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10 September 1991

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DJG/k

For the attention of Mr. David J. Gould

Dear Sirs,

European Patent No. 0244180

We have pleasure in enclosing the Certificate of Grant of European Patent No. 0244180, granted on Application No. 87303681.8, together with a copy of the published patent specification.

Publication of the grant took place on 7 August 1991 and the patent will be open to opposition for a period of nine months from that date.

The patent will remain in force for a term of 20 years from the application filing date, i.e. from 27 April 1987 subject to the payment of annual renewal fees in each of the designated states in which it has been registered, i.e. Belgium, Germany, France, United Kingdom, the Netherlands and Spain.

The patent may be maintained in all or any of these designated states. The Associates in each of these countries have been instructed to attend to the payment of the first renewal fee after grant and also to forward the certificate of renewal and their debit notes direct to Du Pont. We have entered the European Patent (UK) on our maintenance system.

As you know the European (U.K.) Patent can be extended by registration to several overseas territories including Hong Kong (within 5 years of grant), and Singapore (within 3 years of grant). We can deal with these if you wish.

Yours faithfully,

Miss Jill Routh
BROOKES & MARTIN

Europäisches Patentamt	European Patent Office	Office européen des brevets

Urkunde Certificate Certificat

Es wird hiermit bescheinigt, daß für die in der beigefügten Patentschrift beschriebene Erfindung ein europäisches Patent für die in der Patentschrift bezeichneten Vertragsstaaten erteilt worden ist.

It is hereby certified that a European patent has been granted in respect of the invention described in the annexed patent specification for the Contracting States designated in the specification.

Il est certifié qu'un brevet européen a été délivré pour l'invention décrite dans le fascicule de brevet ci-joint, pour les Etats contractants désignés dans le fascicule de brevet.

Europäisches Patent Nr. **European Patent No.** **Brevet européen n°**

0244180

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München, den
Munich,
Fait à Munich, le 07.08.91

Paul Braendli

Präsident des Europäischen Patentamts
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(54) **Titanium dioxide pigment coated with cerium cations, selected acid anions, and alumina.**

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Description

BACKGROUND OF THE INVENTION

The present invention relates generally to pigments composed of coated TiO_2 particles, and particularly to TiO_2 pigments having coatings comprising cerium cations, selected acid anions, and an outer coating of alumina.

TiO_2 has a high refractive index for its density, which renders it a superior pigment for use in coatings, e.g., paints. However, TiO_2 is photoactive; exposure to ultraviolet radiation results in generation of free radicals on the surface of TiO_2 particles. Thus, where a TiO_2 pigment is employed in a paint exposed to sunlight, free radicals are generated which can migrate to the film-forming component of the paint, resulting in coating degradation or failure.

Therefore, minimizing free radical migration is desirable in order to provide lightfast and stable pigments for coating use. Heretofore, the majority of commercial TiO_2 pigments have been coated with dense silica or densified alumina to provide lightfastness. However, some patent references have disclosed use of cerium in association with TiO_2 pigments to promote lightfastness.

Lederer, U. S. Patent 3,513,007, discloses TiO_2 particles having coatings formed from dispersions containing water-soluble hydrolyzable compounds of silicon, titanium, zirconium, or phosphorus, to which water-soluble hydrolyzable compounds of aluminum, cerium, and or calcium and alkali are added.

Barnard, U.S. Patent 4,239,548, discloses pigments having inner coatings comprising cerium and phosphate radicals and outer coatings comprising aluminum and phosphate radicals and optionally hydrous alumina.

Jacobson, U.S. Patent 4,460,655, describes pigments of TiO_2 particles associated with compounds selected from the group consisting of $Na_7Ce_6F_{31}$, $K_7Ce_6F_{31}$, $Li_7Ce_6F_{31}$, and $(NH_4)_7Ce_6F_{31}$.

Jacobson, U.S. Patent 4,461,810, discloses pigments of TiO_2 particles, the surfaces of which are associated with cerium cations and sulfate, phosphate, or silicate anions. The particles are also provided with an outer coating of alumina.

Newland et al., U.S. Patent 4,022,632, describes TiO_2 pigments treated with carboxylate salts of cobalt, cerium or manganese.

Bramekamp, U.S. Patent 3,506,466, discloses TiO_2 pigment particles coated with inorganic oxides, where the inorganic oxide bears on its surface an amine salt of an oxycarboxylic acid selected from the group consisting of lactic, citric, malic, tartaric and glycolic acids.

GB-A-1580882 describes a method of making a coated inorganic pigment which performs adequately in terms of gloss and dispersibility both organic and aqueous-based paint media. The inorganic pigment particles, which are preferably TiO_2 are coated with alumina and then contacted with one or more organic hydroxy acids or salts or with a water-soluble reaction product of one or more di- or polyhydric alcohols and one or more di- or poly-basic organic hydroxy acids.

It has now been found that pigments of TiO_2 particles treated with cerium cations in association with certain polyfunctional water-soluble acid anions or borate ions, and then topcoated with alumina, exhibit excellent lightfastness, gloss and dispersion characteristics.

SUMMARY OF THE INVENTION

The present invention provides a pigment consisting essentially of rutile TiO_2 particles bearing coatings of alumina or alumina-silica, the particle surfaces having associated therewith 0.05-2%, by weight of the TiO_2, of cerium cations and an associated quantity of borate anions or polyfunctional organic acid anions having a solubility in water of at least 10 grams per liter at 25° C.

DETAILED DESCRIPTION OF THE INVENTION

The pigments of the present invention are composed of rutile TiO_2 particles treated with cerium cations in association with selected polyfunctional organic acid anions such as citrate anions, and then topcoated with alumina or alumina-silica. Optionally, the acid anions can be borate. In extreme lightfastness exposures, the pigments of this invention provide performance equivalent to TiO_2 coated with 6% by weight silica and 2% by weight alumina. It is believed that cerium citrate in association with the TiO_2 particle surfaces provides recombination centers for electron/hole pairs produced when pigments containing such particles are exposed to actinic radiation. Quenching of electron/hole pairs eliminates free radical production which might otherwise degrade a paint film or other organic materials in proximity to pigment particles.

The TiO_2 used to prepare the pigment of the invention can be of the conventional rutile variety, prepared by either the chloride or sulfate process.

Associated with the particle surfaces of the TiO_2 are cerium cations and selected acid anions. "Associated with the particle surfaces" means that the ions are bound to the TiO_2 particles by a chemical or physical attraction.

The acid anions associated with the cerium cations are borate anions or polyfunctional organic acid anions having water solubilities greater than 10 grams per liter at 25°C. Exemplary of such organic acid anions are citrate, succinate, fumarate, adipate, tartrate, and maleate ions. Of the foregoing, citrate ions are preferred.

The cerium cations can be supplied by any water-soluble cerium salt, e.g., ceric sulfate or ceric nitrate, which are added to rutile slurries at pH 2-7. Polyfunctional organic acid anions are supplied by addition of the appropriate acid. Borate anions are supplied by addition of $Na_2B_2O_4$. The cerium ion content of the pigment can be determined by ion plasma chromatography. The polyfunctional organic acid anion content can be determined using a Leco or other total carbon analyzer.

The amount of alumina or alumina-silica which the particles bear as coatings can be varied depending primarily upon the pigment's intended use. Ordinarily, the alumina coating will constitute 0.5-10% of the total weight of the particles. Preferably, the alumina coating constitutes 1-6%, and most preferably, 2-4%, of the total weight of the pigment particles. The amount of alumina the particles bear as coatings, expressed as percent by weight, is calculated by first determining, by ion plasma spectroscopy, the alumina content of the coated pigment. The alumina content of the uncoated rutile TiO_2 is similarly determined, and the alumina content attributable to the coating is determined by computing the difference between coated and uncoated alumina contents.

The pigment of the present invention can be prepared from an aqueous slurry containing 200-450 grams per liter TiO_2. This slurry is brought to 45°-70°C and is held at that temperature throughout the preparation procedure. The slurry is adjusted to a pH at which added cerium ions will remain in solution by addition of mineral acid, e.g., HCl, and then sufficient cerium salt is added to provide a cerium ion concentration in the slurry of 0.05-2%, by weight of the TiO_2. For example, if cerium ions are supplied by addition of ceric nitrate, pH should be adjusted to 2-4; if cerium ions are added in the form of ceric sulfate, pH should be adjusted to the range 2-7.

At this point, a sufficient quantity of a selected anion species (i.e, organic acid or borate) is added to the slurry to provide a concentration of added anion ranging from 100% to 300% of the cerium ion concentration. As a result, cerium will precipitate upon the surfaces of the TiO_2 particles in association with the added anion.

Alumina is then precipitated on the TiO_2 particles by slowly adding enough sodium aluminate to the slurry to provide a concentration of about 2-8% by weight of the TiO_2. Acid, normally sulfuric or hydrochloric, is added at the same time to maintain the pH of the slurry within the range 6-9 during the precipitation step. After addition of aluminate is complete, the slurry is allowed to cure, with continuous stirring, for 15-30 minutes.

The resulting pigment is then separated from the liquid by filtration or centrifugation, washed with water, and dried.

Coating compositions can be prepared with the pigments of the invention in conventional ways, e.g., by blending the pigment with a film-forming component and a liquid carrier.

The following examples illustrate particular aspects of the present invention. In the examples, all parts and percentages are by weight and all degrees are Celsius unless otherwise indicated.

Example 1

In a large plastic vessel equipped with stirring apparatus and a pH probe, 11,000 parts water are mixed with 5000 parts rutile TiO_2.

The resulting slurry is heated to 60°, and the pH is adjusted to about 3.0 by addition of HCl. 42 parts of a 1.5 M $Ce(NO_3)_4$ solution are then added, followed by 40 parts citric acid. The resulting mixture is then stirred for a period of about 5 minutes, and then the pH is increased to about 7.5 by addition of NaOH.

A coating of 2% hydrous alumina is then deposited on the pigment by simultaneously adding 250 mL $NaAlO_2$ solution (containing the equivalent of 400 g Al_2O_3 per liter solution) and HCl, such that the pH of the slurry is continuously maintained from about 7.0 to about 7.5.

The resulting coated pigment is cured by holding for about 30 minutes at 60° and pH 7.5. The pigment is then filtered from the slurry, washed free of salts with deionized water, and air-dried. The pigment is then micronized, using 3 lbs. superheated steam per lb. pigment. The resulting pigment, containing about 0.2%

CeO_2 as $Ce_3(C_6H_5O_7)_4$, and a 2.0% alumina coating, is suitable for use in paint systems.

Example 2

A mill base is made by mixing

Pigment of Example 1	387 parts
alkyd resin (Syntex ® 3145; Celanese Coatings Co.)	149.6 parts
n-butanol	9.4 parts
xylol	79 parts.

This mixture is sand ground, and then the sand is filtered from the mill base. A paint is made by mixing 100 parts of the mill base with the following:

xylol	1.4 parts
alkyd resin (Syntex ® 3145; Celanese Coatings Co.)	71.8 parts
melamine resin solution (Cymel ® 248-8, 55% solids, American Cyanamid Co.)	38.5 parts.

Claims

1. A pigment consisting essentially of rutile TiO_2 particles bearing a coating of alumina or alumina-silica, the TiO_2 particle surfaces having bound therewith 0.05-2%, by weight of the TiO_2, of cerium cations and an associated quantity of borate anions or polyfunctional organic acid anions having a solubility in water of at least 10 grams per liter at 25 °C, said coating of alumina or aluminasilica forming a top coat on the TiO_2 particles.

2. A pigment according to claim 1, wherein the alumina or alumina-silica coating constitutes 0.5-10% of the total weight of the TiO_2 particles.

3. A pigment according to claim 2, wherein the alumina or alumina-silica coating constitutes 1-6% of the total weight of the TiO_2 particles.

4. A pigment according to claim 3, wherein the alumina or alumina-silica coating constitutes 2-4% of the total weight of the TiO_2 particles.

5. A pigment according to any one of the preceding claims wherein the associated anions are borate ions.

6. A pigment according to claim 1, wherein the associated anions are polyfunctional organic acid anions having a solubility in water of at least 10 grams per liter at 25 °C.

7. A pigment according to any one of claims 1 to 4, wherein the associated anions are citrate, succinate,

fumarate, adipate, tartrate or maleate ions.

8. A coating composition comprising a pigment according to any one of claims 1 to 7, a film-forming material, and a liquid carrier.

9. A method of producing coated TiO_2 pigment particles which comprises (a) forming an aqueous slurry containing 200 to 450 grams per litre of TiO_2 and having a pH at which cerium ions will remain in solution, (b) adding sufficient cerium salt to provide a cerium ion concentration in the slurry of 0.05 to 2% by weight of TiO_2, (c) adding a sufficient quantity of a source of borate or polyfunctional organic acid anions to provide a concentration of said anions of from 100 to 300% of the cerium ion concentration thereby causing the cerium ions to precipitate onto the surfaces of the TiO_2 particles in association with the said borate or polyfunctional organic acid anions and (d) depositing an alumina or silicaalumina coating on the treated TiO_2 particles.

10. A method according to claim 9 wherein in step (d) alumina is precipitated onto the treated TiO_2 particles by adding enough sodium aluminate to the slurry to provide a concentration of abut 2 to 8% by weight of the TiO_2 and adjusting the pH to within the range of 6 to 9 during the precipitation step.

Revendications

1. Un pigment constitué essentiellement de particules de TiO_2 de la variété rutile portant un enrobage d'alumine ou d'alumine-silice, les surfaces des particules de TiO_2 comportant 0,05 à 2 %, par rapport au poids du TiO_2, de cations cérium qui leur sont liés ainsi qu'une quantité associée d'anions borate ou d'anions d'acide organique polyfonctionnel ayant une solubilité dans l'eau d'au moins 10 grammes par litre à 25° C, ledit enrobage d'alumine ou d'alumine-silice formant une couche supérieure sur les particules de TiO_2.

2. Un pigment selon la revendication 1, dans lequel l'enrobage d'alumine ou d'alumine-silice constitue 0,5 à 10 % du poids total des particules de TiO_2.

3. Un pigment selon la revendication 2, dans lequel l'enrobage d'alumine ou d'alumine-silice constitue 1 à 6 % du poids total des particules de TiO_2.

4. Un pigment selon la revendication 3, dans lequel l'enrobage d'alumine ou d'alumine-silice constitue 2 à 4 % du poids total des particules de TiO_2.

5. Un pigment selon l'une quelconque des revendications précédentes, dans lequel les anions associés sont des anions borate.

6. Un pigment selon la revendication 1, dans lequel les anions associés sont des anions d'acide organique polyfonctionnel ayant une solubilité dans l'eau d'au moins 10 grammes par litre à 25° C.

7. Un pigment selon l'une quelconque des revendications 1 à 4, dans lequel les anions associés sont des ions citrate, succinate, fumarate, adipate, tartrate ou maléate.

8. Une composition de revêtement comprenant un pigment selon l'une quelconque des revendications 1 à 7, une matière filmogène et un véhicule liquide.

9. Un procédé de production de particules de pigment de TiO_2 enrobées, qui consiste à (a) former une suspension aqueuse contenant 200 à 450 grammes par litre de TiO_2 et ayant un pH auquel les ions cérium restent en solution, (b) ajouter une quantité suffisante de sel de cérium pour obtenir une concentration d'ions cérium dans la suspension de 0,05 à 2 % par rapport au poids de TiO_2, (c) ajouter une quantité suffisante d'une source d'anions borate ou d'anions d'acide organique polyfonctionnel pour obtenir une concentration desdits anions qui soit de 100 à 300 % de la concentration des ions cérium, pour faire ainsi précipiter les ions cérium sur les surfaces des particules de TiO_2 en association avec lesdits anions borate ou d'acide organique poiyfonctionnel et (d) déposer un enrobage d'alumine ou de silice-alumine sur les particules de TiO_2 traitées.

10. Un procédé selon la revendication 9, dans lequel, dans l'étape (d), on fait précipiter de l'alumine sur les particules de TiO_2 traitées en ajoutant suffisamment d'aluminate de sodium à la suspension pour obtenir une concentration d'environ 2 à 8 % par rapport au poids du TiO_2 et en ajustant le pH dans l'intervalle de 6 à 9 pendant l'étape de précipitation.

Patentansprüche

1. Pigment, das im wesentlichen aus Rutil-TiO_2-Teilchen mit einer Beschichtung aus Aluminiumoxid oder Siliciumaluminiumoxid besteht, wobei die Oberflächen der TiO_2-Teilchen 0,05 bis 2 %, bezogen auf das Gewicht des TiO_2, Cerkationen und eine assoziierte Menge Boratanionen oder polyfunktionelle organische Säureanionen mit einer Löslichkeit in Wasser von wenigstens 10 g/l bei 25° C aufweisen und wobei die Beschichtung aus Aluminiumoxid oder Siliciumaluminiumoxid eine Deckschicht auf den TiO_2-Teilchen bildet.

2. Pigment nach Anspruch 1, worin die Aluminiumoxid- oder Siliciumaluminiumoxidbeschichtung 0,5 bis 10 % des Gesamtgewichts der TiO_2-Teilchen ausmacht.

3. Pigment nach Anspruch 2, worin die Aluminiumoxid- oder Siliciumaluminiumoxidbeschichtung 1 bis 6 % des Gesamtgewichts der TiO_2-Teilchen ausmacht.

4. Pigment nach Anspruch 3, worin die Aluminiumoxid- oder Siliciumaluminiumoxidbeschichtung 2 bis 4 % des Gesamtgewichts der TiO_2-Teilchen ausmacht.

5. Pigment nach einem der vorstehenden Ansprüche, worin die assoziierten Anionen Boratlonen sind.

6. Pigment nach Anspruch 1, worin die assoziierten Anionen polyfunktionelle organische Säureanionen mit einer Löslichkeit in Wasser von wenigstens 10 g/l bei 25° C sind.

7. Pigment nach einem der Ansprüche 1 bis 4, worin die assoziierten Anionen Citrat-, Succinat-, Fumarat-, Adipat-, Tartrat- oder Maleationen sind.

8. Überzugszusammensetzung, welche ein Pigment nach einem der Ansprüche 1 bis 7, ein filmbildendes Material und einen flüssigen Träger umfaßt.

9. Verfahren zur Herstellung von beschichteten TiO_2-Pigmentteilchen durch (a) Bilden einer wässrigen Aufschlämmung mit 200 bis 450 g/l TiO_2 und einem pH-Wert, bei dem Cerionen in Lösung bleiben, (b) Zugeben von ausreichend Cersalz zur Bereitstellung einer Cerionenkonzentration in der Aufschlämmung von 0,05 bis 2 % des Gewichts des TiO_2, (c) Zugeben einer ausreichenden Menge einer Quelle von Boratoder polyfunktionellen organischen Säureanionen zur Bereitstellung einer Konzentration dieser Anionen von 100 bis 300 % der Cerionenkonzentration, wodurch die Cerionen zur Niederschlagung auf den Oberflächen der TiO_2-Teilchen in Assoziation mit den Borat- oder polyfunktionellen organischen Säureanionen veranlaßt werden, und (d) Aufbringen einer Aluminiumoxid- oder Siliciumaluminiumoxidbeschichtung auf den behandelten TiO_2-Teilchen.

10. Verfahren nach Anspruch 9, worin in Schritt (d) Aluminiumoxid auf den behandelten TiO_2-Teilchen niedergeschlagen wird, indem genügend Natriumaluminat zur Aufschlämmung zugegeben wird, um eine Konzentration von etwa 2 bis 8 % des TiO_2-Gewichts bereitzustellen, und der pH-Wert innerhalb des Bereiches von 8 bis 9 während des Ausfällungsschritts eingestellt wird.