grace, MD, U.S.A., which can be used as the seed particle of the present invention.

The aforementioned type(s) of seed particles can be used alone, or in combination with a second type of seed particle. An example of such a second type of seed particle is clay. The clay can be used together with a composite pigment particle type as described in the above-identified particles described in U.S. Pat. Nos. 5,262,239, 5,219,660, 5,312,485, and 5,352,287, with the clay preferably comprising at least 20% by weight of the total seed pigment solids. A commercially available source of this combination of pigments is distinguished by the trademark Hysnap®, and is commercially available from by J.M. Huber Corporation, Havre de Grace, MD, U.S.A.

The high refractive index particles used in this invention can be any white inorganic pigment. Preferably, the high refractive index particles have a refractive index above at least about 1.6. The high refractive index materials may be selected, for example, from among high refractive index metal oxides such as TiO_2, ZnO, BaO, ZrO, $BaSO_4$, Al_2O_3, MgO, as used either alone or in combinations thereof.

Two basic classes of titanium dioxide which can be used in the practice of this invention are anatase and rutile types thereof. Anatase has a refractive index of 2.52 and rutile 2.76. While rutile has a slightly higher refractive index, anatase is less expensive and less abrasive than rutile. Suitable commercially sources of titanium dioxide are available from Dupont, Millennium, Kerr-McGee, Tioxide, Kronos, or Kemira. Titanium dioxide particles used in this invention can have regular or irregular particle shapes with an average particle size being approximately 0.1 to 0.5 microns, and more typically 0.2 to 0.3 microns. A titanium dioxide size in the range of 0.2 to 0.5 μm is preferred.

The composite pigment products of this invention should contain between 0.1 to 30%, and preferably between 1 to 15%, and more preferably between 5 to 15%, by weight, of the high refractive index pigment particle material, such as titanium dioxide, based on the total weight of the finished composite pigment product (on a dry basis). If the amount of high refractive index pigment is too small, no significant improvements in the optical properties of the finished composite pigment will be realized, while, on the other hand, if too much high refractive index pigment is used, less than optimum light scattering will arise and undue costs are incurred. With the above considerations in mind, it is preferred that the high refractive index pigment particles coat at least 5% of the exterior surface of a seed particle.

In the processing scheme used to make the composite products of this invention, the starting material pigments, i.e., the seed particles, are dispersed in an aqueous medium, if not already supplied in that form. The pH reducing agent is first added to a slurry of the seed particles with agitation or stirring so that the reaction medium has a uniformly reduced pH provided throughout before addition of the high refractive index particles thereto. In any event, a surface potential modifying reaction is performed via pH reduction in the reaction medium to create opposing surface potentials as between the seed particles and the high refractive index particles. To accomplish this surface modifying reaction, the pH of the reaction medium must be sufficently reduced such that an anionic surface potential typically present on the high refractive index particles, such as titanium dioxide, at basic pH values is converted to a cationic charge.

In one mode of this invention, where the production line for the seed particles per se is also under the control of the practitioner, then an aqueous slurry of the seed particles conveniently can be treated with the pH reducing agent during the seed particle production per se (prior to any milling) by treating the cake slurry of the raw seed particles during recovery with the pH reducing agent (e.g., alum) in amounts effective to cause the prescribed pH reduction in the slurry which, in turn, will cause a surface potential modification to high refractive index particles when subsequently added thereto. Otherwise, if the seed particles are obtained from a supplier, they can be used in the provided slurry form or slurried, as needed, if obtained in dry form, and then sequentially subjected to steps of pH reduction and addition of the high refractive index particles.

The pH reducing agent used to cause the surface-potential modification of the high refractive index particles should be water-soluble or water-dispersible. Also, the pH reducing agent can be inorganic or organic in composition as long as it provides the desired function. In any event, the treatment of the high refractive index particles with the pH-reduced reaction medium in the presence of the seed particles causes the high refractive index material to associate with the surfaces of the seed particles in a manner which permits the full benefit of the enhanced refractive index of the composite to be achieved.

From a practical standpoint, alum is a preferred choice of pH reducing agent out of cost considerations. However, besides alum, other water-soluble or water dispersible inorganic pH reducing reagents useful in practicing this invention include poly aluminum silica sulfate, poly aluminum chloride, titanyl sulfate, zirconyl sulfate and mixtures thereof.

The addition of the inorganic pH reducing agent effectively reduces the pH of the slurry of seed particles to 7 or less, preferably to a pH of 3 to 6, and more preferably 4 to 5.5, such as in the case of alum.

Preferably, the alum is dosed into the reaction medium at a steady rate over a relatively short period of time. As a caveat, even though increasing the addition amount of alum effective to drive the pH of the reaction medium below about 4 may further increase the level of modification in surface potential of the high refractive index particles that is achieved, it nonetheless may not be desirable in cases as it can lead to undesirable amounts of sodium sulfate by-product in the reaction medium.

Organic surface modifying reagents can also be used in the practice of this invention, such as water-soluble or water dispersible polymers substituted with quaternary ammonium groups. For example, polyacrylamides substituted with quaternary ammonium groups could be used in this regard.

In one embodiment of this invention, where the pH reducing agent has already been added during the seed particle production per se by treatment of the cake slurry of the raw seed particles during recovery with the pH reducing agent (e.g., alum) in amounts effective to lower the pH to 7 or less, then the high refractive index metal oxide pigment is added to the slurry of the seed particles with agitation in a reactor or in-line mixer. For instance, the pH-adjusted slurry of seed pigments first optionally can be pumped to a Cowles type mixer for introducing the high refractive index metal oxide to the pH-reduced slurry of seed particles. Preferably, whether pre-mixed in the Cowles type mixer or not, the pH-modified slurry is pumped through an in-line mixing system with high shear. A useful high shear in-line mixer can be obtained from Silverson Machines, Inc. (e.g., Models 500LS and 600LS, which are single sealed models with a Nema C-Face Motor).

An optional step that can be included during the mixing of the high refractive index pigments and the seed particles in the pH-reduced medium is the addition of a small amount of an alkali solution, e.g., sodium silicate, sodium carbonate, sodium hydroxide or similar materials to the dispersion for purposes of even further enhancing the overall scattering power achieved. Addition amounts of the alkali solution, preferrably sodium silicate solution, of 0.1-2% by weight, can suffice in this regard.

The above-discussed pH-reduction and high refractive index pigment/seed particle attachment steps are carried out at about 20 - 50°C, inclusive of ambient temperature and pressure conditions.

The resulting raw composite pigment product is then ground by wet dispersion milling, e.g., media milling such as pebble or bead milling, to produce finely dispersed particles. This dispersion can be dried, e.g., spray dried, and dry milled if desired by conventional dry milling techniques known to one skilled in the art, such as hammer milling, pendulum milling, or other impact type milling, as used in one or multiple passes for comminuting and fine grinding. Alternatively, extreme milling can be performed by fluid energy, air mill, jet mill or other particle to particle impact type processes.

The desired product composite average particle size generally is less than 7 microns, and preferably between 3-7 microns, especially where the composite product is destined for active paper pigment applications.

Another embodiment for practicing the process of the present invention is set forth in the process flow diagram of FIG. 5. This flow diagram illustrates the alternate embodiment where seed pigments supplied in slurry form have not yet been subjected to the pH reduction procedure. In this embodiment, a slurry of seed pigments from tank 1 and alum from tank 2 are combined and conducted through line 9 through screen 5 into mixer 6, e.g., an in-line mixer of the same type as described hereinabove. Titanium dioxide particles, supplied from tank 3, are separately fed via line 10 using pump 4 to the outlet side of mixer 6 where the titanium dioxide particles are combined with the mixture of alum and seed pigments at the inlet side of pump 7 and before the resulting mixture is introduced to pump 7. Pump 7 can be any conventional pump used for slurries. Then, the resulting raw product slurry is conducted from pump 7 to mill 8 for grinding to a desired product size.

The inventive composite pigment product is useful either in dry form or in slurry form depending on the specific application. The slurry form of the product is attractive for many active paper pigment applications of the inventive composite product pigment. In this application, an "active paper pigment" means any material which will enhance the optical characteristics of paper when incorporated therein, where optical characteristics can include light scattering, opacity, sheet brightness or other conventional standard methods of measurement of optical performance of paper. They are additionally useful to enhance the print quality of papers as determined by conventional standard methods of measurement such as print-through resistance. Papers which include the composite product of this invention used as the active paper pigments demonstrate 10% and even higher increases in light scattering coefficients, paper opacity, paper brightness and print-through resistance as compared to the untreated seed particles.

The following non-limiting examples will further illustrate the present invention. All parts, ratios, concentrations, and percentages are based upon weight unless otherwise specified.

EXAMPLE 1

In this example, HYDREX® amorphous aluminosilicate was used as the seed pigment particle. Unmilled seed pigment cake slurry (~25% solids, ave. size of 18 microns) was conducted to a vessel into which clarified alum (48% $Al_2(SO_4)_3$) was added with agitation at a rate of 10 mL/min until a pH of 4.0 in the slurry was achieved. Then, 5%, by weight (dry basis) of titanium dioxide (0.4 μm), obtained as slurry, was injected to the inlet of a Silverson in-line mixer to provide the TiO_2 content (dry product basis). The slurry was then pebble milled for 2.5 hours to an average particle size (APS) of between about 4-6 μm before being analyzed for paper optical performance.

EXAMPLE 2

In this example, the procedures of EXAMPLE 1 were followed, except clarified alum was added until a pH of 5.0. Then, 10%, by weight (dry basis) of titanium dioxide (0.4 μm), obtained as slurry, was injected to the inlet of a Silverson in-line mixer to provide the TiO_2 content (dry product basis). The slurry was then pebble milled for 2.5 hours to an average particle size (APS) of between about 4-6 μm before being analyzed for paper optical performance.

EXAMPLE 3

In this example, the procedures of EXAMPLE 1 were followed, except clarified alum was added until a pH of 4.0. Then, 5%, by weight (dry basis) of titanium dioxide (0.4 μm), obtained as slurry, was injected to the inlet of a Silverson in-line mixer to provide the TiO_2 content (dry product basis). Then 0.5%, by weight sodium silicate solution (~38% solids) was added and mixed with the slurry. The slurry was then pebble milled for 2.5 hours to an average particle size (APS) of between about 4-6 μm before being analyzed for paper optical performance.

Paper Optical Performance Analysis Protocol:

The paper optical performance of the composite pigments representing this invention as made according to the Examples described herein, were evaluated and compared with the same properties as measured for commercially available HYDREX®P pigment, as Comparison

Examples, at an equivalent average particle size and paper filler amount, by preparing handsheets using an M-K 801 sheet former. In all cases, samples of the pigments were added as slurries to a standard mechanical pulp to yield the single filler wood-containing paper furnish with a pigment filler amount of 1-10%. Handsheets were evaluated using standard TAPPI methods for determining paper opacity (TAPPI Method T425 om-91) and brightness (TAPPI Method T452 om-92). Performance in paper can typically be related to a pigment's ability to scatter light. Therefore, the Kubelka Munk Scattering Coefficient, S, values were also calculated using the appropriate equations. In this regard, the scattering power of the base paper and a "filled" paper permit calculation of the respective filler's scattering power. Optical properties were measured using a Technidyne, Technibright TB-1C. Print-through was evaluated using SCAN method P 36:77. Sheets were printed with black offset news ink to achieve an optical density of 0.9. and allowed to equilibrate for 12 hours before measuring reflectance values.

The Scattering Coefficients of Examples 1-6 herein were measured using a Britt Jar screening method at an average 2% filler loading level. The filler was dispersed in 1 liter of deionized water and mixed in a Britt Jar for 30 seconds. After 30-45 additional seconds, the valve was opened, vacuum applied and the filler collected on #5 Whatman filter paper. This provided an even dispersion of filler on the filter paper surface and provided a rapid means to test numerous samples. The filter paper containing experimental fillers was dried at 105°C for 15 minutes. Scattering Coefficients were thereby determined using the methods above.

In Table 1 below, the scattering coefficient results for the composite pigment products of Examples 1-3 are summarized along with the result for a Comparison

Example 1 using untreated HYDREX®P pigment as the paper filler.

Table 1

Pigment	pH, @end of alum addition	Scatt. Coeff., S (cm^2/g)	APS, microns	TiO_2,%	Silicate wt.%
Example 1	4.0	302	5.3	5	0
Example 2	5.0	266	5.3	10	0
Example 3	4.0	356	4.8	5	0.5
Comp.Ex. 1*	N.A.**	216	5.7	0	0

*: Hydrex®P pigment

**: N.A.= not applicable

As clearly demonstrated in TABLE 1 above, the composite pigments of EXAMPLES 1, 2 and 3 each showed superior light scattering power as indicated by higher S values, than the comparison example based on a paper filled with untreated Hydrex®P pigment. Also, increased performance was observed with the lower pH @ end of alum addition examples where silicate was added.

EXAMPLE 4

In this example a composite pigment particle type as described in U.S. Pat. No. 5,262,239, in Example 2 thereof, was produced in combination with 40% Fiberex® clay (a product manufactured by J.M. Huber Corporation, Macon, GA, U.S.A.), and this composite pigment was used as the seed pigment. Unmilled seed pigment cake slurry (~32% solids) containing this seed pigment was conducted to a vessel into which clarified alum (48% $Al_2(SO_4)_3$) was added with agitation at a rate of 10 mL/min until a pH of 5.5 in the slurry was achieved. Then, 10%, by weight (dry basis) of titanium dioxide (0.4 μm), obtained as slurry, was injected to the inlet of a Silverson in-line mixer to provide the TiO_2 content (dry product basis). The slurry was then pebble milled for 2.5 hours to an average particle size (APS) of between about 4-6 μm before being analyzed for paper optical performance using the analysis protocol described above. Reference is made thereto. A Comparison Example 2 was prepared and tested utilizing Hydrex®P pigment.

In Table 2 below, the scattering coefficient results for the composite pigment product of Example 4 is summarized along with the result for the Comparison Example 2.

Table 2

Pigment	pH, @end of alum addition	Scatter. Coeff., S (cm^2/g)	APS, microns	TiO_2,%	Silicate wt.%
Example 4	5.5	265	4.6	10	0
Comparison Example 2	N.A.	216	5.7	0	0

It is clearly demonstrated in TABLE 2 above that the composite pigments of EXAMPLE 4 show superior light scattering power as indicated by higher S values, than the comparison example that used untreated Hydrex®P pigment.

EXAMPLE 5

In this example an amorphous aluminosilicate product was used as the seed pigment. Unmilled seed pigment cake slurry (~25% solids, ave. size of 18 microns) was conducted to a vessel into which poly aluminum silica sulfate solution (referred to hereafter as PASS) was added with agitation at a rate of 10 mL/min until a pH of 6.0 in the slurry was achieved. Then, 5%, by weight (dry basis) of zinc oxide (0.2 μm), obtained in dry form and mixed to provide an aqueous suspension, was added while mixing using a Lightning mixer with a paint dispersing blade, to provide the ZnO content (dry product basis). The slurry was then pebble milled for 2.5 hours to an average particle size (APS) of between about 3-6 μm before being analyzed for paper optical performance using the analysis protocol described above. Reference is made thereto. A Comparison Example 3 was prepared and tested utilizing Hydrex®P pigment. In Table 3 below, the scattering coefficient results for the composite pigment product of Example 5 is summarized along with the result for the Comparison Example 3.

Table 3

Pigment	pH, @end of PASS addition	Scatt. Coeff., S (cm^2/g)	APS, microns	ZnO,%	Silicate wt.%
Example 5	6.0	354	4.2	5	0
Comparison Example 3	N.A.	216	5.7	0	0

It is clearly demonstrated in TABLE 3 above that the composite pigments of EXAMPLE 5 show superior light scattering power as indicated by higher S values, than the reference sample containing the Hydrex®P pigment.

EXAMPLE 6

In this example, the procedures of EXAMPLE 3 were followed while using poly aluminum silica sulfate (PASS) to reduce the seed pigment slurry pH to 5.0 while using TiO_2 to produce composite pigments representing this invention. These samples were evaluated for paper optical performance using the analysis protocol described above.

Reference is made thereto. A Comparison Example 4 was prepared and tested utilizing the Hydrex®P pigment. In Table 4 below, the scattering coefficient results for the composite pigment product of Example 6 is summarized along with the result for the Comparison Example 4.

Table 4

Run	pH, @end of PASS addition	Scatt. Coeff., S cm^2/g)	APS, microns	TiO_2,%	Silicate wt.%
Example 6	5.0	274	4.8	5	0
Comparison Example 4	N.A.	216	5.7	0	0

It is clearly demonstrated in TABLE 4 above that the composite pigments of EXAMPLE 6 show superior light scattering power as indicated by higher S values, than the reference sample containing the Hydrex®P pigment.

EXAMPLES 7-10

A series of samples of composite pigments of this invention were prepared by the procedures of EXAMPLE 3 while using alum to reduce the seed pigment pH to 5.0, except with certain variations in the levels of TiO_2 and in certain examples adding various amounts (by weight) of sodium silicate solution during titanium dioxide addition, as indicated in Table 5, to produce composite pigments representing this invention. The produced composite pigments were then analyzed for paper optical performance using the analysis protocol described above. Reference is made thereto. A Comparison Example 5 was prepared and tested based on Hydrex®P as the pigment. The superior optical properties of the composite pigment products were experimentally tested by producing handsheets. Handsheets were prepared using TAPPI standard methods and procedures well know to those trained in the art. A Comparison Example 5 was also prepared and tested based on Hydrex®P as the pigment.

Table 5

Run	pH, @end of alum addition	APS, microns	TiO_2,%	Silicate wt.%
Example 7	5.0	5.6	5	0
Example 8	5.0	5.6	5	1
Example 9	5.0	5.1	10	0
Example 10	5.0	5.3	10	2

FIGS. 1-4 graphically summarize and show the superior optical performance properties displayed by the inventive composite products as represented by Examples 7-10 versus the Comparative Example 5 containing the HYDREX®P pigment as is, at various filler levels. The increase in performance realized by use of the processing protocol of this invention is the result of improved light scattering capability imparted to the composite pigment of this invention. The data also shows its superiority to a leading pigment commonly used as a filler in paper.

EXAMPLE 11

The protocol described in EXAMPLE 3 was repeated except use was made of unmilled Hysnap® cake slurry in full production scale as the seed pigment. The unmilled seed pigment cake slurry (~35% solids, ave. size of 18 microns) was recovered and into which clarified alum (48% $Al_2(SO_4)_3$) was added, with agitation at a rate, of 10 L/min until a pH of 4.5 in the slurry was achieved. Then, 7%, by weight (dry basis) of titanium dioxide (0.4 μm), obtained as slurry, was injected to the inlet of a positive displacement type pump to provide the TiO_2 content (dry product basis). The slurry was passed through an in-line mixer, then media milled to an average particle size (APS) of about 6 μm. The composite product pigment displayed excellent optical performance.

Even though the inventive composite pigment has been illustrated hereinabove as a paper pigment, it will be understood that the inventive composite pigment also can be used as a coating pigment and/or filler for other applications, such as for rubbers, plastics, paints, lacquers, printing inks, bodycare agents and cosmetics, and so forth.

While the invention has been described in terms of its preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.

CLAIMS

1. A composite product comprising a seed particle including an exterior surface having an anionic surface potential to which exterior surface is attached a plurality of smaller sized high refractive index pigment particles.

2. The composite product of claim 1, where said high refractive index pigment particles are discrete particles having a refractive index of at least 1.6 or higher.

3. The composite product of claim 1, wherein said high refractive index pigment particles are selected from the group consisting of TiO_2, ZnO, BaO, ZrO, $BaSO_4$, Al_2O_3 and MgO.

4. The composite product of claim 1, wherein said high refractive index pigment particles comprise titanium dioxide.

5. The composite product of claim 1, wherein said high refractive index pigment particles coat at least 5% of said exterior surface of said seed particle.

6. The composite product of claim 1, wherein said high refractive index pigment particles have an average size of 0.2 to 0.5 μm.

7. The composite product of claim 1, wherein said high refractive index pigment particles comprise between 1 to 15%, by weight, based on the total weight of said composite product.

8. The composite product of claim 1, wherein said seed particle is selected from the group consisting of kaolins, calcined kaolins, kaolinites, sodium aluminosilicates, acid leached clays, talcs, micas, serpentinite, montmorillonites, hydrated alumina, precipitated calcium carbonate, magnesium carbonate, ground limestone, ultrafine ground limestone, diatomaceous earth, amorphous silicas, and amorphous aluminosilicates, and mixtures and composites thereof.

9. The composite product of claim 1, wherein said seed particle is a composite seed pigment having a nucleus selected from the group consisting of kaolins, calcined kaolins, leached clays, talcs, micas, serpentinite, montmorillonites, hydrated alumina, precipitated calcium carbonate, magnesium carbonate, ground limestone, diatomaceous earth, and mixtures thereof, and wherein said nucleus of said seed particle is coated with a substantially continuous uniform coating to form said exterior surface, wherein said coating comprises discrete particles of less than one micron in size selected from the group consisting of alkali metal silicates, alkali metal alumino-silicates, alkaline earth metal alumino-silicates, alkaline earth metal silicates, alkaline earth aluminocarbonates, precipitated silicas and mixtures thereof.

10. The composite product of claim 1, wherein said high refractive index particles have a cationic surface potential.

11. A paper containing a filler amount of a composite product of claim 1.

12. A method for making a composite product, comprising the steps of:

(a) providing a slurry containing a seed particle including an exterior surface having an anionic surface potential;

(b) adding a pH-reducing agent to said slurry; and

(c) adding high refractive index pigment particles which attach to said exterior surface under aqueous conditions.

13. The method of claim 12, wherein said pH-reducing agent is mixed with said slurry of said seed particle in step (b) with agitation prior to the addition of said high refractive index particles in step (c).

14. The method of claim 12, wherein said step (b) of adding said pH-reducing agent effects reduction in pH of the resulting slurry effective that a surface-

potential change from anionic to cationic is effected on the high refractive index particles as added in step (c).

15. The method of claim 12, wherein said pH-reducing agent is added in an amount effective to reduce the pH of said resulting slurry to a pH value of 7 or less.

16. The method of claim 12, wherein said pH-reducing agent is added in an amount effective to reduce the pH of said resulting slurry to a pH value ranging from 3 to 6.

17. The method of claim 12, wherein said pH-reducing agent is added in an amount effective to reduce the pH of said resulting slurry to a pH value ranging from 4 to 5.5.

18. The method of claim 12, wherein said pH-reducing agent is an inorganic material.

19. The method of claim 12, wherein said pH-reducing agent is alum.

20. The method of claim 12, further comprising the additional steps, in this sequence of:

(d) optionally, during step (c), further adding an alkali silicate solution;

(e) recovering the raw composite product resulting from step (c), or step (d) if used;

(f) grinding said raw composite product to a desired particle size; and

(g) optionally, drying said milled raw composite product.

21. The method of claim 12, where said high refractive index pigment particles are discrete particles having a refractive index of at least 1.6 or higher.

22. The method of claim 12, wherein said high refractive index pigment particles are selected from the group consisting of TiO_2, ZnO, BaO, ZrO, $BaSO_4$, Al_2O_3 and MgO_2.

23. The method of claim 12, wherein said high refractive index pigment particles comprise titanium dioxide.

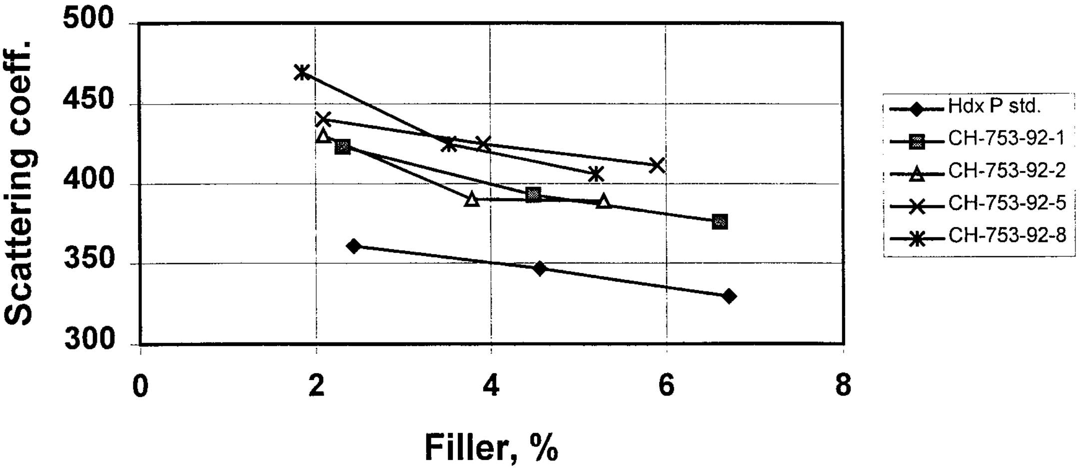
24. The method of claim 12, wherein said high refractive index pigment particles coat at least 5% of said exterior surface of said seed particle.

25. The method of claim 12, wherein said high refractive index pigment particles have an average size of 0.2 to 0.5 μm.

26. The method of claim 12, wherein said high refractive index pigment particles comprise between 5 to 15%, by weight, based on the total weight of said composite product.

27. The method of claim 12, wherein said seed particle is selected from the group consisting of kaolins, calcined kaolins, kaolinites, sodium aluminosilicates, acid leached clays, talcs, micas, serpentinite, montmorillonites, hydrated alumina, precipitated calcium carbonate, magnesium carbonate, ground limestone, ultrafine ground limestone, diatomaceous earth, amorphous silicas, and amorphous aluminosilicates, and mixtures and composites thereof.

28. The composite product of the method of claim 12.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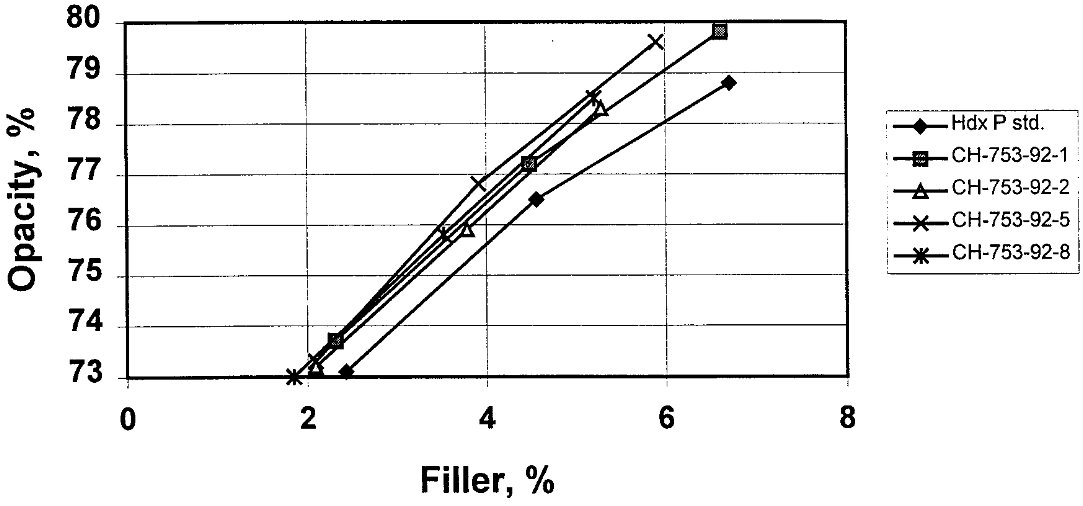
450
400
350
300
0
2
4
6
8
Filler, %
Hdx P std.
CH-753-92-1
CH-753-92-2
CH-753-92-5
CH-753-92-8

FIG. 1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76
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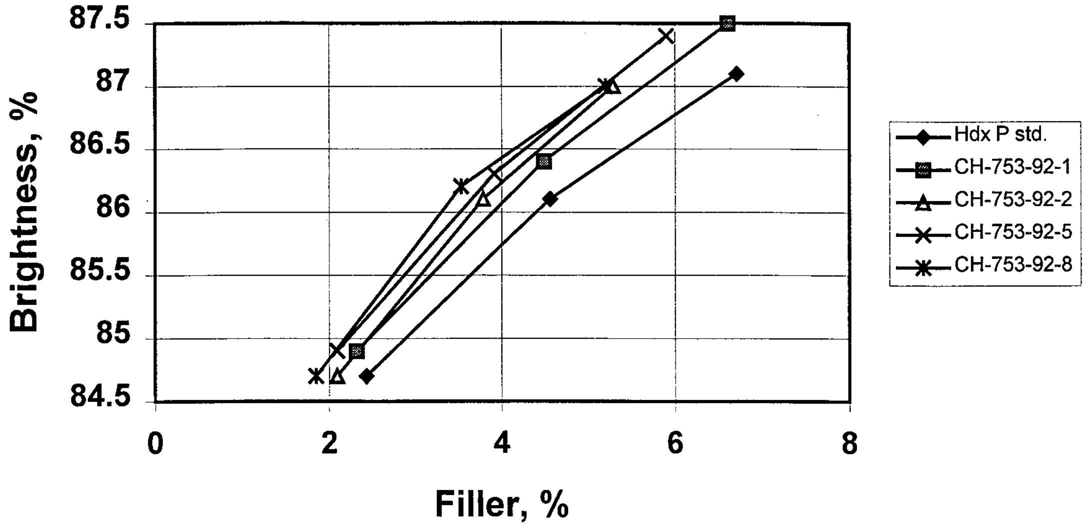
CH-753-92-2
CH-753-92-5
CH-753-92-8

FIG. 2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85
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4
6
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CH-753-92-1
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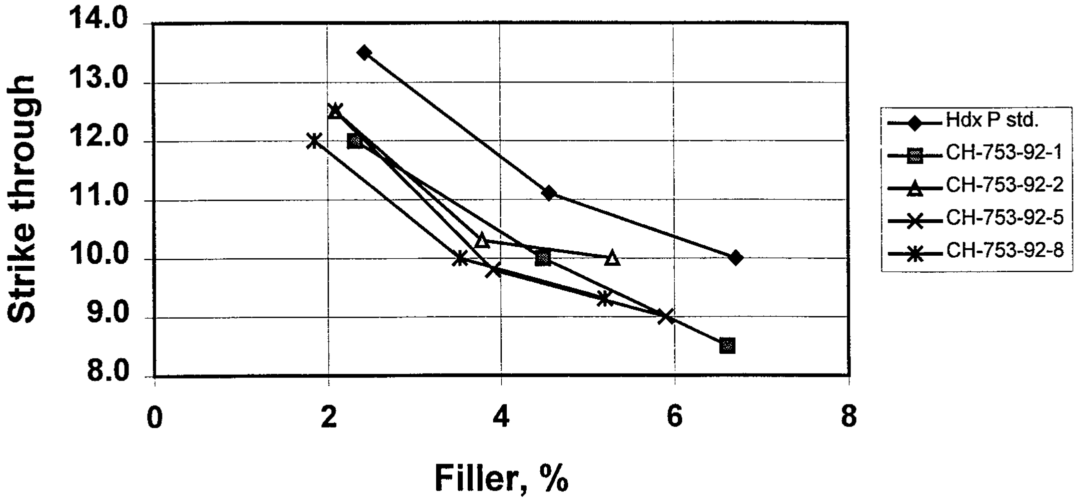
CH-753-92-8

FIG. 3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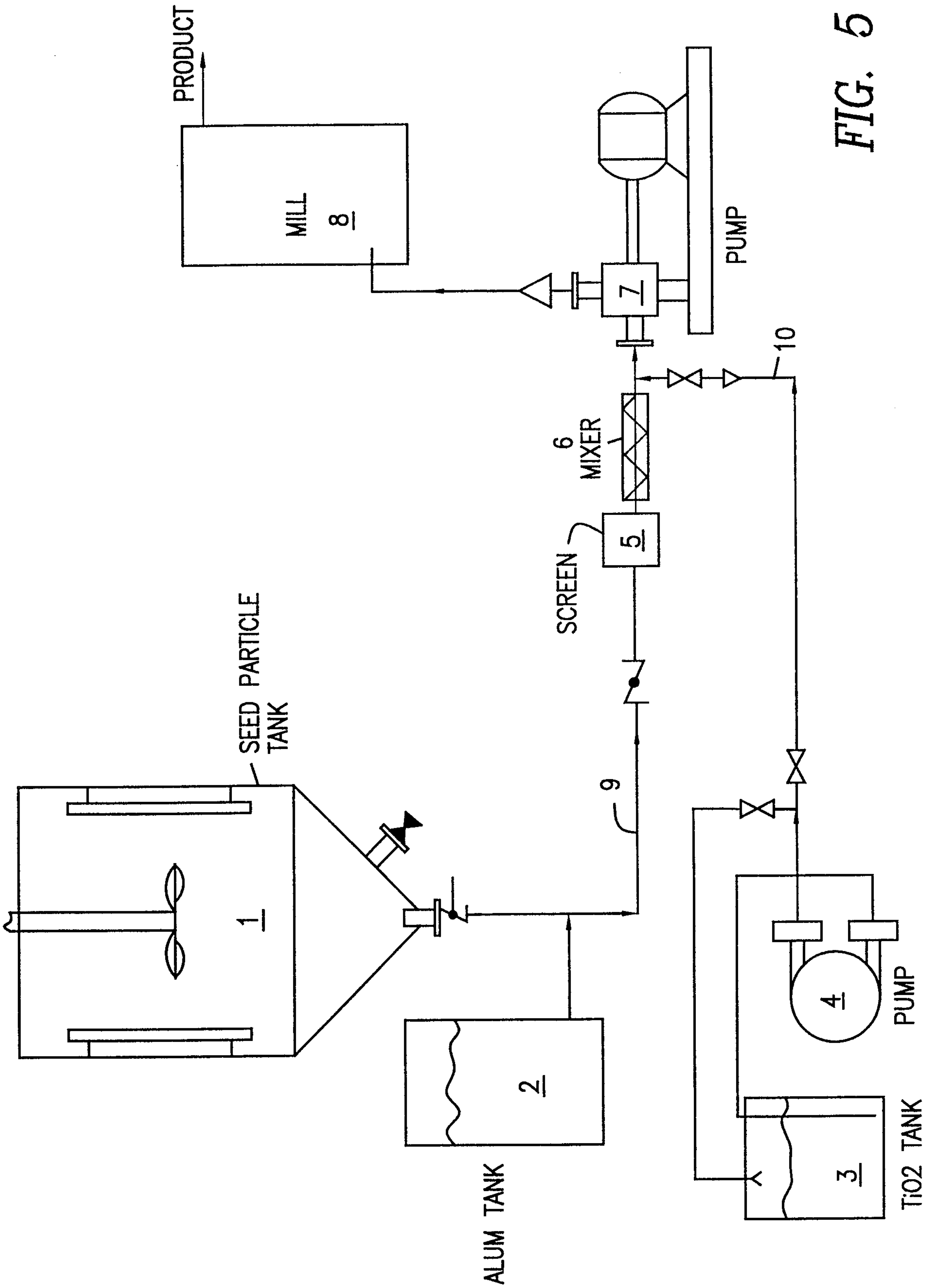
Filler, %
Hdx P std.
CH-753-92-1
CH-753-92-2
CH-753-92-5
CH-753-92-8

FIG. 4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8
PUMP
7
10
6
MIXER
SCREEN
5
9
SEED PARTICLE TANK
1
2
ALUM TANK
4
PUMP
3
TiO2 TANK

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/15230

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09C 1/36, 1/42
US CL :106/425, 426, 436, 442, 444, 446, 450
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)

U.S. : 106/425, 426, 436, 442, 444, 446, 450

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,726,700 A (WILDT) 10 APRIL 1973, col. 2, lines 25-28.	1-28

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

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document published on or after the international filing date	"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
"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)	"&" document member of the same patent family
"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	

Date of the actual completion of the international search 27 SEPTEMBER 1999	Date of mailing of the international search report 22 OCT 1999
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