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OUR REF DCW/VSW

YOUR REF

Mr. David J. Gould
E.I. DU PONT DE NEMOURS AND COMPANY
Legal Department, Patent Records Center
1007 Market Street
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U.S.A.

15 March 1990

Dear David,

European Patent Application No. f87 303 682.6
Your reference : CH-1370

I am pleased to report that the above application has been accepted and I enclose a copy of the notice of acceptance under Rule 51(4). I also enclose a copy of the text of the application in the form in which the EPO propose to grant the application. This corresponds with the form of the application as amended in January of this year.

We have a term of four months expiring on 8 July 1990 for making any last minute voluntary amendments to the application.

If I do not hear from you by 8 June 1990, I will indicate approval of the present text proposed for grant.

Yours sincerely,


DAVID C. WOODCRAFT

FILE CHECKED

Encl:

APR 9 1990

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Datum/Date

- 8. 03. 90

Zeichen/Ref/Réf DCW/CH-1370	Anmeldung Nr./Application No./Demande n°/Patent Nr./Patent No./Brevet n° 87303682.6-1 /
Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire L. L. DU PONT DE NEMOURS AND COMPANY	

COMMUNICATION UNDER RULE 51 (4) EPC

You are hereby informed that the Examining Division intends to grant a European patent on the basis of the above application with the text and drawings as indicated below:

Description:

Page(s):
Page(s): 1-8
Page(s):
Page(s):

of the published patent application
received on 29-4-89 with letter of
received on with letter of
received on with letter of

Claim(s):

No.:
No.: 1-14
No.:

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Drawing(s):

Sheet:
Sheet:
Sheet:

of the published patent application
received on with letter of
received on with letter of

With the following amendments to the above-mentioned documents

(a) In accordance with your request of
Description page(s):

Claims No.:
Drawing(s) sheet:

(b) Proposed by the Examining Division

Description page(s):

Claims No.: 13
Drawing(s) sheet:

A copy of the relevant documents is enclosed.

The title of the invention in the three official languages of the European Patent Office, the international patent classification, the designated Contracting States and the registered name of the applicant are shown on the attached EPO Form 2056.

You are requested to state your approval of the text specified above within four months of this notification.

Failure to do so will result in refusal of the application under Article 97 (1) EPC (Rule 51 (5) EPC).

Further information concerning the acceptability of amendments or the filing of a separate set of claims for one or more designated Contracting States that have entered a reservation under Article 167 (2) (a) EPC will be found in the Guidelines for Examination in the EPO, C-VI, 4.8 to 4.10 and 15.1.2 to 15.1.4 (July 1987).

Enclosures: EPO Form 2056
2 copies

Formalities Officer, Tel.: (089) 2399-4620

Registered letter
EPO Form 2004.1 10.87

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Zeichen/Ref./Réf. DCW/CH-1370	Anmeldung Nr./Application No./Demande n°./Patent Nr./Patent No./Brevet n°. 87303682.6-2112
Anmelder/Applicant/Demandeur/Patentinhaber/Propriétaire/Titulaire E.I. DU PONT DE NEMOURS AND COMPANY	

For the intended grant of a European patent, (1) the title of the invention in the three official languages of the European Patent Office, (2) the International Patent Classification and (3) the designated Contracting States and the applicant's registered name, address and country of residence or principal place of business are set out below.

(1)

- Titandioxid-Pigment, beschichtet mit durch Boroxid modifizierten Siliziumoxiden
- Titanium dioxide pigment coated with boria-modified silica
- Bioxyde de titane pigmentaire revêtu de silice modifiée par de l'oxyde de bore

(2) CLASS STRING: C09C1/36, C09C3/06

(3) BE-DE-ES-FR-GB-NL

E.I. DU PONT DE NEMOURS AND COMPANY
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Wilmington Delaware 19898/US

TITLE
Titanium Dioxide Pigment
Coated with Boric-Modified Silica

BACKGROUND OF THE INVENTION

The present invention relates generally to coated TiO_2 particles for use as pigments, and particularly to TiO_2 particles having densified silica coatings.

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. A widely-used approach to the problem of providing lightfastness involves coating TiO_2 particles with a layer of densified silica. The following patent references disclose conventional silica coating densification techniques.

Werner, U. S. Patent 3,437,502, discloses TiO_2 pigment having high opacity and dispersibility, which is obtained by applying a dense silica coating to TiO_2 followed by topcoating with alumina. The silica coating is applied by increasing the pH of a slurry of TiO_2 particles to above 7. A predetermined quantity of sodium silicate is then added to the slurry, resulting in a rise in pH of the slurry to above 8, generally above 11. The pH is then gradually reduced over a period of several hours by addition of dilute acid, and

the resulting silica-coated particles are cured at pH 6.0 to 7.5, at 60° to 100°C, for 30 minutes to several hours. The resulting product is then coated with alumina.

5 West, U. S. Patent 4,125,412, discloses preparation of durable TiO₂ pigments by slurring silica-coated TiO₂ particles at pH 9 to 10.5 while maintaining slurry temperature at 80° to 100°C.

10 European Patent Application 73,340 describes a similar method for coating TiO₂ particles with amorphous dense silica prior to topcoating with alumina. Silica is applied by adding a soluble silicate to a TiO₂ slurry at a temperature of at least 85°C and at a pH of from 9.8 to 10.1. The slurry is then neutralized in at least
15 three neutralization steps by addition of acid.

Common to the teachings of the foregoing references is a requirement for relatively high temperatures and high alkalinity during the silica densification step. An extremely lightfast white
20 pigment for use in paint systems can be made by depositing 4-6 weight percent amorphous dense silica on rutile TiO₂ pigment. To coat the base TiO₂ pigment with this quantity of dense silica requires several hours at 85°-90°C, during which mineral acids are used to precipitate silica from Na₂SiO₃. This high temperature
25 coating operation requires use of steel tanks, since less costly fiberglass tanks are not rated for use in the 85°-90°C temperature range. Methods for providing dense coatings of more than 4 weight percent silica at lower temperatures, e.g., 65°-80°C, to allow use of
30 fiberglass tanks, would be of significant interest to the TiO₂ pigment industry.

It has now been found that codeposition of B₂O₃ with SiO₂ provides dense silica coatings at process
35 temperatures which permit use of fiberglass slurry tanks. The boria-containing pigments resulting from

this process are highly lightfast, and exhibit excellent gloss and dispersibility.

SUMMARY OF THE INVENTION

5 The present invention provides a pigment consisting essentially of TiO_2 particles bearing coatings comprising SiO_2 and B_2O_3 . In a process aspect, the present invention provides a process for preparing TiO_2 particles bearing coatings of boria-modified silica, comprising:

10 (a) forming an aqueous slurry of rutile TiO_2 at a temperature from about 65°C to about 90°C ;

(b) adjusting pH of the slurry to the range 7-10.5;

15 (c) adding a predetermined quantity of a solution comprising Na_2SiO_3 and B_2O_3 , under conditions which maintain silicate and boria ions in solution;

20 (d) gradually lowering pH of the slurry to about 7.5-8.5 by addition of acid, thereby depositing a coating of silica and boria; and

(e) curing the resulting coated pigment at a temperature from about 65°C to about 90°C for a period of at least 15 minutes.

DETAILED DESCRIPTION OF THE INVENTION

25 In accordance with the present invention, B_2O_3 is codeposited with SiO_2 on TiO_2 particles, providing lightfast, durable pigments. The TiO_2 particles making up the pigments bear dense silica coatings, yet are produced at temperatures significantly lower than those required by other silica densification processes capable of providing dense silica coatings at greater than 4 weight percent.

30 In practice, silica/boria layers are codeposited from a master solution of Na_2SiO_3 and

$\text{Na}_2\text{B}_2\text{O}_4$. A standard acid solubility test can be to measure effectiveness of coating densification. In addition to enhanced densification of SiO_2 in the presence of B_2O_3 , an improvement in pigment brightness is provided.

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.

The amount of silica or silica topcoated with alumina which the particles bear as coatings can be varied depending primarily upon the pigment's intended use. Generally, the silica coatings will constitute from 2-10% of the total pigment weight, and an alumina topcoat, if present, will constitute 0.5-5% of the total weight of the particles. Preferably, the silica coating constitutes 4-8% of the total weight of the pigment particles. Preferably, the alumina topcoat, if present, constitutes 1-4% of the total weight.

The amount of alumina the particles bear as coatings, expressed as percent by weight, is calculated by first determining the alumina content of the coated pigment by ion plasma spectroscopy. 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 $65^\circ\text{--}90^\circ\text{C}$ and is held at that temperature throughout the preparation procedure. The slurry is adjusted to pH 7-10.5, and a sufficient quantity of solution containing Na_2SiO_3 and $\text{Na}_2\text{B}_2\text{O}_4$, or separate solutions of Na_2SiO_3 and $\text{Na}_2\text{B}_2\text{O}_4$, is added to provide a coating of the desired composition and weight. Upon addition of the Na_2SiO_3 and $\text{Na}_2\text{B}_2\text{O}_4$ solution(s), pH of the slurry increases to about 11.

Generally, slurry pH must be maintained above about 10 to maintain silicate and boria ions in solution.

5 Generally, the weight and composition of the coatings to be deposited will be determined by the composition of the master $\text{Na}_2\text{SiO}_3/\text{Na}_2\text{B}_2\text{O}_4$ solution, the quantity added to the slurry containing TiO_2 , and quantity of TiO_2 in the slurry. For TiO_2 slurries containing 400 g/L TiO_2 , about 40-50 mL of a master aqueous solution, containing 400 g SiO_2 equivalent and 10 40 g B_2O_3 equivalent per liter, should be added per liter TiO_2 slurry to provide coatings approximating 5% of pigment weight. The compositions of the coating solutions can be varied as required to provide variations in coating weight and composition.

15 The coatings applied to TiO_2 particles in accordance with the present invention can contain from 60-95 percent by weight SiO_2 and 0.5-30% by weight B_2O_3 , based upon coating weight. Preferably, coatings will contain 80-90 percent by weight SiO_2 and 2-20 percent by weight B_2O_3 . 20

Upon addition of the coating solutions, the pH of the TiO_2 slurry will rise to the range 10.5-11.5. Over a period of 2-4 hours, 15% aqueous HCl or other mineral acid is added to gradually decrease slurry pH to 25 about 8.0. As acid is added, $\text{SiO}_2/\text{B}_2\text{O}_3$ will be deposited and densified on the surfaces of the TiO_2 particles. After all acid is added, the pigment should be cured at 65°-90°C for 30 minutes.

30 If desired, alumina can be precipitated on silica/boria coated TiO_2 particles by adding enough sodium aluminate to the slurry, at a temperature from about 50°-90°C, 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 as the alumina is 35 precipitated. 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, 9000 parts water are mixed with 3000 parts rutile TiO_2 .

The resulting slurry is heated to 75° , and the pH is adjusted to about 7.5 by addition of NaOH. 400 parts of an aqueous solution containing 400 parts SiO_2 equivalent (as Na_2SiO_3) and 40 parts B_2O_3 equivalent (as $\text{Na}_2\text{B}_2\text{O}_4$) per 1000 parts water are added. The pH of the resulting mixture is then determined, and sufficient 15% aqueous HCl is added, over a period of about 3 hours, to reduce the slurry pH to about 8.0. After all HCl has been added, the slurry is cured for 30 minutes at pH 8.0 and 75° .

The resulting coating, which constitutes about 5.5% by weight of the total pigment, contains SiO_2 and B_2O_3 in a ratio by weight of about 90:10.

A coating of 2.5% hydrous alumina is then deposited on the pigment by simultaneous gradual addition of 200 mL NaAlO_2 solution (containing NaAlO_2 equivalent to 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 ambient temperature and pH 7.5. The pigment is then filtered from the slurry, washed free of salts with water, and air-dried. The pigment is then micronized, using 3 lbs. superheated steam per lb. pigment. The resulting pigment is suitable for use in paint systems where lightfastness is required.

Example 2

In this series of experiments, several batches of pigment were prepared to evaluate the effect of B_2O_3 codeposition and various processing temperatures upon acid solubility. Generally, acid solubility is inversely related to chalk-fade resistance for TiO_2 pigments.

The pigments described below were prepared by procedures substantially similar to that described in Example 1, above, except that processing temperatures were varied as indicated in Table 1, below. Acid solubilities were determined as follows.

10 mL 66% sulfuric acid is added to a test tube containing a magnetic stirring bar, and the tube is placed in an aluminum heating block and heated to 175° . A 0.2000 g pigment sample is added to the tube, and digested for 1 hour with stirring. At the conclusion of the digestion period, the tube containing the pigment sample is cooled by pouring the acid mixture into a beaker of ice, and the residue in the tube and beaker is washed with distilled water. The pigment residue in the tube and beaker is collected in a 100 mL volumetric flask, the volume made up to 100 mL by addition of distilled water, and the contents mixed thoroughly. The contents of the volumetric flask are then filtered, and 10 mL of the resulting filtrate are added to a 25 mL volumetric flask, to which 2 mL 20% hydrogen peroxide, and sufficient 10% sulfuric acid to make 25 mL, are

added. The resulting solution is allowed to stand one hour. Absorbance of the solution is then read at 400 nm using a 10 mm cell path. Soluble TiO_2 is determined by reference to a previously prepared spectrophotometric curve obtained by measurement of samples containing known quantities of dissolved TiO_2 .

Table 1

Acid Solubility: (% dissolved TiO_2)

Processing Temp. ($^{\circ}\text{C}$)	Coating Composition:	
	100% SiO_2	90% SiO_2 /10% B_2O_3
90	0.11	0.10
80	0.27	0.12
70	3.34	0.17
65	6.0	0.22

Example 3

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;	
5	Celanese Coatings Co.)	71.8 parts
	melamine resin solution	
	(Cymel ®248-8, 55%	
	solids, American	
	Cyanamid Co.)	38.5 parts.
10		
15		
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