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61492561 2 June 2011 (02.06.2011) US(71) Applicant (for all designated States except US): **ROHM AND HAAS COMPANY** [US/US]; 100 Independence Mall West, Philadelphia, PA 19106 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AULD, Kathleen** [US/US]; 1307 West Pine Street, Feasterville, PA 19053 (US). **BROWN, Ward Thomas** [US/US]; 1203 Barbara's Court, North Wales, PA 19454 (US).(74) Agent: **WILLIS, Reid**; Rohm and Haas Company, 100 Independence Mall West, Philadelphia, PA 19106 (US).

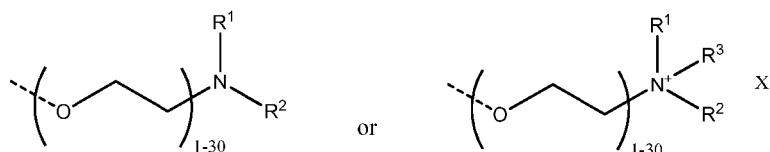
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(54) Title: AMPHOTERIC POLYMER COMPOSITION



(57) Abstract: The present invention relates to a composition comprising an amphoteric polymer having pendant acid groups, or salts thereof, and pendant mono- or dialkylamino ethylene oxide groups or alkylammonium ethylene oxide groups characterized by either of the following formulas: where R1-R3 and X- are as defined herein. The composition of the present invention improves hiding efficiency for coating compositions formulated using associative rheology modifiers, binders, and titanium dioxide.

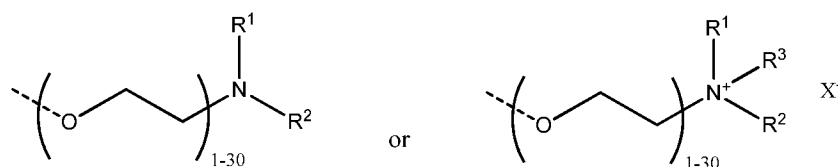
AMPHOTERIC POLYMER COMPOSITION

Background of the Invention

The present invention relates to an amphoteric polymeric composition useful in coatings formulations. Paints containing associative rheology modifiers such as hydrophobically modified ethylene oxide urethane (HEUR), hydrophobically modified alkali soluble emulsion (HASE), and, hydrophobically modified hydroxyethyl cellulose (HMHEC) thickeners cause titanium dioxide (TiO₂) particles to self-associate (crowd), which reduces hiding efficiency as compared to compositions thickened with non-associative thickeners. This crowding effect occurs because associative rheology modifiers create a network with the binder in the paint system, thereby pushing TiO₂ particles closer together. It would therefore be desirable to discover a way to improve the hiding efficiency of coatings formulated with associative rheology modifiers.

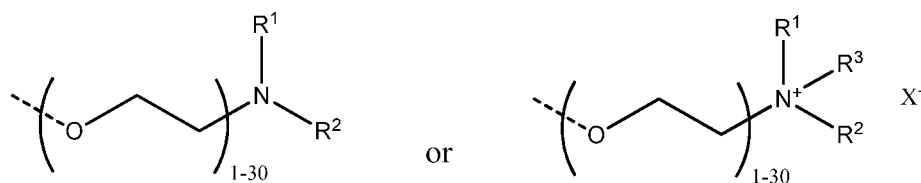
Summary of the Invention

The present invention addresses a need in the art by providing a composition comprising an amphoteric polymer having pendant acid groups, or salts thereof, and pendant mono- or dialkylamino ethylene oxide groups or alkylammonium ethylene oxide groups characterized by either of the following formulas:



where R¹ and R³ are each independently hydrogen or –C₁–C₁₂–alkyl; and R² is C₃–C₁₂ alkyl, and X[–] is a counterion.

In another aspect, the present invention is an aqueous composition comprising a rheology modifier, titanium dioxide particles, a latex binder, and a composition comprising an amphoteric polymer having pendant acid groups, or salts thereof, and pendant mono- or dialkylamino ethylene oxide groups or alkylammonium ethylene oxide groups characterized by either of the following formulas:

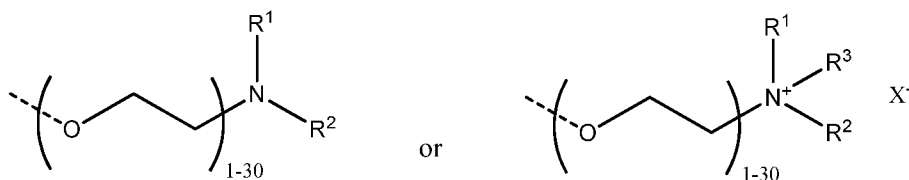


where R^1 , R^2 , R^3 , and X^- are as previously defined.

The present invention addresses a need in the art by providing a way to improve the hiding efficiency compositions containing TiO_2 and associative rheology modifiers.

5 Detailed Description of the Invention

In a first aspect, the present invention is a composition comprising an amphoteric polymer having pendant acid groups, or salts thereof, and pendant mono- or dialkylamino ethylene oxide groups or alkylammonium ethylene oxide groups characterized by either of the following formulas:



Ia

Ib

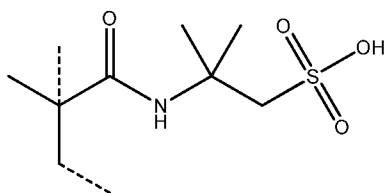
where R^1 and R^3 are each independently hydrogen or $-C_1-C_{12}$ -alkyl; R^2 is C_3-C_{12} alkyl; and X^- is a counterion. Examples of suitable alkyl groups include *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-octyl, *n*-decyl, and 2-ethylhexyl groups.

15 As used herein, the term “pendant acid groups” refers to pendant carboxylic acid, phosphorus acid, or sulfur acid groups or salts thereof; pendant sulfur acid groups refer to $S(O)_2(OH)$, $-OS(O)(OH)$, $-OS(O)(OH)$, or $-S(O)(OH)$ groups, or salts thereof, preferably structural units of one or more sulfur acid monomers, examples of which include
 20 sulfoethyl (meth)acrylate, sulfopropyl (meth)acrylate, styrene sulfonic acid, vinyl sulfonic acid, and 2-(meth)acrylamido-2-methyl propanesulfonic acid, and salts thereof, with 2-acrylamido-2-methyl propanesulfonic acid (AMPS) and salts thereof being

preferred. Examples of suitable phosphorus acid monomers include dihydrogen phosphate esters of an alcohol in which the alcohol contains or is substituted with a polymerizable vinyl or olefinic group. A class of such monomers includes phosphates of hydroxyalkyl(meth)acrylates such as 2-hydroxyethyl (meth)acrylate, 3-hydroxypropyl (meth)acrylates. Another example of a phosphorus acid monomer is 2-(methacryloyloxy)ethyl-2-(trimethylammonio) ethyl phosphate. Examples of suitable carboxylic acid monomers include (meth)acrylic acid and itaconic acid.

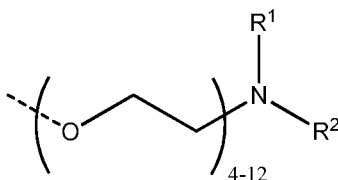
As used herein, the term “(meth)acrylic” refers to acrylic or methacrylic; similarly, the term “(meth)acrylamido” refers to acrylamido or methacrylamido.

- 10 The term “structural units” is used herein to refer to the groups that are formed by the polymerization of the corresponding polymer. Thus, a structural unit of 2-(meth)acrylamido-2-methyl propanesulfonic acid is illustrated below:



where the dotted lines indicate the point of attachment to the polymer backbone.

- 15 In one particular embodiment, the dispersant contains pendant groups having the following formula:



where R^1 and R^2 are each independently C_3 - C_8 -alkyl. In another embodiment, R^1 and R^2 are each *n*-butyl; and structural units of 2-(meth)acrylamido-2-methyl propanesulfonic acid.

The amphoteric polymer can be conveniently prepared by contacting together a) a dialkylamino polyethyleneoxide(1-30) (meth)acrylate monomer, preferably a dialkylamino polyethyleneoxide(3-20) (meth)acrylate monomer, more preferably a dialkylamino polyethyleneoxide(4-12) (meth)acrylate monomer, with b) an acid monomer, preferably a sulfur acid monomer, in the presence of water and a suitable initiator under polymerization conditions. The mole:mole ratio of the dialkylamino polyethyleneoxide methacrylate monomer to acid monomer is typically in range of from 1:20 to 1:1. The amphoteric polymer may also be prepared with additional monomers including (meth)acrylate, styrene, or vinyl ester monomers or combinations thereof.

It is preferred that the weight percent of the acid groups is not less than 15 weight percent, more preferably not less than 30 weight percent, most preferably not less than 50 weight percent, and preferably not more than 95 weight percent, based on the weight of the polymer. The weight average molecular weight (M_w) of the dispersant is typically in the range of from 1000 to 25,000 Daltons.

The amphoteric polymer of the present invention is a dispersant particularly suitable for pigments in a coating containing an associative thickener (e.g., HEUR, HASE, and HMHEC thickeners), although in principle, it can be used for non-associative thickeners such as HEC thickeners. Although not bound by theory, it is believed that the dispersant is effective in improving hiding because of its strong affinity for the surface of the TiO_2 and a hydrophobic portion that interacts with the hydrophobic portion of the associative thickener or latex surface. Accordingly, the dispersant of the present invention provides a network between the TiO_2 particle, rheology modifier and latex that creates more ideally spaced TiO_2 particles with concomitant improvement in hiding.

The present invention is also an aqueous composition comprising a rheology modifier, titanium dioxide particles, the dispersant of the present invention, and a latex binder. The rheology modifier may be any rheology modifier or mixtures thereof, including associative thickeners (e.g., HEURs, HASEs, and HMHECs); as well as non-associative thickeners (e.g., alkali soluble emulsions (ASEs); cellulose such as hydroxyethylcelluloses (HECs), hydroxymethylethylcelluloses (HMECs), and

hydroxypropylcelluloses (HPCs); and synthetic clays such as Laponite. The aqueous composition may also include any of a number of materials including opaque polymers; fillers; pigments, including encapsulated or partially encapsulated pigments and opaque pigments; other dispersants; other rheology modifiers; surfactants; defoamers; 5 preservatives; flow agents; leveling agents; slip ads; and neutralizing agents.

Examples

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

Intermediate 1: Preparation of Dibutylamino-polyethyleneoxide(4)-methacrylate

10 Monomer

Methacrylic anhydride (10 g, 65 mmol.), (4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (4-Hydroxy TEMPO, 0.005 g, 0.03 mmol), and dibutylamino-polyethyleneoxide(4)-alcohol (19.8 g, 65 mmol) were added to a 2-oz glass jar and mixed. The contents of the jar were heated at 50 °C for 1 h. Analysis by ¹H NMR 15 spectroscopy showed 80% conversion to Dibutylamino-polyethyleneoxide(4)-methacrylate.

Intermediate 2: Preparation of Dibutylamino-polyethyleneoxide(1)-methacrylate

Monomer

Methacrylic anhydride (10 g, 65 mmol.), (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl 20 (4-Hydroxy TEMPO, 0.015 g, 0.10 mmol), and dibutylamino-polyethyleneoxide(1)-alcohol (11.2 g, 65 mmol) were added to a 2-oz glass jar and mixed. The contents of the jar were heated at 60 °C overnight. Analysis by ¹H NMR spectroscopy showed near complete (>99%) conversion to Dibutylamino-polyethyleneoxide(1)-methacrylate.

Intermediate 3: Preparation of Dibutylamino-polyethyleneoxide(20)-methacrylate Monomer

Methacrylic anhydride (3.05 g, 20 mmol.), (TEMPO, 0.005 g, 0.03 mmol), and dibutylamino-polyethyleneoxide(20)-alcohol (20 g, 20 mmol) were added to a 2-oz glass jar and mixed. The contents of the jar were heated at 60 °C overnight. Analysis by ¹H NMR spectroscopy showed near complete (>99%) conversion to Dibutylamino-polyethyleneoxide(20)-methacrylate.

Example 1: HEUR-Thickened Paint Composition with TiO₂

A. Polymer Dispersant Synthesis

2-Acrylamido-2-methylpropane sulfonic acid (12.60 g, 61 mmol), dibutylamino-polyethyleneoxide(4)-methacrylate (7.40 g, 20 mmol), 3-mercapto-1 propanol (0.20 g, 2 mmol), Vazo 56 initiator (0.22 g, 1 mmol), and DI Water (27.54 g) were added to a 100-mL round bottom four neck flask ("Flask A") with a Teflon stir bar. The contents of Flask A were dissolved and purged with nitrogen. Flask A was heated to 47.5 °C then heating was removed and the reaction allowed to exotherm to 75 °C and maintained at this temperature for 2 h. Vazo 56 initiator (0.11 g, 0.4 mmol) and DI Water (2.00 g) were added to a 1-oz vial and mixed. Flask A was heated to 82 °C and the contents of the vial were added to the flask and allowed to mix for 1 h at 82 °C. Flask A was cooled to 25 °C. A portion of the sample (25 g) was removed from Flask A and placed into a 4-oz jar, after which DI water (26.25 g) and ammonium hydroxide (2.36 g, 28%) were added to the contents of the 4-oz jar with stirring; the pH was measured to be 3.65 and the percent solids of the material was 21%.

B. Titanium Dioxide Dispersion

DI water (94.66 g) and the polymer dispersant from step A (28.68 g) were added to a grind pot; the grind pot was placed on a high speed dispersator and Ti-Pure R-706 TiO₂ (402 g) was added slowly with mixing. The contents in the grind pot were mixed at high speed for 15 min. The TiO₂ dispersion was filtered through a 325 mesh bag.

C. Paint with Titanium Dioxide Dispersion Containing HEUR Thickeners

RHOPLEX™ SG-10M Acrylic Latex (A Trademark of the Dow Chemical Company or its Affiliates, 55.57 g), the titanium dioxide dispersion from step B, (24.44 g, 16 pigment volume concentration (PVC)), Texanol coalescent (2.22 g), ACRY SOL™ RM-2020NPR Rheology Modifier (A Trademark of the Dow Chemical Company or its Affiliates, 1.00 g), ACRY SOL™ RM-8W Rheology Modifier (A Trademark of The Dow Chemical Company or its Affiliates, 0.13 g), and DI Water (17.05 g) were added one at a time while mixing with an overhead stirrer to a ¼-pint container and mixed for 15 min.

Example 2: HEUR-Thickened Paint Composition with TiO₂

10 A. Polymer Dispersant Synthesis

2-Acrylamido-2-methylpropane sulfonic acid (2.40 g, 12 mmol),
2-(methacryloyloxy)ethyl-2-(trimethylammonio) ethyl phosphate (1.00 g, 3 mmol),
dibutylamino-polyethyleneoxide(4)-methacrylate (1.60 g, 4 mmol), 3-mercapto-1
propanol (0.05 g, 0.5 mmol), Vazo 56 initiator (0.06 g, 0. 2 mmol), and DI Water (6.89 g)
15 were added to a 25-mL round bottom four neck flask ("Flask A") with a Teflon stir bar.
The contents of Flask A were dissolved and purged with nitrogen. Flask A was heated to
73 °C and held for 2 h. Vazo 56 initiator (0.03g, 0. 1 mmol) and DI water (0.5 g) were
added to a 1-oz vial and mixed. Flask A was heated to 82 °C and the contents of the vial
were added to the flask and allowed to mix for 1 h at 82 °C. Flask A was then cooled to
20 25 °C. DI water was added to the contents of Flask A reduce solids content to 20.3% and
ammonium hydroxide (28%) was added to bring the pH to 3.7.

B. Titanium Dioxide Dispersion

DI water (68.06 g) and the polymer dispersant prepared in step A (16.99 g) were added to
a grind pot, which was placed on a high speed dispersator. Titanium Dioxide (Ti-Pure R-
25 706, 230 g) was added slowly to the grind pot with mixing at a high speed for 15 min.
The TiO₂ dispersion was filtered though a 325 mesh bag.

C. Paint with Titanium Dioxide Dispersion Containing HEUR Thickener

RHOPLEX SG-10M Acrylic Latex (55.57 g), Titanium Dioxide dispersion from step B (25.61 g, 16 PVC), Texanol coalescent (2.22 g), ACRY SOL RM-2020NPR Rheology Modifier (1.00 g), ACRY SOL RM-8W Rheology Modifier (0.13 g), and DI Water (16.55 g) were added separately to a ¼ -pint container with mixing for 15 min.

Example 3: HEUR and HEC Thickened Paint Compositions with TiO₂

A. Polymer Dispersant Synthesis

Polymerization was done on a commercially available high throughput polymerization reactor (ScPPR reactor). Amounts and concentration of feeds included DI water: (0.717 g); 2-acrylamido-2-methylpropane sulfonic acid solution in water (5.45 g, 40 wt% solution); dibutylamino-polyethyleneoxide(1)-methacrylate solution in dimethylformamide (DMF) (1.64 g, 50 wt%) solution 3-mercapto-1-propanol in DMF (0.33 g, 9.1 wt% solution); and 2,2,-Azobis(2-methylpropionamidine)dihydrochloride in water (0.33 g, 9.1 wt% solution). The reactor cell was purged with nitrogen followed by an initial charge of water and 10% of monomer, chain transfer agent, and initiator feeds. The temperature was increased to 80 °C, stirring set at 400 rpm and 10 psig of pressure of nitrogen. The remaining 90% of monomer, chain transfer agent and initiator feeds were fed in a series of automated steps over a period of 100 min. A second initiator feed, 2, 2,-Azobis (2-methylpropionamidine) dihydrochloride (0.165 g, 9.1 wt% aqueous solution) was added in 1 shot and the reactor temperature was raised to 85 °C. Stirring was continued for another 30 min after which time the reactor was cooled to room temperature. The pH of the reaction vial was adjusted to pH 8-9 with 28% ammonium. Polymer was precipitated in THF and dried *in vacuo* at 60 °C for 4 days.

B. Titanium Dioxide Dispersion

DI water (14.20 g) and the polymer dispersant prepared in step A (0.59 g) were added to a 60-g capacity mixing cup. Titanium Dioxide (Ti-Pure R-706, 39.49 g) was added to the mixing cup and mixed using a SpeedMixer mixer at a high speed for 3 min.

C. Paint with Titanium Dioxide Dispersion Containing HEUR Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), ACRY SOL RM-2020NPR Rheology Modifier (2.00 g), ACRY SOL RM-8W Rheology Modifier (0.26 g), and DI Water (31.64 g) were added separately to a ½ -pint container with mixing for 10 min.

D. Paint with Titanium Dioxide Dispersion Containing HEC Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), Natrosol 250 MHR hydroxyethylcellulose (HEC, 0.86 g), and DI water (32.94 g) were added separately to a ½ -pint container with mixing for 10 min.

Example 4: HEUR and HEC Thickened Paint Compositions with TiO₂

A. Polymer Dispersant Synthesis

Polymerization was done on a commercially available high throughput polymerization reactor. Amounts and concentration of feeds included: DI water (0.515 g); an aqueous solution of 2-acrylamido-2-methylpropane sulfonic acid solution (2.802 g, 40 wt%); dibutylamino-polyethyleneoxide(20)-methacrylate solution in DMF (4.06 g, 50 wt%); 3-mercapto-1-propanol in DMF (0.33 g, 9.1 wt%); and an aqueous solution of 2,2,-Azobis(2-methylpropionamidine)dihydrochloride (0.33 g of 9.1 wt%). The reactor cell was purged with nitrogen followed by an initial charge of water and 10% of monomer, chain transfer agent and initiator feeds. The temperature was increased to 80 °C, stirring set at 400 rpm and 10 psig of pressure of nitrogen. The remaining 90% of monomer, chain transfer agent and initiator feeds were fed in a series of automated steps over a period of 100 min. A second initiator feed of aqueous 2, 2,-Azobis (2-methylpropionamidine) dihydrochloride (0.165 g of 9.1 wt% solution) was added in 1 shot and the reactor temperature was raised to 85 °C. Stirring was continued for another 30 min after which time the reactor was cooled to room temperature. The pH of the reaction vial was adjusted to 8-9 with 28% ammonium hydroxide solution. Polymer was precipitated in THF and dried *in vacuo* at 60 °C for 4 days.

B. Titanium Dioxide Dispersion

DI water (14.20 g) and the polymer dispersant prepared in step A (0.59 g) were added to a 60-g capacity mixing cup. Titanium Dioxide (Ti-Pure R-706, 39.49 g) was added to the mixing cup and mixed on a SpeedMixer mixer at a high speed for 3 min.

5 C. Paint with Titanium Dioxide Dispersion Containing HEUR Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), ACRY SOL RM-2020NPR Rheology Modifier (2.00 g), ACRY SOL RM-8W Rheology Modifier (0.26 g), and DI Water (31.64 g) were added separately to a ½ -pint container with mixing for 10 min.

10 D. Paint with Titanium Dioxide Dispersion Containing HEC Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), 3.0% solution of Natrosol 250 MHR HEC (0.86 g), and DI water (32.94 g) were added separately to a ½ -pint container with mixing for 10 min.

15 Example 5: HEUR and HEC Thickened Paint Compositions with TiO₂

A. Polymer Dispersant Synthesis

Polymerization was done on a commercially available high throughput polymerization reactor. Amounts and concentration of feeds included: DI water (0.386 g); aqueous 2-acrylamido-2-methylpropane sulfonic acid solution (6.696 g, 40 wt% solution);
20 dibutylamino-polyethyleneoxide(4)-methacrylate solution in DMF (0.536 g, 60 wt% solution); 3-mercapto-1-propanol in DMF (0.33 g, 9.1 wt% solution); and aqueous 2,2,-Azobis(2-methylpropionamidine)dihydrochloride (33 g, 9.1 wt% solution). The reactor cell was purged with nitrogen followed by an initial charge of water and 10% of monomer, chain transfer agent, and initiator feeds. The temperature was increased to
25 80 °C, stirring set at 400 rpm and 10 psig of pressure of nitrogen. The remaining 90% of monomer, chain transfer agent, and initiator feeds were fed in a series of automated steps over a period of 100 min. A second initiator feed of aqueous 2, 2,-

Azobis (2-methylpropionamidine) dihydrochloride (0.165 g of 9.1 wt% solution) was added in 1 shot and the reactor temperature was raised to 85 °C. Stirring was continued for another 30 min, after which time the reactor was cooled to room temperature. The pH of the reaction vial was adjusted to 8-9 with 28% ammonium hydroxide. Polymer was precipitated in THF and dried *in vacuo* at 60 °C for 4 days.

B. Titanium Dioxide Dispersion

DI water (14.20 g) and the polymer dispersant prepared in step A (0.59 g) were added to a 60-g capacity mixing cup. Titanium Dioxide (Ti-Pure R-706, 39.49 g) was added to the mixing cup and mixed on a SpeedMixer mixer at a high speed for 3 min.

10 C. Paint with Titanium Dioxide Dispersion Containing HEUR Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), ACRY SOL RM-2020NPR Rheology Modifier (2.00 g), ACRY SOL RM-8W Rheology Modifier (0.26 g), and DI Water (31.64 g) were added separately to a ½ -pint container with mixing for 10 min.

15 D. Paint with Titanium Dioxide Dispersion Containing HEC Thickener

RHOPLEX SG-10M Acrylic Latex (111.36 g), Titanium Dioxide dispersion from step B (51.34 g, 16 PVC), Texanol coalescent (4.45 g), 3.0% solution of Natrosol 250 MHR HEC (0.86 g), and DI water (32.94 g) were added separately to a ½ -pint container with mixing for 10 min.

20 Comparative Example 1: HEUR-Thickened Paint Composition with TiO₂

RHOPLEX SG-10M Acrylic Latex (55.57g), Ti-Pure R-746 TiO₂ slurry (24.44 g, 16 PVC), Texanol coalescent (2.22 g), ACRY SOL RM-2020NPR Rheology Modifier (1.00 g), ACRY SOL RM-8W Rheology Modifier (0.13 g), and DI Water (17.05 g) were added separately to a ¼ pint container with mixing for 15 min.

25

Comparative Example 2: HEC-Thickened Paint Composition with TiO₂

RHOPLEX SG-10M Acrylic Latex (55.57 g), Ti-Pure R-746 TiO₂ slurry (24.44 g, 16 PVC), Texanol coalescent (2.22 g), Natrosol 250 MHR HEC (0.36 g), and DI Water (17.64 g) were added separately to a ¼ pint container with mixing for 15 min.

- 5 Following the Kubelka-Munk S/mil Test Method and using Equation 1 S/mil was calculated for each paint and results can be found in Table 1. The term AMPS:Amine molar ratio refers to the mole:mole ratio between the amount of AMPS and the amount of the amine added to the polymerization of the dispersant.

Table 1 – Comparison S/mil between Examples and Comparator

Example #	Description	Thickener	AMPS:Amine Molar Ratio	S/mil
1C	Paint with Example 1C TiO ₂ Dispersion	HEUR	3.8:1	6.36
2C	Paint with Example 2C TiO ₂ Dispersion	HEUR	2.8:1	6.37
3C	Paint with Example 3C TiO ₂ Dispersion	HEUR	3.8:1	6.35
4C	Paint with Example 4C TiO ₂ Dispersion	HEUR	3.1:1	7.27
5C	Paint with Example 5C TiO ₂ Dispersion	HEUR	18.4:1	7.11
3D	Paint with Example 3D TiO ₂ Dispersion	HEC	3.8:1	7.46
4D	Paint with Example 4D TiO ₂ Dispersion	HEC	3.1:1	7.58
5D	Paint with Example 5D TiO ₂ Dispersion	HEC	18.4:1	7.52
Comparative 1	Paint with Commercial TiO ₂ Dispersion	HEUR	-	4.65
Comparative 2	Paint with Commercial TiO ₂ dispersion	HEC	-	6.60

Table 1 shows that the HEUR-modified paint containing the dispersant of the present invention shows a marked improvement in hiding over a paint thickened with the same HEUR but containing a dispersant outside the scope of the present invention. The improvement for HEC-modified paint is manifest but not as pronounced.

5 Kubelka-Munk S/mil Test Method

Two draw-downs were prepared on Black Release Charts (Leneta Form RC-BC) for each paint using a 1.5-mil Bird draw down bar and the charts allowed to dry overnight. Using a template, 3.25" x 4" rectangles were cut out with an X-ACTO knife on each chart. The Y-reflectance was measured using a BYK Gardner 45° Reflectometer in each of the scribed areas five times measuring on a diagonal starting at the top of the rectangle and the average Y-reflectance recorded. A thick film draw down was prepared for each paint on Black Vinyl Charts (Leneta Form P121-10N) using a 3" 25 mil block draw down bar and the charts were allowed to dry overnight. The Y-reflectance was measured in five different areas of the draw down and the average Y-reflectance recorded. Kubelka-Munk hiding value S is given by Equation 1:

Equation 1

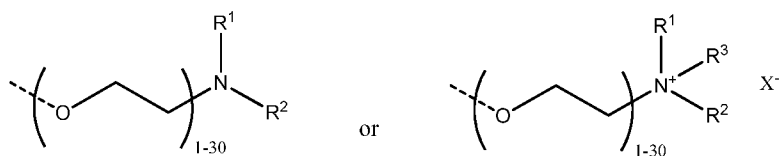
$$S = \frac{R}{X \times (1 - R^2)} \times \ln \frac{1 - (R_B \times R)}{1 - \frac{R_B}{R}}$$

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" x 4" template was 13 in².

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

Claims

1. A composition comprising an amphoteric polymer having pendant acid groups, or salts thereof, and pendant mono- or dialkylamino ethylene oxide groups or alkylammonium ethylene oxide groups characterized by either of the following formulas:

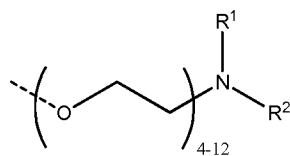


where R^1 and R^3 are each independently hydrogen or $-C_1-C_{12}$ -alkyl; R^2 is C_3-C_{12} alkyl, and X^- is a counterion.

2. The composition of Claim 1 wherein the pendant acid groups are sulfur acid groups.

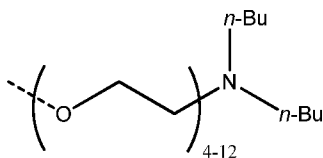
3. The composition of either of Claims 1 or 2 wherein the pendant acid groups are structural units of sulfoethyl (meth)acrylate, sulfopropyl (meth)acrylate, styrene sulfonic acid, vinyl sulfonic acid, or 2-(meth)acrylamido-2-methyl propanesulfonic acid, or salts thereof; and the pendant dialkyl amino ethylene oxide groups characterized by the following formula:

10



15 where R^1 and R^2 are each independently C_3-C_8 -alkyl.

4. The composition of any of Claims 1 to 3 wherein the pendant acid groups are structural units of 2-methacrylamido-2-methyl propanesulfonic acid or styrene sulfonic acid or a salt thereof; and the pendant dialkyl amino ethylene oxide groups characterized by the following formula:



where the mole:mole ratio of the structural units of 2-(meth)acrylamido-2-methyl propanesulfonic acid, or a salt thereof to dialkyl amino ethylene oxide groups is in the range of from 20:1 to 1:1.

- 5 5. The composition of any of Claims 1 to 4 wherein the weight percent of the pendant acid groups is from 50 to 95 weight percent, based on the weight of the amphoteric polymer.
6. An aqueous composition comprising a rheology modifier, titanium dioxide particles, a latex binder, and the composition of any of Claims 1 to 5.
- 10 7. The aqueous composition of Claim 6 wherein the rheology modifier is a HEUR thickener, a HASE thickener, or an HMHEC thickener.
8. The aqueous composition of Claim 6 wherein the rheology modifier is an HEC thickener.
9. The aqueous composition of any of Claims 6 to 8 which is a coating composition.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/039791

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G65/00
ADD.

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)
C08G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2012/081729 A1 (NIPPON CATALYTIC CHEM IND [JP]; YONEDA ATSURO [JP]; MICHITAKA DAISUKE) 21 June 2012 (2012-06-21) copolymers (1)-(14) prepared in examples 1-14; paragraphs [0035], [0036]; claims 1,2	1,5-9
X	Y. YAMAMOTO: "A novel macroinimer of polyethylene oxide: synthesis of hyper branched networks by photoinduced H-abstraction process", EUROPEAN POLYMER JOURNAL, vol. 39, 2003, pages 545-550, XP002681771,	1,5-9
A	"Results and discussion"; Scheme on page 548 table 2 page 549, left column	2-4
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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

14 August 2012

Date of mailing of the international search report

06/09/2012

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

Kositza, Matthias

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/039791

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	page 1, line 29; claims 1-17; examples 1-9 page 20, line 8 - line 21 -----	2-4
A	EP 0 593 151 A1 (ROHM & HAAS [US]) 20 April 1994 (1994-04-20) the whole document -----	1-9
A	JP 5 311194 A (NIPPON CATALYTIC CHEM IND) 22 November 1993 (1993-11-22) the whole document -----	1-9

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/039791

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