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(71) Applicants: **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2040 Dow Center, Midland, MI Michigan 48674 (US). **ROHM AND HAAS COMPANY** [US/US]; 100 Independence Mall West, 7th Floor, Philadelphia, PA Pennsylvania 19106 (US).

(72) Inventors; and

(71) Applicants (for SC only): **LIU, Yang** [CN/CN]; No. 936 Zhang Heng Road, Zhangjiang Hi-Tech Park, Shanghai 201203 (CN). **SUN, Tong** [CN/CN]; No. 936 Zhang Heng Road, Zhangjiang Hi-Tech Park, Shanghai 201203 (CN). **WANG, Tao** [CN/CN]; No. 936 Zhang Heng Road, Zhangjiang Hi-Tech Park, Shanghai 201203 (CN). **CHEN, Junyu** [CN/CN]; No. 936 Zhang Heng Road, Zhangjiang Hi-Tech Park, Shanghai 201203 (CN). **HUANG, Yan** [CN/CN]; No. 936 Zhang Heng Road, Zhangjiang Hi-Tech Park, Shanghai 201203 (CN). **WANG, Tao** [AU/AU]; Hays Road, Point Henry, Geelong, Victoria 3221 (AU).

LAO, Lihong [CN/CN]; No. 35-102, Lane 789, Shuying Road, Minhang District, Shanghai 201100 (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

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(54) Title: SPRAY-DRIED COMPOSITE PARTICLES

(57) Abstract: Provided are spray-dried composite particles comprising by dry weight based on total dry weight of the spray-dried composite particles, from 60% to 90% of inorganic extenders, from 5% to 25% of inorganic pigments, and from 1% to 10% of water-insoluble polymer particles. The spray-dried composite particles have a particle size of from 1 to 100µm. A spray-drying process for preparation of the spray-dried composite particles and a paint formulation comprising the spray-dried composite particles are also provided.



SPRAY-DRIED COMPOSITE PARTICLES

FIELD OF THE INVENTION

The present invention relates to spray-dried composite particles comprising pigments
5 for use in paints to provide economical hiding performance.

INTRODUCTION

Pigments with high refraction index are widely used in the paint industry to provide opacity (i.e., hiding capability). TiO_2 is one such pigment and is very expensive. The huge
10 consumption of such pigments makes the manufacturing of opaque paints not economical.

It is therefore desired to provide spray-dried composite particles comprising at least one pigment for using in paints and providing economical hiding performance.

SUMMARY OF THE INVENTION

15 The present invention provides spray-dried composite particles comprising by dry weight based on total dry weight of the spray-dried composite particles, from 60% to 90% of inorganic extenders, from 5% to 25% of inorganic pigments, and from 1% to 10% of water-insoluble polymer particles. The spray-dried composite particles have a particle size of from 1 to 100 μm .

20 The present invention further provides a spray-drying process for preparation of the spray-dried composite particles comprising the steps of: (a) preparing a slurry for spray-drying comprising by dry weight based on total dry weight of the slurry, from 60% to 90% of inorganic extenders, from 5% to 25% of inorganic pigments, and from 1% to 10% of water-insoluble polymer particles; and (b) adding the slurry into a spray dryer and preparing the
25 spray-dried composite particles.

The present invention further provides a paint formulation comprising the spray-dried composite particles.

DETAILED DESCRIPTION OF THE INVENTION

30 As used herein, the term "average particle size" refers to the median particle size or diameter of a distribution of particles as determined for example, by a Multisizer™ 3 Coulter

Counter™ (Beckman Coulter, Inc., Fullerton, CA) according to the procedure recommended by the manufacturer. The median particle size is defined as the size wherein 50wt% of the particles in the distribution are smaller than the median particle size and 50wt% of the particles in the distribution are larger than the median particle size. It is a volume average particle size.

The spray-dried composite particles of the present invention comprise by dry weight based on total dry weight of the spray-dried composite particles, from 60% to 90%, preferably from 65% to 88%, and more preferably from 70% to 85%, inorganic extenders, from 5% to 25%, preferably from 7% to 20%, and more preferably from 10% to 15%, inorganic pigments, and from 1% to 10%, preferably from 2% to 8%, and more preferably from 3% to 7%, water-insoluble polymer particles.

The inorganic extenders have a particle size of from 0.3 to 30μm, preferably from 0.5 to 20μm, and more preferably from 1 to 10μm.

The spray-dried composite particles have a particle size of from 1 to 100μm, preferably from 3 to 70μm, and more preferably from 5 to 40μm.

The water-insoluble polymer particles

The water-insoluble polymer particles comprise, as polymerization units, at least one α,β-ethylenically unsaturated nonionic monomer, that is, α,β-ethylenically unsaturated monomer without bearing an ionic charge between pH=1-14. Suitable examples of the α,β-ethylenically unsaturated nonionic monomers include (meth)acrylic ester monomers, i.e., methacrylic ester or acrylic ester monomers including methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, decyl acrylate, lauryl acrylate, methyl methacrylate, butyl methacrylate, isodecyl methacrylate, and lauryl methacrylate; (meth)acrylonitrile; styrene and substituted styrene such as α-methyl styrene, and vinyl toluene; butadiene; ethylene; propylene; α-olefin such as 1-decene; vinyl esters such as vinyl acetate, vinyl butyrate, and vinyl versatate; and other vinyl monomers such as vinyl chloride and vinylidene chloride. Preferably, the α,β-ethylenically unsaturated nonionic monomers are ethyl acrylate, methyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl acetate, acrylonitrile, and any combination thereof.

Optionally, the water-insoluble polymer particles further comprise, as polymerization units, from 0.1% to 10%, and preferably from 0.5% to 5%, by dry weight based on total dry

weight of the polymer particles, an ethylenically unsaturated monomer carrying at least one functional group selected from carboxyl, carboxylic anhydride, hydroxyl, amide, amino, ureido, acetoacetate, sulphonate, phosphonate, and any combination thereof. Suitable examples of these monomers are ethylenically unsaturated carboxylic or dicarboxylic acid such as acrylic or methacrylic acid, itaconic acid, and maleic acid; ethylenically unsaturated amide such as (meth)acrylamide; ethylenically unsaturated N-alkylolamide such as N-methylol(meth)acrylamide and 2-hydroxyethyl(meth)acrylamide; hydroxyalkyl ester of the carboxylic or dicarboxylic acid, such as hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; amino-functional monomers such as N,N-dimethylaminoethyl methacrylate; ureido-functional monomers such as methacrylamidoethyl-2-imidazolidinone; monomers bearing acetoacetate-functional groups such as acetoacetoxyethyl methacrylate; and any combination thereof.

The polymerization of the polymer particles can be any methods known in the art, and includes emulsion polymerization and mini-emulsion polymerization.

The inorganic pigments

The inorganic pigment is a particulate inorganic material which is capable of materially contributing to the opacity (i.e., hiding capability) of a composition. Such materials typically have a refractive index of greater than 1.8, and include titanium dioxide (TiO₂), zinc oxide, zinc sulfide, barium sulfate, barium carbonate, and lithopone. TiO₂ is preferred.

The inorganic extenders

The inorganic extender is a particulate inorganic material having a refractive index of less than or equal to 1.8 and greater than 1.3, and including calcium carbonate, clay, calcium sulfate, aluminosilicate, silicate, zeolite, mica, diatomaceous earth, aluminium oxide (Al₂O₃), zinc phosphate, solid or hollow glass, and ceramic bead. Calcium carbonate, clay, mica, and Al₂O₃ are preferred.

Additives

The spray-dried composite particles further comprise less than 3%, preferably less than 2% by dry weight based on total dry weight of the particles, a dispersant. Suitable examples of the dispersant include non-ionic, anionic and cationic dispersants such as polyacid with suitable molecular weight, 2-amino-2-methyl-1-propanol (AMP), dimethyl

amino ethanol (DMAE), potassium tripolyphosphate (KTPP), trisodium polyphosphate (TSPP), citric acid and other carboxylic acids. Preferred dispersants are polyacids, i.e., homopolymers or copolymers of carboxylic acids, hydrophobically or hydrophilically modified polyacids, salts thereof, and any combination thereof. Suitable examples of the hydrophobically or hydrophilically modified polyacids include polyacrylic acid, polymethacrylic acid, and maleic anhydride modified with hydrophilic or hydrophobic monomers such as styrene, acrylate or methacrylate esters, diisobutylene. The molecular weight of such polyacid dispersant is from 400 to 50,000, preferably from 500 to 30,000, more preferably from 1000 to 10,000, and most preferably from 1,500 to 3,000.

The spray-dried composite particles may further comprise less than 3%, preferably less than 2% by dry weight based on total dry weight of the particles, a flow additive. Suitable examples of the flow additive include magnesium stearate, mannitol, stearyl alcohol, glyceryl monostearate, and any combination thereof.

The spray-dried composite particles may further comprise less than 3%, preferably less than 2% by dry weight based on total dry weight of the particles, a defoamer. The defoamer may be any suitable defoamer as known in the art. Suitable examples of the defoamer include siloxane based defoamers and mineral oil based defoamers.

The spray-dried composite particles may further comprise less than 3%, preferably less than 2% by dry weight based on total dry weight of the particles, a thickener. Suitable examples of the thickener include polyvinyl alcohol (PVA), hydrophobically modified alkali soluble emulsions (HASE), alkali-soluble or alkali swellable emulsions (ASE), hydrophobically modified ethylene oxide-urethane polymers known in the art as HEUR, cellulosic thickeners such as hydroxymethyl cellulose (HMC), hydroxyethyl cellulose (HEC), hydrophobically-modified hydroxy ethyl cellulose (HMHEC), sodium carboxymethyl cellulose (SCMC), sodium carboxymethyl 2-hydroxyethyl cellulose, 2-hydroxypropyl methyl cellulose, 2-hydroxyethyl methyl cellulose, 2-hydroxybutyl methyl cellulose, 2-hydroxyethyl ethyl cellulose, and 2-hydroxypropyl cellulose.

The spray-dried composite particles contain less than 2%, preferably less than 0.5%, and more preferably less than 0.1%, by weight based on total weight of the particles, water.

The spray-drying method

The spray-drying method involves the conversion of a slurry droplet into dried powders by evaporation of the solvent/water in a one-step process through a spray dryer. It is well-known in the art that the desired particle morphologies and size distribution are achieved by controlled solids content of the slurry, nozzle diameter, air inlet or air outlet temperature, pump speed, and air pressure of the spray dryer. In this invention, inorganic pigments, inorganic extenders and water-insoluble polymer particles are mixed with by weight based on total weight of the slurry, from 20% to 99% water, and the dispersant, the defoamer, and the optional flow additive to form the slurry. The slurry may be added into any commercially available spray dryer, such as Mini Spray Dryer B-290 from BUCHI Corporation, and GEA Niro Spray Dryer from GEA Process Engineering Inc. to prepare the desired spray-dried composite particles of the present invention.

Paint Formulation

The spray-dried composite particles of the present invention are added into regular paint formulations to replace the usage of inorganic pigments.

For distinction, the fraction of inorganic pigments comprised in the paint formulation but not in the spray-dried composite particles are named hereinafter as “paint pigments”, and the fraction of inorganic pigments comprised in the spray-dried composite particles are named hereinafter as “spray-dried composite pigments”.

In one preferred embodiment, the spray-dried composite particles are higher than 25% by dry weight based on total dry weight of the paint pigments.

The preparation of the paint formulation is a well-known method of the art and involves the process of admixing appropriate paint ingredients in the indicated proportions to provide a paint as well as a final dry paint film with the desired properties.

Application of the paint formulation

The paint formulation may be applied by conventional application methods such as brushing, roller application, and spraying methods such as air-atomized spray, air-assisted spray, airless spray, high volume low pressure spray, and air-assisted airless spray.

Suitable substrates for paint application include concrete, cement board, medium-density fiberboard (MDF) and particle board, gypsum board, wood, stone, metal, plastics, wall paper and textile, etc. Preferably, all the substrates are pre-primed by waterborne or solvent-borne primers.

EXAMPLES

I. Raw materials

Material	Supplier
OROTAN™ 1288 dispersant	The Dow Chemical Company
R-996 TiO ₂	Sichuan Lomon Corporation (China)
AMP-95™ base	The Dow Chemical Company
C-70 calcium carbonate slurry	Omya Minerals Co., Ltd.
EVOQUE™ 1200 emulsion (45% solids)	The Dow Chemical Company
OROTAN™ 731A dispersant	The Dow Chemical Company
FOAMASTER™ NXZ defoamer	Cognis Chemical (China) Co., Ltd.
TI-PURE™ R-706 TiO ₂	DuPont Company
NATROSOL™ 250 HBR rheology modifier	Ashland Aqualon Company
CC-700 calcium carbonate extender	Guangfu Building Materials Group (China)
propylene glycol solvent	Sinopharm Chemical Reagent Co., Ltd.
ACRYSOL™ RM-2020 rheology modifier	The Dow Chemical Company
TEXANOL™ coalescent	The Dow Chemical Company
PRIMAL™ AC-261 acrylic emulsion	The Dow Chemical Company
ROPAQUE™ Ultra E opaque polymer	The Dow Chemical Company
TRITON™ CF-10 wetting agent	The Dow Chemical Company
DB-80 calcined kaolin	Guangfu Building Materials Group (China)
CELITE 499 extender	Celite Corporation

5 II. Test methods

1. Contrast ratio test

Drawdown of Paint Formulations was made with a 100µm Bird Film Applicator™ on a BYKO-chart PA-2810 of BYK-Gardner GmbH, and was then allowed for drying for 1 day in a constant temperature room (CTR). Contrast ratio of dry paint was determined by a BYK-
 10 Gardner 6850 Color-Guide Plus Spectrophotometer. Contrast ratio is a test method for the opacity of paint film, Y values of paint film were tested separately in the white chart (Y_w) and black chart (Y_b). Contrast ratio was defined as Y_b/Y_w. The higher the contrast ratio, the better the opacity.

15 2. Kubelka-Munk hiding test

S/mil was determined for each of the final Paint Formulations as follows: Two draw-downs were prepared on Black Release Charts (Leneta Form RC-BC) for each paint using a 1.5-mil Bird drawdown bar and the charts were allowed to dry overnight. Using a template,

3.25"×4" rectangles were cut out with an X-ACTO knife on each chart. The y-reflectance was measured for five times using a BYK Gardner 45° Reflectometer in each of the scribed areas measuring on a diagonal starting at the top of the rectangle and the average y-reflectance was recorded. A thick film drawdown was prepared for each paint on Black Vinyl Chart (Leneta Form P121-10N) using a 3"25 mil block drawdown bar and the charts were allowed to dry overnight. The y-reflectance was measured in five different areas of the drawdown and the average y-reflectance was recorded. Kubelka-Munk hiding value S (s/mil) is given by Equation 1:

$$S (s/mil) = \frac{R}{X \times (1-R^2)} \times \ln \frac{1-(R_B \times R)}{1-\frac{R_B}{R}} \quad \text{Equation 1}$$

Where X is the average film thickness, R is the average reflectance of the thick film and R_B is the average reflectance over black of the thin film. X can be calculated from the weight of the paint film (W_{pf}), the density (D) of the dry film, and the film area (A). Film area for a 3.25"×4" template was 13in^2 .

$$X(mils) = \frac{W_{pf}(g) \times 1000(mil/in)}{D(lbs/gal) \times 1.964(g/in^3/lbs/gal) \times A(in^2)}$$

III. Experimental examples

1. Preparation of Spray-dried Composite Particles

A slurry was first prepared by mixing 0.8g OROTAN™ 1288 dispersant, 0.2g AMP-95™ base and 28g water at a low-speed mixer. Selected amount of R-996 TiO₂ was then added and mixed with the slurry at an increased 1500rpm shear speed for 30mins. Selected amounts of commercial C-70 calcium carbonate slurry and EVOQUE™ 1200 emulsion (45% solids) were then added at around 700rpm and mixed for 10mins. Additional water was further added to the slurry to keep the solid content of the slurry at 50%. Selected amounts for the above ingredients, R 996 TiO₂, calcium carbonate slurry and EVOQUE 1200 emulsion were different in different examples and were listed in Table 2 as dry weight based on total dry weight of the spray-dried composite particles.

The prepared slurry was added into the Mini Spray Dryer B-290 available from BUCHI Corporation and the device was set so that the nozzle diameter equals to 1mm, the temperature of air inlet equals to 120°C, the temperature of air outlet equals to 100°C, the

pump speed equals to 0.45L per hour, and the air pressure equals to about 196kPa. The Spray-dried Composite Particles (SCP) were collected from the product collection vessel of the spray dryer, and they have a particle size of 10-50 μ m.

5

TABLE 1. Slurry formulation

Slurry Formulation	
Materials	Weight (g)
“Grind”	
water	28.00g
OROTAN™ 1288 dispersant	0.80g
AMP-95™ base	0.20g
R 996 TiO ₂	selected amount*
Mixing with “commercially available slurry”	
C-70 calcium carbonate slurry	selected amount*
“Let-Down”	
EVOQUE™ 1200 emulsion (45% solids)	selected amount*
additional water	to make a solid content of 50%

*selected amounts were described in Table 2

TABLE 2. Selected amounts of critical ingredients in the spray-dried composite particles

Selected amounts (%*)								
Materials	SCP1	SCP2	SCP3	SCP4	SCP5	SCP6 [#]	SCP7	SCP8 [#]
R 996 TiO ₂	29.07	23.26	17.44	29.04	29.01	0	13.64	10.7
C-70 calcium carbonate slurry	66.79	72.60	78.42	68.18	69.56	95.56	84.11	77.36
EVOQUE™ 1200 emulsion (45% solids)	4.07	4.07	4.07	2.71	1.35	4.34	2.18	11.85

* by dry weight percentage based on total dry weight of the spray-dried composite particles

[#] SCP6 and SCP8 are comparative spray-dried composite particles

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Slurry formulation for Spray-dried composite particles 8 (SCP8) could not be collected from the product collection vessel of the spray dryer.

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2. Preparation of Paint Formulations

Comparative Paint Formulations 1 and 2 (Comp. 1 or 2), and Inventive Paint Formulations 1, 2, 3, 4 and 5 (Paint 1, 2, 3, 4, or 5) were prepared according to the procedure of Table 3. The Grind ingredients were mixed using a high speed Cowles disperser. The Let-down ingredients were added using a conventional lab mixer.

TABLE 3. Paint formulations (PVC = 50%)

Coating formulation	
Materials	Weight (g)
“Grind”	
water	126.00g
propylene glycol solvent	15.00g
TRITON™ CF-10 wetting agent	2.00g
FOAMASTER™ NXZ defoamer	1.00g
AMP-95™ base	2.80g
OROTAN™ 731A dispersant	11.20g
NATROSOL™ 250 HBR rheology modifier	2.00g
TI-PURE™ R-706 TiO ₂	Selected amount*
CC-700 calcium carbonate extender	60.00g
DB-80 calcined kaolin	40.00g
CELITE 499 extender	40.00g
“Let-down”	
Spray-dried Composite Particles	See Table 4
PRIMAL™ AC-261 acrylic emulsion	330.00g
TEXANOL™ coalescent	9.45g
ROPAQUET™ Ultra E opaque polymer	80.00g
FOAMASTER™ NXZ defoamer	1.00g
ACRYSOL™ RM-2020 rheology modifier	6.66g
water	62.89g
Total	1000g

*selected amounts were described in Table 4

5 IV. Results

TABLE 4. TiO₂ weight amounts in paint formulations

Paint Formulations	TI-PURE R-706 TiO ₂	Spray-dried Composite Particles		Total TiO ₂	Opacity	
		SCPs	R 996 TiO ₂		Contrast ratio (%)	s/mil
Comp. 1	210g	-	-	210g	95.83	6.1
Comp. 2	210g	107.82g SCP6	-	210g	93.70	5.9
Paint 1	168g	84g SCP1	24.4g	192.4g	96.04	6.3
Paint 2	168g	84g SCP2	19.5g	187.5g	95.86	6.2
Paint 3	168g	84g SCP3	14.6g	182.6g	96.03	6.2
Paint 4	168g	84g SCP4	24.4g	192.4g	96.09	6.4

Paint 5	168g	84g SCP5	24.4g	192.4g	95.97	6.3
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As shown in Table 4, Comparative Paint Formulation 1 (Comp. 1) comprised 210g “paint pigment”, and no Spray-dried Composite Particles. Comparative Paint Formulation 2 (Comp. 2) comprised 210g “paint pigment”, and 107.82g Spray-dried Composite Particles which comprised no “spray-dried composite pigments”. Inventive Paint Formulations 1 to 5 (Paints 1 to 5) comprised 168g “paint pigment”, and different amounts of “spray-dried composite pigments”. Inventive Paint Formulations 1 to 5 (Paints 1 to 5), compared to Comparative Paint Formulation 1, had 8.3% to 13% less total TiO₂ usages, and achieved similar or even better opacity. Since compared to Comparative Paint Formulation 2, which did not comprise any “spray-dried composite pigments”, and its opacity was poorer than the Inventive Paint Formulations 1 to 5. The opacity of Comparative Paint Formulation 2 was even poorer than that of Comparative Paint Formulation 1. This possibly meant the better opacity might not be caused by the spray-drying method, but the pigment comprised in the spray-dried composite particles.

TABLE 5. Spray-dried Composite Particles concentrations in Paint Formulations

Paint Formulations	TI-PURE R-706 TiO ₂	Spray-dried Composite Particles		Concentrations*	Opacity (%)	S/mil
		SCPs	R 996 TiO ₂			
Paint 6	168g	42g SCP7	5.73g	25%	96.00%	6.0
Paint 7	168g	84g SCP7	11.46g	50%	96.70%	6.4
Paint 8	168g	126g SCP7	17.19g	75%	97.10%	6.5

* by dry weight percentage of Spray-dried Composite Particles based on paint pigments, TI-PURE R-706 TiO₂

As shown in Table 5, to achieve better opacity, the Spray-dried Composition Particles of the present invention are recommended to be used in the Paint Formulations, at a concentration of higher than 25% by dry weight based on total dry weight of “paint pigments”.

What is claimed is:

1. Spray-dried composite particles comprising by dry weight based on total dry weight of the spray-dried composite particles, from 60% to 90% of inorganic extenders, from 5% to 25% of inorganic pigments, and from 1% to 10% of water-insoluble polymer particles; wherein the spray-dried composite particles have a particle size of from 1 to 100 μ m.

2. The spray-dried composite particles according to Claim 1 wherein the spray-dried composite particles have a particle size of from 5 to 40 μ m.

3. The spray-dried composite particles according to Claim 1 wherein the inorganic extenders have a particle size of from 0.3 to 30 μ m.

4. The spray-dried composite particles according to Claim 1 wherein the water-insoluble polymer particles comprise, as polymerization units, at least one α,β -ethylenically unsaturated nonionic monomer.

5. The spray-dried composite particles according to Claim 4 wherein the α,β -ethylenically unsaturated nonionic monomers are ethyl acrylate, methyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, vinyl acetate, acrylonitrile, and any combination thereof.

6. The spray-dried composite particles according to Claim 1 wherein the water-insoluble polymer particles further comprise, as polymerization units, from 0.1% to 10% by dry weight, based on total dry weight of the polymer particles, an ethylenically unsaturated monomer carrying at least one functional group selected from carboxyl, carboxylic anhydride, hydroxyl, amide, amino, ureido, acetoacetate, sulphonate, phosphonate, and any combination thereof.

7. The spray-dried composite particles according to Claim 1 wherein the inorganic pigment is selected from titanium dioxide, zinc oxide, zinc sulfide, barium sulfate, barium carbonate, and lithopone.

5 8. The spray-dried composite particles according to Claim 7 wherein the inorganic pigment is titanium dioxide.

9. The spray-dried composite particles according to Claim 7 wherein it contains less than 2% by weight based on total weight of the particles, water.

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10. A spray-drying process for preparation of the spray-dried composite particles according to Claim 1 comprising the steps of:

15 (a) preparing a slurry for spray-drying comprising by dry weight based on total dry weight of the slurry, from 60% to 90% of inorganic extenders, from 5% to 25% of inorganic pigments, and from 1% to 10% of water-insoluble polymer particles; and

 (b) adding the slurry into a spray dryer and preparing the spray-dried composite particles;

 wherein the average particle size of the spray-dried composite particles is from 1 to 100 μ m.

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11. A paint formulation comprising the spray-dried composite particles according to Claim 1.

25 12. The paint formulation according to Claim 11 wherein the spray-dried composite particles that are higher than 25% by dry weight based on total dry weight of the paint pigments.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

C09D 133/00(2006.01)i; C09D 135/00(2006.01)i; C09D 125/00(2006.01)i

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)

C09D 125/-, C09D 133/-, C09D 135/-

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)

CNPAT,CNKI,WPI,EPODOC, calcium, carbonate, sulfate, alumin+, mica, clay, titanium, acrylic+, acrylate, spray+, dry

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 102181205 A (SHANGHAI YUNNI NEW MATERIALS CO. LTD.) 14 September 2011 (2011-09-14) description, paragraphs [0007], [0033] to [0037]	1-12
Y	CN 1176980 A (BAYER AG.) 25 March 1998 (1998-03-25) description, embodiment 1	1-12
A	CN 102002287 A (UNIV. ZHEJIANG) 06 April 2011 (2011-04-06) claims 1-4	1-12
A	CN 104418972 A (HINESE ACAD. SCI. CHEM. INST) 18 March 2015 (2015-03-18) claims 1-11	1-12



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

08 January 2016

Date of mailing of the international search report

26 January 2016

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6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing
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HU,Xinliang

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