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(54) Title: POLYURETHANE COATING COMPOSITION

(57) Abstract: The present invention relates to a composition comprising a stable aqueous dispersion of polyurethane particles and pigment particles partially or fully encapsulated with a soft polymer. The composition of the present invention delivers relatively high gloss as well as gloss stability in coatings formulations.

POLYURETHANE COATING COMPOSITION

Background of the Invention

The present invention relates to a stable aqueous dispersion of polyurethane particles and pigment particles partially or fully encapsulated with polymer.

The ability to obtain and control high gloss in latex-based pigmented coatings is highly desirable; nevertheless, the particulate nature of polymer binder tends to interfere with pigment distribution, causing agglomeration, thereby reducing initial gloss as well as gloss stability over time. Polyurethane latexes, which, in combination with acrylic latexes, offer a binder system for paints with highly desirable properties, as disclosed in U.S. 2009/0318596; however, polyurethane latex-based systems are especially prone to these agglomerative effects, which are especially pronounced for polyurethane latexes made by a pre-polymer followed by a diamine chain-extension process, due to the presence of residual amine or anionic groups, which are known to interact with pigment particles. Accordingly, it would be an advance in the art to discover a polyurethane-based latex binder system that had relatively high gloss and high gloss stability over time.

Summary of the Invention

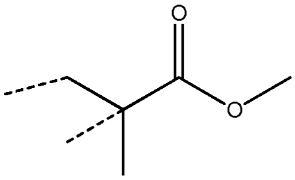
The present invention addresses a need by providing a composition comprising a stable aqueous dispersion of polyurethane particles and pigment particles partially or fully encapsulated with a soft polymer having a T_g not higher than 35 °C; wherein the weight percent of the polyurethane particles is such that the range pigment volume concentration of the composition is in the range of 6 to 25.

The composition of the present invention addresses a need in the art by delivering relatively high gloss as well as gloss stability over time in coatings formulations.

Detailed Description of the Invention

The present invention provides a stable aqueous dispersion of polyurethane particles and pigment particles partially or fully encapsulated with a soft polymer polymer having a T_g not higher than 35 °C; wherein the weight percent of the polyurethane particles is such that the range pigment volume concentration of the composition is in the range of 6 to 25. Preferably, the weight percent of polyurethane particles is from 10 weight percent, more preferably from 20 weight percent, to 70 weight percent, more preferably to 50 weight percent, and most preferably to 40 weight percent, based on the weight of the polyurethane particles and the soft polymer.

The soft polymer is preferably an acrylic, a styrene-acrylic, or a vinyl acrylic polymer. Preferably, the soft polymer includes structural units of styrene or a methacrylate such as methyl methacrylate or ethyl methacrylate; and an acrylate such as ethyl acrylate, butyl acrylate, 2-propylheptyl acrylate, or 2-ethylhexyl acrylate. As used herein, the term "structural unit" of the named monomer, refers to the remnant of the monomer after polymerization. For example, a structural unit of methyl methacrylate is as illustrated:



structural unit of methyl methacrylate

where the dotted lines represent the points of attachment of the structural unit to the polymer backbone.

The polyurethane dispersion is advantageously prepared by contacting under reaction conditions a diisocyanate with a diol, which is typically a polyether polyol, a polyester polyol, a polycaprolactone, or a polycarbonate or a combination thereof. The polyurethane may be thermoplastic and may also contain functionality such as pendant or endcapping hydroxyl, amine, or carboxylic acid groups, which can be cured with crosslinking agents such as polyaziridine, aminoplast resins, epoxies, water dispersible polyisocyanates, and multifunctional aldehydes including (cis, trans)-1,3-cyclohexanecarboxyaldehydes and (cis, trans)-1,4-cyclohexanecarboxyaldehydes. Examples of suitable commercially available polyurethane dispersions include Sancure 815 Polyurethane Dispersion and BayhydrolXP2557 Polyurethane Dispersion.

The pigment particles, preferably TiO_2 particles, are preferably fully encapsulated with the soft polymer having a shell thickness in the range of from 10 nm, more preferably from 30 nm, to 90 nm, more preferably to 70 nm.

Descriptions of partially polymer encapsulated polymers can be found, for example, in U.S. 5,509,960; U.S. 6,080,802; U.S. 6,214,467; U.S. 7,179,531; U.S. 7,081,488; and

U.S. Pat. Pub. 2003/0018103A1. Examples of commercially available partially polymer encapsulated TiO_2 particles include EVOQUE™ Precomposite Polymers (A Trademark of The Dow Chemical Company or its Affiliates).

Examples of fully polymer encapsulated TiO_2 particles are described in U.S. 4,421,660; U.S. Pat. Pub. 2010/0298483, and EP1802662. A preferred general process for fully encapsulating TiO_2 particles in a polymer comprises the steps of a) forming a mixture of i) an aqueous dispersion of TiO_2 particles and an amphoteric polymer; ii) an anionic surfactant; and iii) sodium styrene sulfonate; b) adding to the mixture of step (a) a redox initiator system; then c) adding an aqueous dispersion of a first monomer; and d) polymerizing the first monomer to form an aqueous dispersion of a first polymer that encapsulates the TiO_2 particles.

The first monomer preferably comprises either a) a methacrylate monomer or a styrene monomer, or a combination thereof, and an acrylate monomer; or b) a methacrylate monomer, an acrylate monomer, and a vinyl acetate monomer; or c) a vinyl acetate monomer and an ethylene monomer. More preferably, the first monomer comprises a methacrylate or a styrene monomer, or a combination thereof, and an acrylate monomer.

It may be further desirable to include the following steps after step d): e) adding to the mixture an aqueous dispersion of a second monomer, which preferably comprises a methacrylate or a styrene monomer, or a combination thereof, and an acrylate monomer; and f) polymerizing the second monomer to form an aqueous dispersion of a second polymer that at least partially encapsulates the first polymer.

The first and/or second monomer may further include other polymerizable monomers such as hydroxyl functional acrylates and methacryates including hydroxyethyl methacrylate and hydroxypropylate acrylate; carbamate functional acrylates and methacrylates including hydroxypropyl carbamate acrylate; carboxylic acid functional monomers including acrylic acid and methacrylic acid; and acrylamides including N-methylolacrylamide. These funtionalized groups, when present in the encapsulating polymer, are capable of being crosslinked with crosslinking agents such as polyaziridine, aminoplast resins, epoxy resins, water dispersible polyisocyanates, and multifunctional aldehydes.

The amphoteric polymer, which adsorbs to the surface of the TiO_2 particles, is a polymeric dispersant for TiO_2 particles that contains amine functionality and acid functionality, preferably a polymer that is prepared from the copolymerization of an ethylenically unsaturated amine functional monomer and an ethylenically unsaturated sulfur-acid functional monomer. Examples of suitable ethylenically unsaturated amine functional monomers include dimethylaminoethyl methacrylate, dimethylaminoethyl acrylate, dimethylaminopropyl methacrylamide, dimethylaminopropyl acrylamide, *t*-butylaminoethyl methacrylate and *t*-butylaminoethyl methacrylate, with dimethylaminoethyl methacrylate (DMAEMA) being preferred. Examples of suitable ethylenically unsaturated sulfur-acid functional monomers include sulfoethyl methacrylate, sulfoethyl acrylate, sulfopropyl methacrylate, sulfopropyl acrylate, styrene sulfonic acid, vinyl sulfonic acid, 2-methacrylamido-2-methyl propanesulfonic acid, and 2-acrylamido-2-methyl propanesulfonic acid, and salts thereof, with 2-acrylamido-2-methyl propanesulfonic acid and sulfoethyl methacrylate being preferred.

Suitable anionic surfactants include sodium dodecylbenzene sulfonate (SDS) or dodecyl allyl sulfosuccinate. It is understood that the term “a first monomer” is used to refer to one or more monomers; similarly, “an aqueous dispersion” refers to one or more aqueous dispersions; thus, a methacrylate monomer refers to one or more methacrylate monomers.

The term “redox initiator system” refers to a combination of a reducing agent, an oxidizing agent, and a metal ion catalyst. Examples of suitable oxidizing agents include persulfates such as ammonium and alkali metal persulfates; hydroperoxides, such as *t*-butyl hydroperoxide and cumene hydroperoxide; peroxides such as benzoyl peroxide, caprylyl peroxide, and di-*t*-butyl peroxide; peresters such as *t*-butyl peracetate, *t*-butyl perphthalate, and *t*-butyl perbenzoate; percarbonates; and perphosphates; with *t*-butyl hydroperoxide being preferred.

Examples of suitable reducing agents include ascorbic acid, isoascorbic acid, malic acid, glycolic acid, oxalic acid, lactic acid, and thioglycolic acid; an alkali metal hydrosulfite such as sodium hydrosulfite; a hyposulfite such as potassium hyposulfite; or a metabisulfite such as potassium metabisulfite; and sodium formaldehyde sulfoxylate.

Suitable accelerators include halide and sulfate salts of cobalt, iron, nickel, and copper, used in small amounts. An example of a preferred redox initiator system is *t*-butyl hydroperoxide/isoascorbic acid/Fe^{+2}. Preferably, the accelerator is added prior to the addition of the oxidizing and reducing agents. It is further preferred that the oxidizing and reducing agents are added over time to maintain a relatively even level of radical flux over the course of the addition of monomers.

The dispersion of TiO_2 and the amphoteric polymer are advantageously prepared by slowly adding, with concomitant grinding, the TiO_2 to an aqueous dispersion of the amphoteric polymer. The preferred solids content of the TiO_2/amphoteric polymer dispersion is in the range of 70 to 80 weight percent based on the weight of TiO_2, amphoteric polymer, and water.

To achieve both relatively high gloss and retention of gloss in paint formulations containing the encapsulated pigment polymer, the encapsulating polymer was found to have a T_g of not greater than 35 °C, preferably not greater than 30 °C; and preferably not less -40 °C, more preferably not less than -30 °C.

Though not bound by theory, it is believed that the enhanced gloss observed for formulations that include the soft encapsulating polymer is related to the propensity of this polymer to form a film near ambient temperatures. It has also been discovered that formulations of relatively high gloss and retention of gloss can be prepared in the substantial absence of volatile organic solvents, preferably less than 1000 ppm, more preferably less than 100 ppm, and most preferably less than 10 ppm of volatile organic solvents.

The composition of the present invention is useful as a coating, an adhesive, or a sealant for a suitable substrate or primed include metal, plastic, concrete, wood, asphalt, hair, paper, leather, rubber, foam, or textiles.

Examples

The following examples are for illustrative purposes only and are not intended to limit the scope of the invention.

Abbreviations

SDS = Sodium dodecylbenzene sulfonate (23%)
SSS = Sodium styrene sulfonate
BHP = *t*-Butyl hydroperoxide
EDTA = Ethylene diamine tetraacetic acid
IAA= Isoascorbic acid
PEM = phosphoethyl methacrylate
BA = Butyl acrylate
MMA = Methyl methacrylate
MAA = Glacial methacrylic acid
ALMA = Allyl methacrylate
DI water = Deionized water
SDS = sodium dodecylbenzene sulfonate

Preparation of Encapsulating Polymer Intermediates

Intermediate 1 – Preparation of an Aqueous Dispersion of Fully Polymer Encapsulated TiO_2 Particles, $T_g = 5$ °C

An aqueous dispersion of fully polymer encapsulated TiO_2 particles (the fully encapsulated composite) was prepared substantially in accordance with the following procedure: To a 500-mL four-necked round bottom flask equipped with paddle stirrer, N_2-inlet, reflux condenser, heating mantel, and thermocouple was charged TiO_2-amphoteric polymer slurry (prepared essentially as described in US Pat. Pub. 20100/298483, Example 1; 197.3 g, 73% solids) along with a solution of SDS (1.5 g) mixed in DI water (10 g) and a separate solution of SSS (1.2 g in 10 g DI water). The flask was purged with N_2, and heated to 50 °C, at which time aqueous solutions of 0.1% iron(II) sulfate (4.0 g) and 1 % EDTA (0.4 g) were combined and added to the flask. Two minutes later, co-feed #1 (BHP (1.6 g) dissolved in DI water (25 g) and co-feed #2 (IAA (0.9 g) dissolved in DI water (25 g) were fed to the flask at a rate of 0.25 g/min. Two minutes after the onset of the co-feed solution addition, a monomer emulsion (ME 1) prepared by mixing DI water (6.0 g), SDS (0.75 g), BA (16.8 g), MMA (11.25 g), MAA (0.29 g) and ALMA (0.14 g) was fed to the reactor at a rate of 2.0 g/min at a temperature of 50 °C. When the ME 1 addition was complete, a second monomer emulsion (ME 2) that was prepared previously by mixing DI water (19.0 g), SDS (2.25 g), BA (50.4 g), MMA (33.6 g), and MAA (0.86 g) was fed to the reactor at a rate of 2.0 g minute at 50 C along with the continuation of co-feeds #1 and #2. When ME 2 was complete the co-feed additions were continued for another 20 min until completion. The contents of the reactor were then cooled to room temperature after which time aqua ammonia (1.5 g, 28%) was added. The contents of the reactor were then filtered to remove any gel. The filtered dispersion was found to have a solids content of 61.5% with 0.01 g (~ 23 ppm) of dry gel removed.

Intermediate 2 – Preparation of an Aqueous Dispersion of Fully Polymer Encapsulated TiO_2 Particles, $T_g = 27$ °C

An aqueous dispersion of the fully encapsulated composite was prepared substantially in accordance with the following procedure: To a 500-mL four-necked round bottom flask equipped with paddle stirrer, N_2-inlet, reflux condenser, heating mantel, and thermocouple was charged TiO_2-amphoteric polymer slurry (197.3 g, 73% solids) along with a solution of SDS (1.5 g) mixed in DI water (10 g) and a separate solution of SSS (1.2 g in 10 g DI water). The flask was purged with N_2, and heated to 50 °C, at which time aqueous solutions of 0.1% iron(II) sulfate (4.0 g) and 1 % EDTA (0.4 g) were combined and added to the flask. Two minutes later, co-feed #1 (BHP (1.6 g) dissolved in DI water (25 g) and co-feed #2 (IAA (0.9 g) dissolved in DI water (25 g) were fed to the flask at a rate of 0.25 g/min. Two minutes after the onset of the co-feed solutions addition, a monomer emulsion (ME 1) prepared by mixing DI water (6.0 g), SDS (0.75 g), BA (13.0 g), MMA (15.1 g), MAA (0.29 g) and ALMA (0.14 g) was fed to the reactor at a rate of 2.0 g/min at a temperature of 50 °C. When the ME 1 addition was complete, a second monomer emulsion (ME 2) that was prepared by mixing DI water (19.0 g), SDS (2.25 g), BA (39.0 g), MMA (44.5 g), and MAA (0.86 g) was fed to the reactor at a rate of 2.0 g minute at 50 C along with the continuation of co-feeds #1 and #2. When ME 2 was complete, the co-feed additions were continued for another 20 min until completion. The contents of the reactor were then cooled to room temperature, after which time aqua ammonia (1.5 g, 28%) was added. The contents of the reactor were then filtered to remove any gel. The filtered dispersion was found to have a solids content of 60.5% with 0.01 g (~ 56 ppm) of dry gel removed.

Intermediate 3 – Preparation of an Aqueous Dispersion of Fully Polymer Encapsulated TiO_2 Particles, $T_g = 42$ °C

An aqueous dispersion of the fully encapsulated composite was prepared substantially in accordance with the following procedure: To a 500-mL four-necked round bottom flask equipped with paddle stirrer, N_2-inlet, reflux condenser, heating mantel, and thermocouple was charged TiO_2-amphoteric polymer slurry (197.3 g, 73% solids) along with a solution of SDS (1.5 g) mixed in DI water (10 g) and a separate solution of SSS (1.2 g in 10 g DI water). The flask was purged with N_2, and heated to 50 °C, at which time aqueous solutions of 0.1% iron(II) sulfate (4.0 g) and 1 % EDTA (0.4 g) were combined and added to the flask. Two minutes later, co-feed #1 (BHP (1.6 g) dissolved in DI water (25 g) and co-feed #2 (IAA (0.9 g) dissolved in DI water (25 g) were fed to the flask at a rate of 0.25 g/min. Two minutes after the onset of the co-feed solution addition, a monomer emulsion (ME 1) prepared by mixing DI water (6.0 g), SDS (0.75 g), BA (12.8 g), MMA (15.4 g), MAA (0.14 g) and ALMA (0.14 g) was fed to the reactor at a rate of 2.0 g/min at a temperature of 50 °C. When the ME 1 addition was complete, a second monomer emulsion (ME 2) that was prepared by mixing DI water (19.0 g), SDS (2.25 g), BA (29.9 g), MMA (46.6 g), AAEM (6.4 g) and MAA (2.7 g) was fed to the reactor at a rate of 2.0 g minute at 50 °C along with the continuation of co-feeds #1 and #2. When ME 2 was complete, the co-feed additions were continued for another 20 min until completion. The contents of the reactor were then cooled to room temperature, after which time aqua ammonia (2.5 g, 28%) was added. The contents of the reactor were then filtered to remove any gel. The filtered dispersion was found to have a solids content of 60.5% with 0.01 g (~ 51 ppm) of dry gel removed.

Differential Scanning Calorimetry

T_gs for the encapsulating polymers of Intermediates 1 – 3 were determined using differential scanning calorimetry (DSC) as follows: The samples were dried overnight in an oven at 60 °C before T_g measurement by temperature-modulated DSC. The temperature of each sample was ramped to 150 °C at a heating rate of 20 C°/min, and equilibrated at 150 °C for 5 min. The T_gs were taken as the inflection point of the second heating scan from -90 °C to 200 °C at a heating rate of 7 C°/min. The degree of modulation was set at ±1 C°, every 40 s.

Paint Formulations

A typical industrial paint formulation containing TiO_2 pigments and polyurethane dispersions was used in this study. The solid content of the encapsulating polymer dispersion was typically from 59-61%.

The gloss values were obtained according to ASTM D523 - 89(1999) Standard Test Method for Specular Gloss. Drawdowns over chromate pre-treated aluminum panels were prepared using 10-mil Dow Latex Film Applicator, and allowed to dry in the constant temperature room. The gloss measurement was performed using micro-TRI-gloss meter from BYK Gardner after 1 day, 7 days, and 1 month on the same drawdowns. Each value reported here is an average over three measurements on different positions of the same drawdown on the same date.

The description of the paint formulations including PVC, T_g of the encapsulating polymer, and component amounts by weight percent are shown in Tables 1 and 2. C1 – C9 refer to Comparative Examples 1 – 9; Encapsulating Polymer refers to Intermediates 1, 2, or 3, as evident by the T_g; Acrylic Polymer 1 is RHOPLEX ™ VSR-2015 Acrylic Emulsion Polymer; Acrylic Polymer 2 is RHOPLEX™ AC-261LF Acrylic Emulsion Polymer; Acrylic Polymer 3 is RHOPLEX™ HG-98B Acrylic Emulsion Polymer; PUD is Sancure 815 Aliphatic Waterborne Polyurethane Dispersion; Defoamer is Foamex 1488 Defoamer; TiO_2 is Ti-Pure R-746 TiO_2; Coalescent is Texanol ester alcohol; RM1 is ACRYSOL™ RM-2020NPR Rheology Modifier; and RM2 is ACRYSOL™ RM-8W Rheology Modifier. (RHOPLEX and ACRYSOL are Trademarks of The Dow Chemical Company or Its Affiliates.)

Table 1 – Paint Formulations

Example #	1	2	3	C1	C2	C3	C4	C5
PVC	17	19	8	17	19	20	20	8
T_g (°C)	5	27	5				42	42
Intermediate 1	67.44		33.59					
Intermediate 2		67.85						
Intermediate 3							71.17	30.62
Acrylic Polymer 1			27.75	39.28				
Acrylic Polymer 2					38.04			
Acrylic Polymer 3						41.83		28.35
PUD	24.03	23.26	28.96	24.05	23.29	23.05	23.02	33.47
Defoamer	0.20	0.20	0.09	0.20	0.20	0.18	0.09	0.08
TiO_2				27.05	29.05	30.29		
$NaNO_3$ (15%)	0.87	0.86	1.08	0.87	0.86	0.85	0.85	0.88
Coalescent						2.23	2.23	2.74
RM1	0.91	0.89	1.22	0.91	0.90	0.76	0.76	0.92
RM2	0.31	0.30	0.65	0.31	0.30	0.19	0.19	0.48
Water	6.34	6.74	6.66	7.33	7.38	0.61	1.70	2.46
Totals	100	100	100	100	100	100	100	100

Table 2 – Paint Formulations

Example #	4	C6	5	C7	1	C1	6	C8	7	C9
PVC	21	21	19	19	17	17	15	15	13	13
T_g (°C)	5		5		5		5		5	
Intermediate 1	52.90		60.49		67.44		73.71		79.50	
Acrylic Polymer 1		30.84		35.27		39.28		42.99		46.38
PUD	43.99	44.05	33.53	33.59	24.03	24.05	15.32	15.35	7.34	7.36
Defoamer	0.20	0.20	0.20	0.20	0.20	0.20	0.19	0.20	0.19	0.18
TiO_2		21.20		24.24		27.05		29.55		31.88
$NaNO_3$ (15%)	0.90	0.90	0.88	0.89	0.87	0.87	0.86	0.86	0.85	0.85
RM1	0.94	0.94	0.92	0.93	0.91	0.91	0.90	0.90	0.88	0.89
RM2	0.32	0.32	0.31	0.31	0.31	0.31	0.30	0.30	0.30	0.30
Water	0.75	1.55	3.66	4.58	6.34	7.33	8.72	9.85	10.94	12.16
Totals	100	100	100	100	100	100	100	100	100	100

Table 3 illustrates gloss and gloss retention for paints formulated using polyurethane dispersions (PUDs) and dispersions of TiO_2 that are either: a) unencapsulated (Comp. Examples 1 – 3); or b) encapsulated and with an acrylic polymer (Comp. Example 4 and Examples 1 and 2). The PUD was Sancure 815 Waterborne Urethane Polymer Dispersion; the weight-to-weight ratio of acrylic solids to PUD solids was 70:30; the coalescent was Taxanol ester alcohol; and "NA" means not applicable (since C1 –C3 were prepared without encapsulation of TiO_2).

Table 3 – Gloss and Gloss Retention for Polymer Encapsulated and Unencapsulated TiO_2 Particles

Ex #	Coalescent level (%)	PVC	T_g °C	20° Gloss			60° Gloss		
				1-day	7-day	1-mo	1-day	7-day	1-mo
C1	0	17	NA	24.1	20.9	20.5	62.8	60.2	59.9
C2	0	19	NA	28.1	26.9	25.5	65.5	64.5	62.9
C3	8.3	20	NA	23	18.6	17.1	60.5	56.8	55.2
C4	8.3	20	42	22.2	23.5	23.4	56.1	57.3	57.5
1	0	17	5	42.5	43.4	43.4	71.3	72.0	72.0
2	0	19	27	43.6	44.0	44.4	71.0	70.9	70.8

The data from Table 3 show that both 20° and 60° gloss is markedly lower for the comparative examples C1 to C4; for the formulations containing unencapsulated TiO_2 (C1 to C3), the gloss drifts downward; Comparative Example 4, which includes pigment particles encapsulated with above ambient temperature T_g encapsulating polymer. Only the formulations with pigment particles encapsulated with the softer encapsulating polymer (ambient temperature or below) show both high gloss and retained gloss.

Table 4 illustrates gloss improvement for a low T_g encapsulating polymer with respect to a high T_g encapsulating polymer at low PVC.

Table 4 – Gloss and Gloss Retention for a low PVC Composition

Ex #	Coalescent level (%)	PVC	T_g °C	20° Gloss			60° Gloss		
				1-day	7-day	1-mo	1-day	7-day	1-mo
C5	8.3	8	42	42.4	43.2	43.2	71.5	71.9	71.9
3	0	8	5	57.3	57.3	57.7	79.2	79.4	79.3

The formulation of Comparative Example 5 (C5), which uses the high T_g polymer encapsulated TiO_2, shows a reduced gloss as compared to the formulation of Example 3, which shows improved gloss over the comparative example.

Table 5 illustrates the effect of Acrylic:PUD weight-to-weight ratio on gloss and gloss retention. T_g for the encapsulating polymer was 5 °C. Comparative examples C1, and C6 – C9 are unencapsulated TiO_2.

Table 5 – Effect of Acrylic:PUD ratio on Gloss and Gloss Retention

Ex #	Acrylic/PUD Blend Ratio	PVC	20^0 Gloss			60^0 Gloss		
			1-day	7-day	1-mon	1-day	7-day	1-mon
C6	90:10	21	14.6	13.5	14.0	55.3	54.2	54.5
4	90:10	21	34.2	35.2	36.2	66.3	66.9	67.3
C7	80:20	19	16.6	14.7	14.0	56.5	54.8	53.9
5	80:20	19	39.8	40.1	40.4	69.1	69.6	69.7
C1	70:30	17	24.1	20.9	20.5	62.8	60.2	59.9
1	70:30	17	42.5	43.4	43.4	71.3	72.0	72.0
C8	60:40	15	32.2	30.3	29.2	67.6	66.4	65.6
6	60:40	15	49.8	50.4	50.3	75.6	76.0	75.8
C9	50:50	13	42.0	39.5	39.0	73.0	71.8	71.1
7	50:50	13	54.5	53.8	53.4	78.7	78.3	77.9

The data show gloss retention and gloss improvement over unencapsulated TiO_2 through a broad range of acrylic:PUD.

Claims:

1. A composition comprising a stable aqueous dispersion of polyurethane particles and pigment particles partially or fully encapsulated with a soft polymer having a T_g not higher than 35 °C; wherein the weight percent of the polyurethane particles, based on the weight of the polyurethane particles and the soft polymer, is such that the pigment volume concentration of the composition is in the range of 6 to 25.

2. The composition of Claim 1 wherein the weight percent of polyurethane particles is from 10 to 70 weight percent, based on the weight of the polyurethane particles and the soft polymer, the pigment particles are fully encapsulated with the soft polymer having a shell thickness in the range of from 10 nm to 90 nm and a T_g of not greater than 30 °C.

3. The composition of either of Claims 1 or 2 wherein the soft polymer is an acrylic, styrene-acrylic, or vinyl acrylic polymer.

4. The composition of any of Claims 1 to 3 wherein the weight percent of polyurethane particles is from 20 to 50 weight percent, based on the weight of the polyurethane particles and the soft polymer.

5. The composition of any of Claims 2 to 4 wherein the soft encapsulating polymer is an acrylic or styrene acrylic copolymer than contains structural units of a) methyl methacrylate or styrene; b) butyl acrylate and c) sodium styrene sulfonate.

6. The composition of any of Claims 1 to 5 which is substantially free of volatile organic solvents.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/026388

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09C1/36 C09C3/10 C09D5/02 C09D7/12 C09D133/08 C09D133/12 C09D175/04

ADD. C08F220/14 C08K9/10 C08F220/18

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)

C09C C08F C09D C08K

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 7 179 531 B2 (BROWN WARD THOMAS [US] ET AL) 20 February 2007 (2007-02-20) cited in the application column 2, lines 39-52 column 9, lines 5-24 column 25, lines 3-25; claims 2-4; examples 1,2 column 10, lines 21-24 -----	1-6
X	US 2010/298483 A1 (ALLEN NATHAN T [US] ET AL) 25 November 2010 (2010-11-25) cited in the application paragraphs [0014], [0016], [0020], [0038]; examples 7-11 ----- -/--	1-6

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 24 June 2013	Date of mailing of the international search report 04/07/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Krätzschmar, Ulrike

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/318596 A1 (FU ZHENWEN [US] ET AL) 24 December 2009 (2009-12-24) cited in the application examples 1-13 -----	1-6
E	EP 2 578 647 A1 (ROHM & HAAS [US]) 10 April 2013 (2013-04-10) claims 1,6-8 -----	1-6

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7179531 B2	20-02-2007	AR 041114 A1	04-05-2005
		AU 2003243988 A1	01-04-2004
		BR 0303452 A	08-09-2004
		CA 2439338 A1	12-03-2004
		CN 1488693 A	14-04-2004
		EP 1398333 A1	17-03-2004
		JP 3717501 B2	16-11-2005
		JP 4468249 B2	26-05-2010
		JP 2004099901 A	02-04-2004
		JP 2005336498 A	08-12-2005
		KR 20040024507 A	20-03-2004
		MX PA03007953 A	15-10-2004
		NZ 527905 A	27-08-2004
		NZ 533653 A	29-07-2005
		SG 132502 A1	28-06-2007
		TW I246518 B	01-01-2006
		US 2004054063 A1	18-03-2004
US 2010298483 A1	25-11-2010	AU 2010347747 A1	20-09-2012
		CN 101891971 A	24-11-2010
		EP 2253677 A1	24-11-2010
		SG 183520 A1	30-10-2012
		US 2010298483 A1	25-11-2010
		WO 2011112171 A1	15-09-2011
US 2009318596 A1	24-12-2009	AT 546472 T	15-03-2012
		BR PI0904407 A2	21-09-2010
		EP 2133376 A1	16-12-2009
		US 2009318596 A1	24-12-2009
EP 2578647 A1	10-04-2013	AU 2012233014 A1	18-04-2013
		CN 103031013 A	10-04-2013
		EP 2578647 A1	10-04-2013
		US 2013085222 A1	04-04-2013