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(54) Title: METHOD FOR MAKING A PHOTODURABLE AQUEOUS TITANIUM DIOXIDE PIGMENT SLURRY		
(57) Abstract <p>This invention relates to a new method for making a photodurable, aqueous titanium dioxide (TiO₂) pigment slurry. This method involves reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO₂ pigment. A sufficient amount of aluminum chloride is added to provide at least 2 wt.% alumina in the TiO₂ pigment. The TiO₂ pigment is separated from the reaction gases; and mixed with sufficient water to produce a TiO₂ slurry comprising at least 78 wt.% TiO₂ solids. The slurry may be used in coating formulations such as paints.</p>		

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TITLE

METHOD FOR MAKING A PHOTODURABLE AQUEOUS TITANIUM DIOXIDE PIGMENT SLURRY

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BACKGROUND OF THE INVENTIONField of the Invention

10 This invention relates to a new method for making a photodurable, aqueous titanium dioxide (TiO_2) pigment slurry, where a high level of aluminum co-oxidant is used to make the TiO_2 pigment. The resulting photodurable, aqueous TiO_2 pigment slurry is particularly useful for incorporating into coating
15 formulations such as paints.

Description of the Related Art

20 In the "chloride" process for production of titanium dioxide (TiO_2) pigment, titanium tetrachloride (TiCl_4) is oxidized in the vapor phase with an oxygen-containing gas, typically in the presence of aluminum chloride (AlCl_3), to produce a hot gaseous suspension of TiO_2 solid particulate. This crude TiO_2 particulate
25 is then subjected to certain finishing and grinding treatments depending on which type of final TiO_2 pigment product is desired.

 Generally, the finishing and grinding treatment involves the steps of: (a) dispersing the
30 crude TiO_2 particles in an aqueous medium to form a slurry having a low TiO_2 solids concentration; (b) precipitating an inorganic oxide coating. (e.g., alumina, and/or silica) onto the surfaces of the TiO_2 particles; (c) recovering the inorganic oxide surface-
35 treated TiO_2 particles from the aqueous medium by filtering; (d) washing the TiO_2 particles to remove by-product salts and impurities therefrom; (e) drying the washed TiO_2 pigment particles; (f) dry-grinding the dried TiO_2 pigment particles to a desired particle size

using a fluid-energy mill, and optionally, if an aqueous TiO₂ pigment slurry is desired, (g) dispersing the pigment product in water to produce a slurry typically having a TiO₂ solids content of 72 to 78 wt.%.
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The resultant aqueous TiO₂ pigment slurry may be used in many end-use applications such as in the manufacture of coatings (e.g., paints). The TiO₂ pigment efficiently scatters visible light, thereby imparting whiteness, brightness, and opacity when incorporated into coating formulations. Since many coatings containing TiO₂ pigment are exposed to severe weather conditions, it is important that the TiO₂ pigment be photodurable in order to provide these coatings with good resistance to chalking and discoloration. Particularly, many paints contain organic binders which are susceptible to photochemical attack and degrade over time on exposure to sunlight, moisture, temperature change, and other conditions to form oxygenated species that solubilize and wash away from the surface of the paint. Chalking occurs as increased amounts of organic binder are removed from the paint's surface, causing TiO₂ and extender pigments to protrude through the paint's surface and producing a white, chalky appearance. By itself, the surface of the TiO₂ pigment particle is photochemically active and can promote degradation of the organic binders under certain conditions. However, this form of degradation can be controlled by the application of inorganic oxide coatings (e.g., alumina and/or silica) onto the surfaces of the TiO₂ particles. The inorganic oxide surface treatment forms a barrier between the surfaces of the TiO₂ particles and the organic binders.
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Co-pending, co-assigned U.S. Patent Application entitled "A Method For Making a Photodurable Aqueous Titanium Dioxide Pigment Slurry"
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(CH-2323 - Filing Date: May 14, 1997 - Serial No.:
08/856,062) discloses a method for making a
photodurable, aqueous TiO₂ pigment slurry. This method
involves the steps of mixing amorphous alumina, TiO₂
5 pigment particles, water, and at least one dispersant
to form the slurry. The amount of alumina used is at
least about 3 wt.% based on the total weight of TiO₂
solids in the slurry. The resulting slurry can be
diluted to a lower TiO₂ solids content, and the slurry
10 can then be screened and media-milled. The slurry is
described as being particularly useful in coating
formulations such as paints.

Ott and Sullivan, U.S. Patent 5,356,470
discloses a process for making an aqueous TiO₂ pigment
15 slurry, wherein the amount of oversized TiO₂ particles
having a particle size greater than 1 micron are
reduced in the slurry. The process involves making an
aqueous slurry having about 79 to 83% by weight TiO₂
solids. The TiO₂ particles are produced by oxidizing a
20 mixture of TiCl₄ and AlCl₃ with oxygen, with the amount
of AlCl₃ used being sufficient to form 0.1 to 1.5% Al₂O₃
in the TiO₂. The slurry is viscous shear-processed,
diluted, and then media-milled to reduce the size of
the TiO₂ particles. The resulting TiO₂ slurry is
25 described as being particularly suitable for coating
paper products, but the slurry does not have good
photodurability, since there is no wet-treatment of the
TiO₂ particles with an alumina or silica coating.

British Patent 686,570 describes a process to
30 prepare titanium dioxide containing at least 90%
rutile, whereby the decomposition of titanium
tetrachloride is performed in the presence of a
volatile aluminum compound which is converted to
alumina under process conditions. The amount of
35 aluminum compound is such to obtain 0.01-10%,

preferably 0.5-2% by weight of alumina in the titanium dioxide.

Krchma, U. S. Patent 2,559,638 describes a process to prepare TiO_2 pigment, wherein aluminum chloride is added as a co-oxidant during vapor phase oxidation of titanium tetrachloride. The amount of aluminum chloride added is sufficient to provide 0.1-10% by weight alumina, and preferably 0.3-3%, based on the TiO_2 being produced. Water vapor is also present in the oxidation medium at 0.05-10%, preferably 0.1-3%.

Hitzemann et al., U. S. Patent 3,547,671 discloses a process to prepare rutile TiO_2 pigment, wherein oxidation of $TiCl_4$ takes place in the presence of $AlCl_3$ and a phosphorus chloride. Subsequently, the pigment is subjected to wet-treatment with aluminum and silicon salts to precipitate alumina and silica coatings, respectively. The amounts of $AlCl_3$ and phosphorus chloride added achieve preferably 2-4% by weight alumina and 0.5-3% P_2O_5 by weight in the pigment base.

In Dietz, U. S. Patent 3,640,744 and Goodspeed, U.S. Patent 3,650,793, a process to prepare TiO_2 by vapor phase oxidation of a titanium halide is disclosed, wherein aluminum and silicon compounds are added to the oxidation step such that 1-2.5 wt.% alumina and 0.3-0.75 wt.% silica are provided in the final TiO_2 product.

Glaeser, U. S. Patent 4,214,913 discloses a process to prepare rutile TiO_2 by vapor phase oxidation of a mixture of $TiCl_4$ and $AlCl_3$ and after at least 80% of the $TiCl_4$ has been converted to TiO_2 , adding PCl_3 to form P_2O_5 . $AlCl_3$ is present to provide 0.1-1.5% Al_2O_3 in the TiO_2 . Sufficient PCl_3 is added to provide 0.1-0.5% P_2O_5 in the TiO_2 .

As described in the above references, it is known to add volatile aluminum compounds in the

oxidation reaction of titanium tetrachloride (TiCl_4), primarily to increase the rutile content of the TiO_2 pigment being produced. Typically, the amount of aluminum compound added is sufficient to form 1 to 1.5 wt.% alumina based on the TiO_2 pigment product, and this amount helps achieve greater than 99% rutile in the pigment product.

However, for some end-use applications, these TiO_2 pigments may not have sufficient photodurability; thus, the pigment is often wet-treated. In a wet-treatment process, metal oxide coatings, preferably silica and alumina, are applied to the surface of the TiO_2 particles to enhance the photodurability of the pigment. While wet-treatment processes provide high photodurability, they involve a number of steps, including filtration, drying, coating steps, refiltration, etc. which add substantial cost to the overall process.

Further, as also described above, the TiO_2 pigment must then usually be formulated into a slurry in order to make it suitable for coating applications. Conventional processes used to prepare a TiO_2 pigment slurry involve several energy-intensive steps and the processing equipment requires high capital investment.

In view of the forgoing, it would be desirable to have a direct slurry-manufacturing process, where the steps of wet-treatment, filtering, washing, drying, grinding, and reslurrying the TiO_2 particles could be eliminated.

The present invention provides a new method for making a photodurable, aqueous TiO_2 pigment slurry having significantly improved photodurability. In the direct slurry manufacturing method of this invention, the cost-intensive and conventional processing steps of wet-treatment, filtration, drying, and grinding are eliminated. Particularly, in this method, the alumina

content of the TiO₂ pigment is at least 2 wt.% after the oxidation reaction. At this higher level of alumina, an enhancement in photodurability of the TiO₂ pigment is achieved so that this pigment can be directly incorporated into a slurry without first being subjected to a conventional wet-treatment process. The resulting photodurable, aqueous TiO₂ pigment slurry can be used in coating formulations such as paints.

SUMMARY OF THE INVENTION

The present invention provides a method for preparing a photodurable, aqueous TiO₂ slurry comprising the steps of:

- (a) reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO₂ pigment, wherein sufficient aluminum chloride is added to provide at least 2 wt.% alumina in the TiO₂ pigment based on total weight of TiO₂ solids;
- (b) separating the TiO₂ pigment from the reaction gases; and
- (c) mixing the TiO₂ pigment with sufficient water to produce a TiO₂ slurry comprising at least 78 wt.% TiO₂ solids, based on total slurry weight.

Preferably, the alumina content is at least 3 wt.% and more preferably about 3 to about 5 wt.%. Also, the slurry preferably contains about 80 to about 88 wt.% TiO₂ solids. The reaction of titanium tetrachloride, aluminum chloride and oxygen-containing gas may occur in the presence of a phosphorus chloride to provide 0.1 to 0.5 wt.% P₂O₅ in the TiO₂ pigment.

The TiO₂ pigment can optionally undergo injector-treatment, wherein the pigment is treated with a gas selected from the group consisting of steam, air, nitrogen, and mixtures thereof, at a sonic or

supersonic velocity, a pressure of about 25-600 psi, and a temperature of 140-650°C subsequent to step (b) and prior to step (c) as described above. The treated TiO₂ pigment may then be separated from the gasses which were used to treat the pigment.

In preparing the slurry, the TiO₂ pigment is preferably mixed with water in the presence of a dispersant. Preferred dispersants include those selected from the group consisting of citric acid, polyacrylates, triethanolamine, 2-amino-2-methyl-1-propanol, monoisopropylamine, and mixtures thereof.

The slurry produced by the above method can subsequently be diluted. Preferably, the slurry is diluted to a TiO₂ solids content in the range of about 68 to about 78 wt.% based on total slurry weight. Optionally, the slurry can then be screened to remove grit and media-milled to reduce particle size and enhance pigmentary properties.

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BRIEF DESCRIPTION OF THE FIGURE

Figure 1 shows a schematic diagram for a preferred embodiment of making the photodurable, aqueous TiO₂ slurry of this invention.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for preparing an aqueous titanium dioxide pigment slurry, wherein the pigment contains at least 2 wt.% alumina, based on the total pigment weight. This TiO₂ slurry has high photodurability, for example, when incorporated into coating formulations.

The production of TiO₂ by vapor phase oxidation of TiCl₄, i.e., "the chloride process", is well known and disclosed in Schaumann, U. S. Patent 2,488,439, the disclosure of which is hereby incorporated by reference. In the chloride process, TiCl₄ is reacted with an oxygen-containing gas in the

vapor phase in a reactor at a temperature of about 900° to 1600°C to produce a hot gaseous suspension of TiO₂ solid particulate and free chlorine.

Particularly in the method of the present invention, TiCl₄ is evaporated and preheated to temperatures from about 300° to 650°C and introduced into the reaction zone of a reactor. A volatile aluminum compound, such as aluminum halides, including AlCl₃, AlBr₃, and AlI₃, preferably AlCl₃, is added to the reaction zone. Typically, the aluminum compound is thoroughly premixed with the TiCl₄ prior to its introduction into the reaction zone. In alternative embodiments, the aluminum compound can be added partially or completely downstream from the point of where the TiCl₄ and oxygen-containing gas are initially contacted.

The aluminum compound added becomes incorporated as alumina and/or an alumina mixture in the TiO₂, meaning the alumina and/or alumina mixture is dispersed in the TiO₂ particles and/or on the surface of the TiO₂ particles as a surface coating. The amount of aluminum compound added is sufficient to provide at least 2 wt.%, and preferably about 2.5 to about 6 wt.%, and more preferably about 3 to about 5 wt.% Al₂O₃ based on the total TiO₂ solids formed in the oxidation reaction. Levels of aluminum compound added, measured as amount of alumina, greater than 2 wt.% provide enhanced durability for the TiO₂ product and subsequent TiO₂ slurry prepared according to this invention.

Other co-oxidants and rutile promoters may be added at the point of addition of the aluminum compound or further downstream in the process. For example, PCl₃ may be added at one or more points downstream from where the TiCl₄ and oxygen-containing gas are initially contacted as described in Glaeser, U.S. Patent 4,214,913, the disclosure of which is hereby

incorporated by reference. The phosphorous compound becomes incorporated on the surface of the TiO_2 particles as phosphorus oxide (P_2O_5). In the present invention, it can be advantageous for the TiO_2 pigment to contain about 0.1 to about 0.5 wt.% P_2O_5 , since the P_2O_5 improves the deagglomeration of the base TiO_2 pigment.

The oxygen-containing gas is preheated to at least 1200°C and is continuously introduced into the reaction zone through a separate inlet from an inlet for the TiCl_4 feed stream. By "reaction zone", it is meant the length of the reactor in which substantial reaction of the reactants takes place. The reaction of O_2 and TiCl_4 in the vapor phase is extremely fast and provides a hot gaseous suspension comprising TiO_2 particles and free chlorine. This reaction step is followed by a brief period of TiO_2 particle growth.

The oxygen containing gas which is introduced into the reaction zone contains a nucleant. By "nucleant", it is meant any substance which can reduce the particle size of the pigment such as metals, oxides, salts, or other compounds of sodium, potassium, lithium, rubidium, cesium, calcium, barium, strontium, or mixtures thereof. The salts, CsCl and KCl , are preferred for use in this invention.

The hot gaseous suspension of TiO_2 solid particulate is then rapidly cooled in order to prevent undesirable particle size growth. Cooling of the hot gaseous suspension may be performed by methods known in the art. These methods typically involve passing the hot gaseous suspension through a cooling conduit (flue) having relatively cool walls in comparison to the gaseous suspension. Granular scouring particles (scrubs), such as calcined TiO_2 , sand, and mixtures thereof may be added to the flue to reduce the

formation of TiO_2 particulate deposits on the internal walls of the flue.

The TiO_2 pigment can be recovered from the cooled reaction products by conventional separation treatments, including cyclonic or electrostatic separating media, filtration through porous media, or the like. The recovered TiO_2 pigment contains residual chlorides, but this pigment may be used after the particles have been treated to remove the residual chlorides.

In a preferred embodiment to remove these residual chlorides, the TiO_2 pigment undergoes injector-treatment (IT) as described in Schurr, U. S. Patent 4,083,496, the disclosure of which is hereby incorporated by reference. This treatment involves treating the TiO_2 pigment with a gas selected from the group consisting of steam, air, nitrogen, and mixtures thereof, at a sonic or supersonic velocity, a pressure of about 25-600 psi and a temperature of 140-650°C, followed by separating the pigment from the gas. The TiO_2 pigment can be separated from the gas and chloride impurities by using any suitable separating devices such as a cyclone or a bag filter. Injector-treatment reduces the TiO_2 pigment acidity/chlorides which can reduce the amount of dispersant needed for pH control of a product slurry. Prior to injector-treatment, there can be steps to grind or mill the pigment. By partial deagglomeration of the pigment, injector-treated pigment can be processed at an increased solids content during the dispersion step. Injector-treatment provides the advantages of improved durability, low chlorides and improved slurry processability.

The chloride-free base TiO_2 pigment is then used for direct aqueous slurry processing. The TiO_2 pigment is mixed with water in the presence of a dispersant to provide a TiO_2 slurry. Commercially-

available dispersants can be used to prepare the aqueous TiO₂ pigment slurry of this invention. These dispersants include, for example, sodium or potassium pyrophosphate; sodium hexametaphosphate; sodium, 5 potassium, or ammonium polyphosphate; aliphatic carboxylic acid; citric acid; polyhydroxy alcohols; polyacrylates and the like; and alcohol amines such as 1-amino-2-ethanol; 2-amino-1-ethanol, 1-amino-2-propanol, 2-amino-2-methyl-1-propanol, diethanolamine, 10 di-isopropanolamine, 2-methylamino-1-ethanol, monoisopropanolamine, triethanolamine, and the like, and mixtures thereof. The pH of the slurry is preferably adjusted to a level in the range of about 6.0 to about 9.0 by the addition of these dispersants 15 to the slurry.

The mixing of the TiO₂ pigment particles, dispersant, and water is best done at greater than 78% TiO₂ solids where viscous sheer conditions can produce deagglomeration of the TiO₂ particle agglomerates. The 20 mixing process can be carried out continuously or batchwise.

In a batch process, the TiO₂ pigment is mixed with water and stirred under high shear conditions using a high speed mixer. The pH of the slurry may need 25 to be adjusted to about 6.0 to 9.0 by adding at least one dispersant to the slurry. As the TiO₂ solids content is increased, the viscosity of the slurry increases. It is important that the TiO₂ particles be sufficiently dispersed and incorporated into the 30 slurry. Under high shear conditions at a high solids content, the TiO₂ particle agglomerates are broken-up by the high shear stress zones resulting in improved dispersion of the TiO₂ particles into the slurry. With such processing conditions, the incorporation of the 35 TiO₂ particles into the slurry is improved by increasing the mixing speed of the mixer.

In a continuous process, the TiO₂ pigment is continuously and simultaneously added to a tank along with water and a dispersant, such that the tank is always maintained at the required TiO₂ solids content for good high shear processing. Simultaneously, with the addition of new material, a portion of the processed aqueous TiO₂ slurry can be removed by any suitable means, typically from the bottom of the tank by gravity flow or a conveying screw.

The water content of the slurry is dependent on the desired viscosity and TiO₂ solids content of the slurry. However, it is important that the initial TiO₂ solids content be at least 78 wt.% based on total weight of the slurry in order that high shear stress zones may be created during the viscous shear processing of the slurry. The TiO₂ particle agglomerates are broken-up by the high shear stress zones resulting in improved dispersion of the TiO₂ particles into the slurry. Generally, the initial TiO₂ solids content of the slurry is at least 78 wt.% and is preferably in the range of about 80 to about 88 wt.%, more preferably in the range of about 83 to about 86 wt.%.

The slurry may then be diluted to a desired TiO₂ solids content to provide an aqueous slurry which can be more easily handled and transported to other sites such as a paint manufacturing facility. For example, in many applications, it is desirable that the slurry be diluted to a final TiO₂ solids content of less than about 80 wt.%, preferably about 68 to about 78 wt.%, and more preferably about 72 to about 78 wt.%. This resulting aqueous slurry has rheological properties similar to those of conventional slurries made by mixing micronized TiO₂ pigment particles with water.

The slurry may then be subjected to a screening process to remove any grit, and the screened slurry may be media-milled to reduce the size of the TiO₂ particles by techniques known in the art such as those described in Ott et al., U.S. Patent 5,356,470. These screening and media-milling steps do not affect the photodurability of the pigment, but they may improve rheological and end-use properties such as the gloss of paints containing these pigments.

In summary, the method of this invention involves the following steps, some of which are optional. The overall method steps are also illustrated in Figure 1:

- (a) reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO₂ pigment, wherein sufficient aluminum chloride is added to provide at least 2% by weight alumina in the TiO₂ pigment;
- (b) separating the TiO₂ pigment from the reaction gases;
- (c) optionally treating the TiO₂ pigment with a gas selected from the group consisting of steam, air, nitrogen, and mixtures thereof, at a sonic or supersonic velocity, a pressure of about 25-600 psi, and a temperature of 140-650°C;
- (d) separating the treated pigment from the gases;
- (e) mixing the TiO₂ pigment with sufficient water, optionally in the presence of a dispersant, to prepare a TiO₂ slurry comprising at least 78 wt.% solids, based on total slurry weight;
- (f) optionally diluting the slurry; and
- (g) optionally screening and media-milling the slurry to reduce the size of the TiO₂ particles.

Test MethodsChalk/Fade (C/F)

The method used for measuring the chalk/fade degradation of paints containing TiO₂ pigment from the following examples is discussed by W. H. Daiger and W. H. Madson in "Journal of Paint Technology," 1967, vol. 39, no. 510, pp. 399-410.

The basis of this test is that white objects (including TiO₂ particles) scatter all wavelengths of visible light equally. A paint is prepared with the desired pigment and then tinted blue with a copper phthalocyanine pigment. Panels coated with these paints are exposed in Florida for a specified period of time. The reflectance of red light from the panel is measured using a colorimeter. Since the fresh panels are blue (i. e., reflect all colors but red), red reflectance values are initially very low. The red reflectance increases as pigment particles are exposed and scatter all wavelengths of visible light equally.

Since the absolute rate of chalking depends on a number of variables, standards are used and sample results should be considered as relative to the standards.

Viscosity

In the following examples, slurry viscosity data are based on Brookfield viscosity measurements made on slurries at 25°C, and 100 rpm, using a number 4 spindle for values up to 2000 centipoise (cp) and an appropriate spindle for higher viscosities.

Rheology

In the examples, slurry rheology data are obtained by measurements with a Hercules high shear device, operating at a shear rate of 2000 reciprocal seconds. The Hercules rheometer, made by Kaltec

Scientific, Novi, Michigan, has a rotating bob inside a cup filled with the slurry which transmits shear forces and deflects the spring. Results are reported in centipoise (cp) units.

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EXAMPLES

Comparative Example 1

Base pigment was made as follows. A stream of oxygen preheated to 1550°C was introduced into one end of a tubular reactor. About 15 ppm of KCl was added to the oxygen stream to control particle size. Titanium tetrachloride vapor stream containing aluminum trichloride to provide about 1% Al₂O₃ was introduced into the reactor at 450 to 500°C. The AlCl₃ was produced by reacting aluminum with Cl₂ in the presence of the TiCl₄ stream, as it was beneficial to use this exothermic reaction to heat the TiCl₄ stream to 450°C or higher. PCl₃ in a vapor phase was added subsequently to produce about 0.3% P₂O₅ on a pigment basis. Scrub solids were added to the reaction stream before it exited the reactor into cooling flues. The pigment was cooled to less than 160°C, and separated from by-product Cl₂. This base pigment was used to make a slurry.

Surfactant premix was prepared by mixing 50 g of water, 2.0 g of 50% citric acid solution, and 5.4 g of amino-methyl-propanol (AMP). About 138 g of water were added to a vessel with agitation provided by an IKA mixer. Base pigment, as prepared above, (1000 g) was added along with the surfactant premix to the vessel over a period of about 8 minutes. The addition rate was slowed as slurry solids and viscosity increased, resulting in 83.8% TiO₂ solids at about pH 8.6. Agitation was continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 112 g of water were added to dilute the slurry to about 76% TiO₂

solids. The properties for the resultant slurry are shown below in Table 1.

Comparative Example 2

5 For this example, the base TiO₂ pigment of Comparative Example 1 was first subjected to Injector-Treatment (IT) with 450°C steam (as described in US Patent 4,083,946). The IT reduced the base pigment acidity/chlorides, which reduced the amount of alcohol
10 amine needed for pH control. By giving partial deagglomeration of the base pigment, IT processed pigment can be processed at increased percent solids during the dispersion step.

This injector-treated base TiO₂ pigment was
15 used to make a slurry following a similar procedure as described in Comparative Example 1. Surfactant premix was prepared by mixing 50 g of water, 2.0 g of 50% citric acid solution, and 2.1 g of AMP. About 110 g of water were added to a vessel with agitation provided by
20 an IKA mixer. 1000 g of injector-treated base pigment were added along with surfactant premix to the vessel over about 5 minutes. The addition rate was slowed as slurry solids and viscosity increased, resulting in 86.2% TiO₂ solids at about pH 8.8. Agitation was
25 continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 137 g of water were added to dilute the slurry to about 76% TiO₂ solids. The properties for the resultant slurry are shown below in Table 1.

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Example 3

The base pigment produced under identical conditions from Comparative Example 1, except that the amount of aluminum trichloride was increased to give
35 pigment with about 3.0% Al₂O₃. This pigment was used to make the slurry. Pre-mixed surfactant was separately

prepared, consisting of 50 g of water, 2.0 g of 50% citric acid solution, 5.5 g of AMP. About 138 g of water were added to a vessel with agitation provided by an IKA mixer. 1000 g of the base pigment were added
5 along with surfactant premix to the vessel over about 8 minutes. The addition rate was slowed as slurry solids and viscosity increased, resulting in 83.8% TiO₂ solids at about pH 8.6. Agitation was continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 112 g
10 of water were added to dilute the slurry to about 76% TiO₂ solids. The properties for the resultant slurry are shown below in Table 1.

Example 4

15 The base TiO₂ pigment from Example 3 was subjected to the same injector-treatment of Comparative Example 2 and was used to make a slurry. Surfactant premix was prepared by mixing 50 g of water, 2.0 g of 50% citric acid solution, and 2.8 g of AMP. About 110 g
20 of water were added to a vessel with agitation provided by an IKA mixer. 1000 g of injector-treated base pigment were added along with surfactant premix to the vessel over about 5 minutes. The addition rate was slowed as slurry solids and viscosity increased,
25 resulting in 86.1% TiO₂ solids at about pH 8.6. Agitation was continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 137 g of water were added to dilute the slurry to about 76% TiO₂ solids. The properties for the resultant slurry are
30 shown below in Table 1.

Example 5

35 A base TiO₂ pigment was produced by the same process as that of Comparative Example 1, except the amount of aluminum trichloride was increased to give pigment with about 3.0% Al₂O₃, and no P₂O₅ co-ox was

used. This pigment was used to make the slurry. Surfactant pre-mix was prepared by mixing 50 g of water, 2.0 g of 50% citric acid solution, and 5.5 g of AMP. About 138 g of water were added to a vessel with agitation provided by an IKA mixer. 1000 g of the base pigment were added along with surfactant premix to the vessel over about 8 minutes. The addition rate was slowed as slurry solids and viscosity increased, resulting in 83.7% TiO₂ solids at about pH 8.6. Agitation was continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 112 g of water were added to dilute the slurry to about 76% TiO₂ solids. The properties for the resultant slurry are shown below in Table 1.

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Example 6

The base TiO₂ pigment of Example 5 was subjected to the injector-treatment process of Comparative Examples 2 and 4 and used to make a slurry. Surfactant premix was prepared by mixing 50 g of water, 2.0 g of 50% citric acid solution, and 2.6 g of AMP. About 110 g of water were added to a vessel with agitation provided by an IKA mixer. 1000 g of injector-treated base pigment were added along with surfactant premix to the vessel in about 5 minutes. The addition rate was slowed as slurry solids and viscosity increased, resulting in 86.1% TiO₂ solids at about pH 9.0. Agitation was continued for 5 minutes to obtain a uniform deagglomerated slurry. Then, 137 g of water were added to dilute the slurry to about 76% TiO₂ solids. The properties for the resultant slurry are shown below in Table 1.

TEST RESULTS

5	<u>Example</u>	<u>C/F</u>	<u>Brookfield Viscosity</u>	<u>Rheology in cp</u>
	1 (Comparative)	2	900	7
	2 (Comparative)	9	230	3
	3	10	740	7
10	4	14	200	3
	5	12	760	4
	6	16	200	3

15 These results demonstrate the improvement in photodurability when about 3% Al₂O₃ co-ox was used and an even larger improvement when this base TiO₂ pigment was used in conjunction with injector-treatment.

CLAIMS

1. A method for making a photodurable, aqueous titanium dioxide pigment slurry, comprising the steps of:
- 5 (a) reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO_2 pigment, wherein sufficient aluminum chloride is added to provide at least 2 wt.% alumina in the TiO_2 pigment based on
- 10 total weight of TiO_2 solids;
- (b) separating the TiO_2 pigment from the reaction gases; and
- (c) mixing the TiO_2 pigment with sufficient water to produce a TiO_2 slurry comprising at least 78
- 15 wt.% TiO_2 solids, based on total slurry weight.
2. The method of claim 1, wherein about 3 to about 5 wt.% alumina is in the TiO_2 pigment.
- 20 3. The method of claim 1, wherein the slurry comprises about 80 to about 88 wt.% TiO_2 solids.
- 25 4. The method of claim 1, wherein the reaction of titanium tetrachloride, aluminum chloride, and oxygen-containing gas occurs in the presence of a phosphorus chloride to provide 0.1 to 0.5 wt.% P_2O_5 in the TiO_2 pigment.
- 30 5. The method of claim 1, wherein the TiO_2 pigment is treated with a gas selected from the group consisting of steam, air, nitrogen, and mixtures thereof, at a sonic or supersonic velocity, a pressure of about 25-600 psi, and a temperature of 140-650°C subsequent to step (b) and prior to step (c).

6. The method of claim 5, wherein the treated TiO₂ pigment is subsequently separated from the gasses which were used to treat the pigment.

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7. The method of claim 1, wherein the TiO₂ pigment is mixed with sufficient water in the presence of a dispersant selected from the group consisting of citric acid, polyacrylates, triethanolamine, 2-amino-2-methyl-1-propanol, monoisopropylamine, and mixtures thereof.

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8. A method for making a photodurable, aqueous titanium dioxide pigment slurry, comprising the steps of:

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(a) reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO₂ pigment, wherein sufficient aluminum chloride is added to provide at least 2 wt.% alumina in the TiO₂ pigment based on total weight of TiO₂ solids;

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(b) separating the TiO₂ pigment from the reaction gases;

(c) mixing the TiO₂ pigment with sufficient water to produce a TiO₂ slurry comprising at least 78 wt.% TiO₂ solids, based on total slurry weight; and

25

(d) diluting the slurry.

9. A method for making a photodurable, aqueous titanium dioxide pigment slurry, comprising the steps of:

30

(a) reacting titanium tetrachloride, aluminum chloride and an oxygen-containing gas in the presence of a nucleant in the vapor phase to produce TiO₂ pigment, wherein sufficient aluminum chloride is added to provide

at least 2 wt.% alumina in the TiO₂ pigment based on total weight of TiO₂ solids;

(b) separating the TiO₂ pigment from the reaction gases;

5 (c) mixing the TiO₂ pigment with sufficient water to produce a TiO₂ slurry comprising at least 78 wt.% TiO₂ solids, based on the total slurry weight;

(d) diluting the slurry;

(e) screening the slurry to remove grit; and

10 (f) media-milling the slurry to reduce the size of the TiO₂ particles.

10. The method of claim 8 or 9, wherein about 3 to about 5 wt.% alumina is in the TiO₂ pigment.

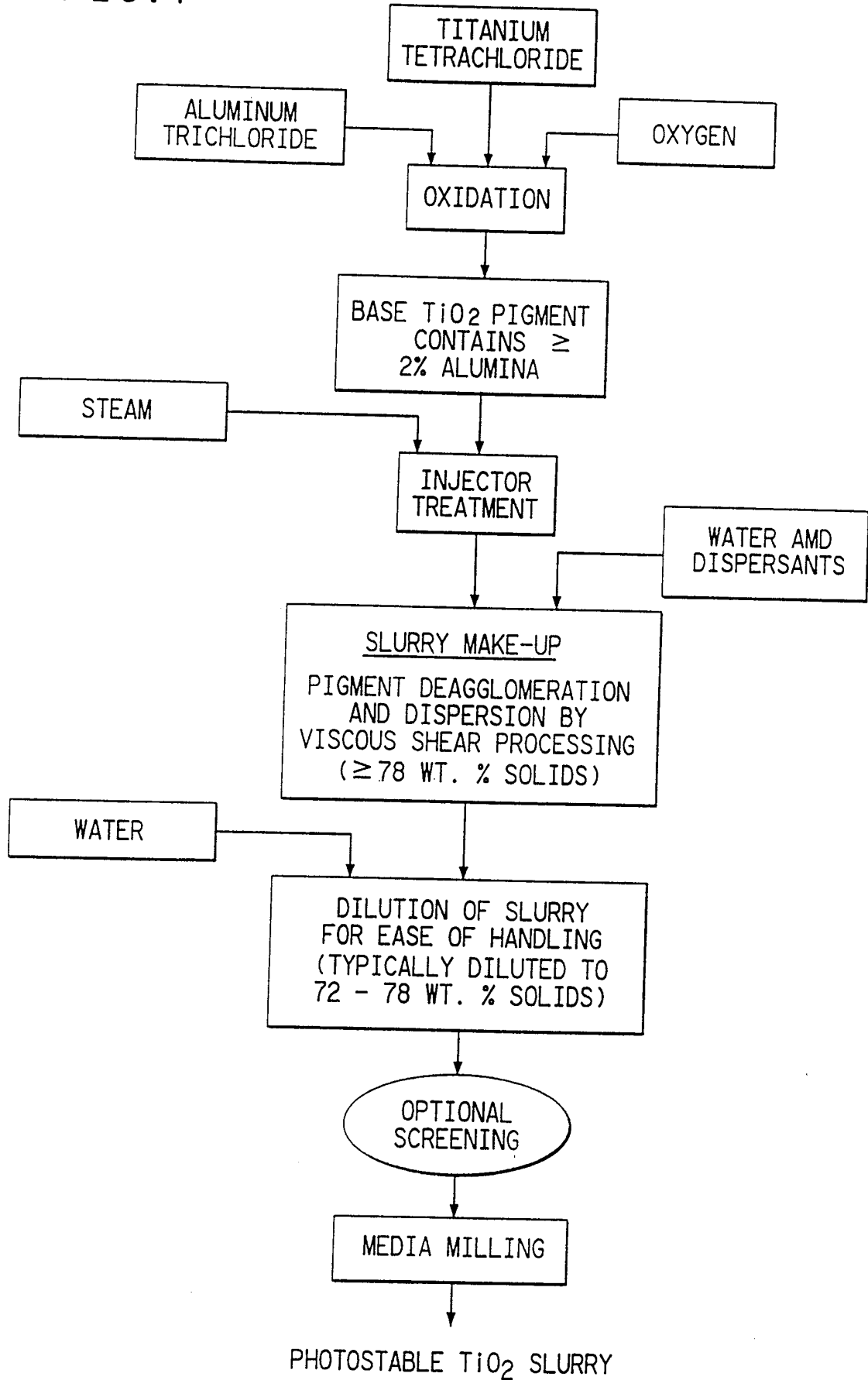
15

11. The method of claim 8 or 9, wherein the slurry produced in step (c) comprises about 80 to about 88 wt.% TiO₂ solids.

20

12. The method of claim 8 or 9, wherein the slurry produced in step (d) is diluted to a TiO₂ solids content in the range of about 68 to about 78 wt.%.

FIG. 1



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/13612

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09D17/00 C09C1/36

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)

IPC 6 C09D 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 practical, 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 4 214 913 A (H. H. GLAESER) 29 July 1980 cited in the application see claims 1,2; example 3	1-4,7,8, 10,11
A	---	9
A	WO 97 05204 A (E. I. DU PONT DE NEMOURS AND COMPANY) 13 February 1997 see page 2, line 22-25 see page 4, paragraph 1; claim 11	1,3,7-9, 11
A	GB 686 570 A (SAUREFABRIK SCHWEIZERHALL) 28 January 1953 cited in the application see claim 1	1

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Interr. Patent Application No

PCT/US 98/13612

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 035 076 A (AMERICAN CYANAMID COMPANY) 9 September 1981 see page 2, last paragraph - line 29; claim 1 -----	1
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