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(54) Titre : LIANTS D'ACETATE DE VINYLE DANS UNE COMPOSITION DE REVETEMENT A CONCENTRATION VOLUMIQUE EN PIGMENT SUR-CRITIQUE

(54) Title: VINYL ACETATE BINDERS IN ABOVE-CRITICAL PIGMENT VOLUME CONCENTRATION COATINGS COMPOSITION

(57) Abrégé/Abstract:
Above-critical coating composition comprises an aqueous dispersion of polymer particles, pigment particles, and extender particles wherein the polymer particles comprise, in a single phase and based on the weight of the polymer particles, from 35 to 79.9 weight percent structural units of vinyl acetate and from 0.1 to 6 weight percent structural units of a phosphorus acid monomer or a salt thereof, wherein the polymer particles have a particle size by dynamic light scattering of from 250nm to 500nm. The above-critical coating composition shows surprising improvements in hiding with increasing particle size of the polymer particles.

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VINYL ACETATE BINDERS IN ABOVE-CRITICAL PIGMENT VOLUME CONCENTRATION COATINGS COMPOSITION

Background of the Invention

The present invention relates to a coatings composition comprising a stable aqueous dispersion of vinyl acetate functionalized polymer particles adsorbed to pigment particles in an above-critical pigment volume concentration (PVC) paint formulation.

Coating formulations are complex mixtures of polymers particles (binder), pigments, extenders, and additives. The pigment of choice in most coatings formulations is TiO_2, which is effective for creating opacity, but expensive. The expense can be mitigated somewhat by functionalizing the binder with phosphate groups to promote adsorption of the binder particles to TiO2 particles to form composites with increased spacing between the pigment particles, thereby providing a mechanism for reducing the levels of expensive TiO2 to achieve the same degree of hiding.

Especially attractive binders for architectural coatings are vinyl acetate polymers and copolymers, which are known to have high scrub resistance at relatively low cost. Vinyl acetate polymers functionalized with phosphate groups are especially desirable as film-forming polymers due to the cost benefits provided by reduced TiO_2 usage. Cost benefits of vinyl acetate based paints are further realized in above critical paint formulations, which are widely used in spite of their relatively poor performance. It would desirable to improve performance, particularly hiding (opacity), in these above-critical vinyl acetate based paint formulations economically.

Summary of the Invention

The present invention addresses a need in the art by providing a coating composition comprising an aqueous dispersion of polymer particles, pigment particles, and extender particles wherein the polymer particles comprise, in a single phase and based on the weight of the polymer particles, from 35 to 79.9 weight percent structural units of vinyl acetate and from 0.1 to 6 weight percent structural units of a phosphorus acid monomer or a salt thereof, wherein the polymer particles have a particle size by dynamic light scattering of from 250 nm to 500 nm, and wherein the coating composition has an above-critical pigment volume concentration. The present invention

addresses a need in the art by economically improving hiding in above-critical vinyl acetate based paint formulations without adversely impacting other desirable properties in the coating.

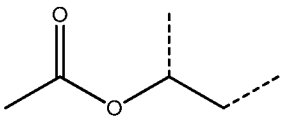
Detailed Description of the Invention

The present invention is a coating composition comprising an aqueous dispersion of polymer particles, pigment particles, and extender particles wherein the polymer particles comprise, in a single phase and based on the weight of the polymer particles, from 35 to 79.9 weight percent structural units of vinyl acetate and from 0.1 to 6 weight percent structural units of a phosphorus acid monomer or a salt thereof, wherein the polymer particles have a particle size by dynamic light scattering of from 250 nm to 500 nm, and wherein the coating composition has an above-critical pigment volume concentration.

As used herein, the term "in a single phase" refers to the fact that the polymer particles comprise one or more copolymers comprising structural units of vinyl acetate and the phosphorus acid monomer with the described proportions.

As used herein, the term "extender particles" refer to inorganic materials that are used to increase the pigment volume concentration of the coating composition. Extender particles are generally distinguished from pigment particles by their lower index of refraction (typically from 1.3 to 1.6 as compared to above 2.0 for pigments). Examples of suitable extenders include, calcium carbonate, clays, aluminum silicates, silica, calcium silicates, mica, talc, and nephilene syenite.

As used herein, the term "structural units" refers to the remnant of the recited monomer after polymerization. For example, a structural unit of vinyl acetate is as illustrated:

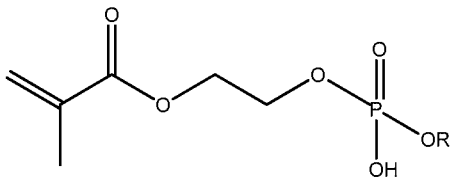


structural unit of vinyl acetate

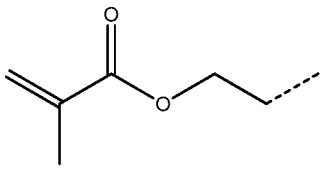
where the dotted lines represent the points of attachment of the structural unit to the polymer backbone. Preferably, the concentration of structural units of vinyl acetate is from 40, more preferably from 50, and most preferably from 60, to 75, more preferably to 70 weight percent based on the weight of the polymer particles

Examples of suitable phosphorus acid monomers include phosphonates and dihydrogen phosphate esters of an alcohol in which the alcohol contains or is substituted with a polymerizable vinyl or olefinic group. Preferred dihydrogen phosphate esters are phosphates of hydroxyalkyl acrylates and methacrylates, including phosphoethyl methacrylate and phosphopropyl methacrylate, with phosphoethyl methacrylate or a salt thereof being especially preferred. A preferred phosphonate is 2-(methacryloyloxy)ethyl phosphonic acid or a salt thereof.

"Phosphoethyl methacrylate" (PEM) is used herein to refer to the following structure:



where R is H or



where the dotted line represents the point of attachment.

A preferred concentration of structural units of the phosphorus acid monomer, preferably PEM, is from 0.2 to 4, more preferably to 2 weight percent, based on the weight of the polymer particles.

The polymer particles preferably comprise 0.1 to 2 weight percent, based on the weight of the polymer particles, structural units of a sulfur acid monomer or a salt thereof. Examples of suitable sulfur acid monomers include sulfoethyl methacrylate, sulfopropyl methacrylate, vinyl sulfonic acid, 2-acrylamido-2-methyl propanesulfonic acid, and 2-methacrylamido-2-methyl propanesulfonic acid, and salts thereof. Preferred sulfur acid monomers are 2-acrylamido-2-methyl propanesulfonic acid and vinyl sulfonic acid, and salts thereof. The polymer particles more preferably comprise 0.5 to 1.5 weight percent, based on the weight of the polymer particles, structural units of 2-acrylamido-2-methyl propanesulfonic acid or a salt thereof.

The polymer particles preferably adsorb to the surface of the pigment particles. For example, when TiO_2 is blended with a VA-PEM latex, adsorption can be seen by way of scanning electron microscopy or centrifugation. As used herein, "adsorb" refers to polymer particles contacting or attaching to the surface of the TiO_2 particles in a manner other than covalent bonding.

Preferably, the polymer particles are film-forming at room temperature. The polymer particles include structural units of monomers resulting in polymer particles with a T_g, as calculated using the Fox equation, of from -20 °C, more preferably from -10 °C, to 20 °C, more preferably to 10 °C. The polymer particles preferably comprise from 20 weight percent to 64.8, more preferably to 50, and most preferably to 40 weight percent structural units of one or more acrylate monomers, based on the weight of the polymer particles. Examples of suitable acrylate monomers include ethyl acrylate, butyl acrylate, or 2-ethylhexyl acrylate, or combinations thereof. More preferably, the polymer particles include from 200 to 40 weight percent structural units of butyl acrylate, based on the weight of the polymer particles. Preferably, the polymer particles have a particle size by dynamic light scattering of from 300 nm to 450 nm.

The polymer particles may optionally include up to 20 weight percent structural units of a vinyl ester of a branched alkyl carboxylic acid (also known as a vinyl versatate), based on the weight of the polymer particles. An example of a commercially available vinyl versatate is VA-VeoVa 10 monomer.

The aqueous dispersion of polymer particles is preferably prepared by forming an at least partially neutralized solution of the phosphorus acid monomer, then contacting the solution with vinyl acetate and optionally the sulfur acid monomer, or salt thereof. As used herein, the term "at least partially neutralized phosphorus acid monomer" refers to an aqueous solution of a phosphorus acid monomer containing not less than ½ the molar amount of neutralizing agent required to neutralize the monomer, up to the amount required to completely neutralized the monomer, preferably up to the amount required to reach a pH equal to the highest pK_a (preferably the second pK_a) of the monomer. For example, if the neutralizing agent is ammonia, and the phosphorus acid monomer is PEM, the suitable molar ratio of ammonia to PEM would be at least 1:1 and preferably up to 2:1. Suitable neutralizing agents include, for example, ammonia, KOH, NaOH, ethanol amine, and aminomethyl propanol. It is preferred that pH of the aqueous solution of the phosphorus acid monomer, prior to contact with the vinyl acetate and

optionally one or more additional monomers, be in the range of from 4.5, more preferably from 5.0, most preferably from 5.5; to 8.0, more preferably to 7.5, and most preferably to 7.2. The pH of the polymerization medium is maintained at such a level to minimize the hydrolysis of the vinyl acetate monomer or of the polymer, and is preferably buffered throughout the polymerization process to maintain a pH in the range of from 4.5, more preferably from 5.5; to 8, more preferably to 7. Because the polymerization reaction is carried out at a pH that does not promote the hydrolysis of vinyl acetate, very low levels of acetic acid or a salt thereof (i.e., the hydrolysis products of vinyl acetate) are formed during the polymerization process. Consequently, yields of useful polymer are improved, VOCs are reduced, and production of a less desirable hydrophilic polymer (due to generation of pendant OH groups as a consequence of hydrolysis) is reduced.

In a first step of preparing the composition of the present invention the stable aqueous dispersion of the polymer particles is contacted with pigment particles, preferably an aqueous dispersion of pigment particles (also known as a slurry), more preferably a TiO_2 slurry, to form the aqueous dispersion of polymer particles that preferably adsorb to the surface of the pigment particles. The aqueous dispersion of polymer particles is advantageously adjusted to a pH in the range of 8 to 10 before, during, or after contacting the pigment particles, preferably an aqueous dispersion of TiO_2 particles, to form the composite of polymer particles and the pigment particles. This combination can then be admixed with extender particles to form the above critical PVC composition.

Furthermore, the stable aqueous dispersion of polymer particles can be combined with extender first and this mixture can be combined with the pigment particles, preferably as an aqueous dispersion. Also, the extender particles can be combined with pigment particles, preferably as an aqueous dispersion, which can then be admixed with the aqueous dispersion of polymer particles (i.e., the latex).

In above critical PVC paints there is a relatively low concentration of opacifying pigment and it is well known that a large proportion of the opacity (or hiding) comes from air voids that are present due to the absence of adequate film forming binder to encapsulate the entirety of the pigments and extenders present in the formulation. Optimizing opacity in low pigment content

coatings is especially important to maintaining the low cost advantage of these types of formulations.

The term "critical pigment volume concentration" (CPVC) refers to the lowest concentration of polymer required to wet the surface of the pigment particles. Below CPVC there is an excess amount of polymer relative to the amount of pigments and extenders. As such, at PVCs at or below CPVC, an adequate relative amount of binder volume to pigment/extender volume is present, leading to a substantially nonporous dry coating.

Above CPVC, the volume of binder is insufficient to coat all pigment and extender to form a porous dry coating, resulting in a deterioration of the properties and performance of the consequent coating. For example, abrasion resistance and stain resistance and removal are superior for coatings at or below CPVC as compared to coatings above CPVC. Nevertheless, the cost advantages of above-CPVC paints sometimes outweigh the disadvantages of diminished properties.

The CPVC of a coating can be conveniently determined using reflectance (integrated sphere, spectral reflectance included, 10 degree observer/D65), as follows: The difference in reflectance of a coated film in the dry state is compared to the same film that has been rewetted with a penetrating solvent that has refractive index similar to that of the polymer (such as Isopar L solvent) that fills the air voids of the dry coating. When a coating is above CPVC, the Y-reflectance of the re-wetted coating will decrease by at least 2% from the initial Y-reflectance value of the dry coating. Preferably, the above-critical PVC is at least 60, more preferably at least 65, and preferably not greater than 90.

It has surprisingly been discovered that hiding is improved in above-critical paint formulations with an increase in binder particle size; in contrast, for below-critical paint formulations, the relationship between particle size and hiding is inverse: higher particle sizes result in reduced hiding.

For binders that are not film forming at room temperature, that is, binders with a T_g of preferably not less than 25 °C, more preferably not less than 30 °C, hiding also increases with increased particle size; the improvement, however, can be seen at much lower particles sizes than for the

low T_g binders. For these relatively high T_g binders, the particle size of the binder particles is preferably not less than 150 nm and preferably not greater than 450 nm.

Abbreviations

Abbreviation	Chemical name or description (%'s in water are indicated)
PEM	Phosphoethyl methacrylate, 60% active
NaPS	Sodium persulfate
FES-77	Disponil FES-77 fatty ether sulfate (33% aq)
15-S-40*	TERGITOL™ Secondary Alcohol Ethoxylate (70% aq)
TMN-10	TERGITOL™ TMN-10
DS-4	Rhodacal DS-4 sodium dodecylbenzene sulfonate (22% aq)
Na-AMPS	Sodium 2-acrylamido-2-methyl-1-propanesulfonate (50% aq)
BA	Butyl acrylate
VA	Vinyl acetate
IAA	Isoascorbic acid
t-BHP	*t*-Butyl hydroperoxide
PS	Particle Size
TiO_2 slurry	Ti-Pure R-746 TiO_2 slurry
RM2020 NPR*	ACRYSOL™ RM2020 NPR Rheology Modifier
RM8W*	ACRYSOL™ RM8W Rheology Modifier
Natrosol	Natrosol 250 MHR
Natrosol soln	Natrosol 250 MHR (3% in water)
HMHEC	Natrosol Plus 330
CF-10*	TRITON™ CF-10 Surfactant
Foamaster	Foamaster VL Defoamer
Texanol	Texanol Coalescent
TiO_2 PVC	TiO_2 Pigment Volume Concentration in the Paint
731A	TAMOL™ 731A Dispersant

*ROVACE, TRITON, ACRYSOL, TAMOL, CELLOSIZE, and TERTIGOL are Trademarks of The Dow Chemical Company or its Affiliates.

Comparative Example 1 – Preparation of BA/VA/PEM/AMPS Latex

Deionized (DI) water (861 g), $FeSO_4$ (11.6 g), Brugolite FF6 reducing agent (0.3 g) and 15-S-9 (17.1 g) were charged to a 5-L 4-necked round bottom flask equipped with a mechanical stirrer, nitrogen gas blanket, thermometer, condenser, heating mantel and temperature controller. The reactor contents were heated to 68 °C. The monomer emulsion was prepared by first mixing DI water (335.9 g) and PEM (17 g) in a vessel and adjusting the pH to 6.8 with NaOH (50% aq, 10.2 g). FES-77 (27.4 g), 15-S-40 (49.9 g), and DS-4 (32.6 g) were then added followed by BA (569 g), VA (1109 g) and Na-AMPS (19.18 g). An initiator solution was prepared separately by mixing DI water (75 g), t-BHP (1.73 g) and NaPS (2.56 g). A separate solution of DI water (75 g) and IAA (3.34 g) was prepared. Flow of the monomer emulsion, the NaPS/*t*-BHP, and the IAA solutions to the reactor flask were started at the same time. The monomer emulsion was added over 120 min while the *t*-BHP/NaPS solution and the IAA solution were added over 155 min. After the monomer emulsion, initiator solution, and IAA solution additions were complete a redox pair was added to reduce residual monomers. The reaction temperature was maintained at 72.5 °C for the duration of the entire reaction (4 h), after which time the latex was cooled to and a biocide added. The pH of the final latex was adjusted to 7.5 with NH_3 (28% aq) Water was added to adjust to the listed solids.

Example 1 – Preparation of BA/VA/PEM/AMPS Latex

Example 1 was prepared substantially as described for Comparative Example 1 except that the monomer emulsion was prepared by first mixing DI water (330 g) and PEM (17 g) in a vessel and adjusting the pH to 6.8 with NaOH (50% aq, 10.2 g). FES-77 (27.4 g), 15-S-40 (49.9 g), and DS-4 (32.6 g) were then added followed by BA (569 g), VA (1100g) and Na-AMPS (38.36 g).

The particle sizes (determined using a Brookhaven BI90 particle size analyzer) and T_g (calculated using the Fox equation) of the latex binder compositions are shown in Table 1.

Table 1 – VA/BA/PEM Latex Compositions

Binder Ex.	Binder Monomer Composition	PS (nm)	T_g (°C)
Comp 1	VA/BA/AMPS/PEM[a] 65.0/33.4/0.6/1.0	230	-4.2
1	VA/BA/AMPS/PEM 64.5/33.4/1.1/1	307	-3.9

a – %PEM is uncorrected for active amount, which is ~60% of the reported percentage

Above-critical PVC Paint Formulation

An above critical PVC paint (60.6 PVC (total)) was prepared using the following procedure:

Binder emulsion was added to a paint container and mixed using a 3-blade pitched metal stirrer; aqueous ammonia (28% aq) was added to neutralize the binder to a pH of 8-9. After the addition of the base was complete, TiO_2 and Defoamer were added sequentially to the emulsion. In a separate container the mill based (part B) was prepared on a Cowles disperser. After preparation, the mill based was added to part A while mixing. Finally, Part C was added in order to the mixture of Part A and Part B while mixing. Adequate level of thickener was added until a Krebs Unit viscosity of 90-100 was obtained. Table 2 shows the ingredients and amounts used to make Paint Formulation 1. The amount of VA-PEM binder used was that amount sufficient to obtain 39.4 vol % based on the dry volume of binder, pigment, and extender.

Method for Reflectance Measurement

Both dry coating samples and Iso-Par L re-wetted coating samples were measured for Y- reflectance using a Xrite USA model Xrite8400, XriteColor Master CM-2 using the spectral component included mode and under D65/10° observer conditions. The Iso-par L oil was applied to the dry coating using a 1-inch nylon paint brush and allowed to penetrate for 5 min prior to making reflectance measurements.

Table 2 – Above-Critical Paint Formulation 1 (60.6 PVC)

Part A	
Binder	
NH_3 (28% aq)	Sufficient achieve pH of 8-9
TiO_2 slurry	76.0 g
CF-10	0.52 g
Foamaster	0.52 g
Mill base part B	
Natrosol	2.95 g
Water	164.2 g
CF-10	0.80 g
Foamaster	0.80 g
NH_3 (28% aq)	0.08 g
731A	9.73 g
Omyacarb 5 extender	90.00 g
Minex 10 extender	48.00 g
Optiwhite extender	48.00 g
Grind Sub-total	364.60 g
Part C	
Texanol	5% based on binder T_g
Natrosol soln	sufficient to achieve 90-100 KU viscosity
Water	sufficient to achieve 34.8% volume solids

Below-critical Paint Formulation

A below-critical PVC paint (39.9 PVC (total)) was prepared using the procedure substantially described to make Paint Formulation 1. Table 3 shows the ingredients and amounts used to make Paint Formulation 2. The amount of VA-PEM binder added was that amount necessary to obtain 60.1 vol %, based on the volume of binder, pigment, and extender.

Table 3 – Below Critical Paint Formulation 2 (39.9 PVC)

Part A	
Binder	
NH_3 (28% aq)	1.30
Foamaster	1.00
TiO_2 slurry	254.33
Mill Base Part B	
Premix	
Water	107.28
HMHEC	3.22
NH_3 (28% aq)	0.54
731A	7.94
TMN-10	1.61
Foamaster	2.15
Minex 7 extender	48.27
Icecap-K extender	48.27
Omyacarb 5 extender	101.90
Water	62.22
LetDown Part C	
T 15-s-40	2.00
Foamaster	1.00
RM-2020 NPR	8.28
RM-8W	28.80
Water	Quantity to achieve 37% volume solids

Kubelka-Munk S/mil Test Method

The paints were evaluated for hiding using the in accordance with the Kubelka-Munk S/mil test method, as described in the following procedure.

Four 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 on each chart. The Y-reflectance was measured using a X-Rite Color i7 Spectrophotometer in each of the scribed areas five times and the average Y-reflectance recorded. A thick film draw down was prepared for each paint on the Black Release Charts

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 in^2.

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

The comparison in trends in hiding versus particle size for above critical PVC paint formulation 1 (PVC = 60.6) and below-critical paint formulation 2 (PVC = 39.9) is illustrated in Table 4.

Table 4 – Hiding Data for Above- and Below-critical PVC Paint Formulations

Binder example	Comp 1	1
Particle size (nm)	230	307
T_g (°C)	-4.2	-3.9
S/mil above critical PVC Paint (Paint Formulation 1)	5.10	5.30
S/mil below critical PVC Paint (Paint Formulation 2)	5.21	5.02
stdev	0.01	0.04

Inexplicably, hiding decreases with increasing particle size for the below-critical PVC paint formulation (Formulation 3), but increases with increasing particle size for the above critical PVC formulation (Formulation 1).

Claims

1. A coating composition comprising an aqueous dispersion of polymer particles, pigment particles, and extender particles wherein the polymer particles comprise, in a single phase and based on the weight of the polymer particles, from 35 to 79.9 weight percent structural units of vinyl acetate and from 0.1 to 6 weight percent structural units of a phosphorus acid monomer or a salt thereof, wherein the polymer particles have a particle size by dynamic light scattering of from 300 nm to 450 nm, and wherein the coating composition has an above-critical pigment volume concentration (CPVC) of at least 60.

2. The coating composition of Claim 1 wherein the polymer particles comprise, based on the weight of the polymer particles, from 40 to 70 weight percent structural units of vinyl acetate and from 0.2 to 2 weight percent of a phosphorus acid monomer or a salt thereof; wherein the polymer particles further comprise from 20 to 50 weight percent structural units of one or more acrylate monomers; and wherein the pigment particles are TiO_2 particles.

3. The coating composition of either of Claims 1 or 2 wherein the phosphorus acid monomer is phosphoethyl methacrylate or a salt thereof.

4. The coating composition of any one of Claims 1 to 3 wherein the polymer particles comprise 0.2 to 2 weight percent structural units of phosphoethyl methacrylate or a salt thereof, based on the weight of the polymer particles, and wherein the polymer particles further comprise from 0.2 to 1.5 weight percent structural units of a sulfur acid monomer or a salt thereof, based on the weight of the polymer particles.

5. The coating composition of claim 4, wherein the polymer particles comprise from 0.5 to 1.5 weight percent structural units of the sulfur acid monomer or salt thereof, based on the weight of the polymer particles.

6. The coating composition of any one of Claims 1 to 5 wherein the polymer particles have a T_g as calculated by the Fox equation of from -10 °C to 10 °C.

7. The coating composition of any one of Claims 1 to 6 wherein the above-CPVC of the composition is from 60 to 90.

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8. The coating composition of any one of Claims 1 to 7 wherein the above-CPVC of the composition is measured using a spectrophotometer.

Date Reçue/Date Received 2020-11-10