

# PATENT SPECIFICATION

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## (54) METHOD OF DISPERSING SOLID PIGMENTS IN AQUEOUS MEDIA

(71) We, ROHM & HAAS COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Independence Mall West, Philadelphia, Pennsylvania 19105, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of dispersing solid pigments in aqueous media, particularly but not exclusively, coating compositions comprising an aqueous latex of a film-forming polymer, and especially those containing an alkylene glycol intended to yield moderate to high specular gloss coatings. The method of the invention is also applicable to the production of fluid pigment pastes of high solids and low water content. The invention also relates to pigmented coating and other aqueous compositions obtained using a dispersant for the pigment.

The use of low molecular weight polyelectrolytes as dispersing agents for pigments in water-based coatings is well known. U.S. 2,930,775 discloses that salts of copolymers of olefins and maleic anhydride are operable therefore. However, while these dispersants are excellent for many uses, formulations containing these dispersants often exhibit a tendency to foam, sometimes produce coatings having inadequate adhesion, and may exhibit poor stability, especially in the presence of divalent cations deriving either from so-called reactive pigments containing zinc, barium, lead, etc., or from paint formulation additives containing such cations.

British Patent 998,380 (and its counterpart, U.S. 3,223,751) teach that anionic copolymers of three moles of acrylamide and one mole of itaconic acid, or the salts thereof, are pigment dispersing agents. U.S. 3,230,275 deals with interpolymers of 5—45% acrylamide, at least 20% of an acrylic ester, 2—25% of a hydroxyalkylester of an unsaturated acid, and up to 15% of a carboxylic acid monomer which heat cure to form hard, flexible, solvent resistant coatings; however, the use of these resins in aqueous system formulations is not suggested or contemplated.

U.S. 3,840,487 describes dispersing agents which are the salts of the copolymers of 40—95 mole percent acrylic or methacrylic acid and 5 to 60 mole percent of non-functional alkyl acrylate ester. Although such disclosed polyacrylate type compositions are good dispersing agents, we have found they confer greater foaming tendency, have poor stability, and confer generally poorer adhesion and less gloss to latex paint formulations than the copolymers used herein. Such differences may be due to the fact that the prior patentees rely on a balance between a hydrophobic comonomer and(meth)acrylic acid to achieve solubility of the copolymer dispersant in alkylene glycols, whereas we rely on hydrophilic and hydrogen-bondable, yet nonionic, comonomers to promote solubility.

U.S. Patents 3,646,099 and 3,859,260 disclose water-soluble oligomers of the formulas H-(hydroxyethyl acrylate)<sub>10</sub>-(acrylic acid)<sub>10</sub>-SO<sub>3</sub>Na and H-(hydroxypropyl acrylate)<sub>5</sub>-(acrylic acid)<sub>15</sub>-SO<sub>3</sub>Na which are described as useful as conductive agents and surface active agents. There is no suggestion that such sulfonate

(sulfamate) salts of said oligomers could be used as pigment dispersants in paint formulations.

In accordance with the broadest aspect, the present invention provides a method of dispersing solid pigments in aqueous media with the aid of from 0.01 to 5.0% by weight based on the weight of the pigment, of a water-soluble, alkali metal (e.g., sodium potassium), ammonium or amine (e.g. triethyl amine, dimethylamino-ethanol, 2-amino-2-methyl-1-propanol, ethyl amine, diethyl amine, butyl amine, ethanol amine, N-methyl ethanol amine, and the like) salt of a copolymer consisting essentially of polymerized units of

(A) 25—90 weight percent, preferably 45 to 90 weight percent, more preferably 55 to 80%, and most preferably 60—75%, of at least one hydroxyalkylester of acrylic acid or methacrylic acid, wherein the alkyl group of the ester moiety has from two to six carbon atoms, preferably two or three, (representative esters include 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate and 2,3-dihydroxypropyl acrylate);

(B) 10—75 weight percent, preferably 10 to 55 weight percent, more preferably 20 to 45%, and most preferably 25—40%, of one or more of acrylic acid, methacrylic acid, itaconic acid and half esters, half amides of itaconic acid; and

(C) from 0—35 percent by weight, and preferably not more than 30%, of one or more other ethylenically unsaturated comonomers which, in such limited amounts, do not effect the solubility of the copolymer. Such comonomers include methyl acrylate, ethyl acrylate, n-butyl acrylate, sec-butyl acrylate, isobutyl acrylate, t-butyl acrylate, the corresponding methacrylate analogs, acrylamide, acrylonitrile, and diacetone acrylamide.

As is conventional in the art, when a monomer is referred to, the technically pure material is meant. By "technically pure" of course is meant a material as sold under the name of the designated monomer. For example, hydroxyethyl methacrylate refers to technically pure hydroxyethyl methacrylate. It is typically composed of, on a weight basis, 90% hydroxyethyl methacrylate, 5.5% higher boiling methacrylates, principally hydroxyalkoxyalkyl methacrylates, 3% methacrylic acid, 0.9% ethylene dimetacrylate, and 0.4% water. A monomer data sheet, published by Rohm & Hass Company, Independence Mall West, Philadelphia Pa. 19105 in August of 1976 and bearing identifying number CM—43, shows typical analyses of hydroxyethyl methacrylate and hydroxypropyl methacrylate.

Those skilled in the art in following the teachings of a patent, concerning the use of particular monomers, conventionally use the commercial grade of the material, which typically contains a small percentage of impurities.

The number average molecular weight of the copolymer dispersant employed herein is in the range 500 to 15,000, preferably from 1,000 to 10,000, determined by gel permeation chromatography.

The copolymer dispersants are prepared by solution polymerisation techniques in aqueous media which optionally for economy and convenience may contain the desired alkylene glycol diluent. The appropriate monomeric mixture is generally reacted under oxygen-free conditions at temperatures within the range of 30 to 150°C in the presence of such free radical initiators as t-butyl peroxyvalate, t-butyl peracetate, ammonium persulfate, t-butyl hydroperoxide, cumene hydroperoxide, and like free radical catalysts including free radical redox polymerisation initiators. Catalyst concentrations of 1 to 15% by weight of the monomers are useful to obtain the low molecular weight polymers desired. Sufficient alkali metal hydroxide, ammonium hydroxide, or water-soluble amine, preferably a slight excess, is added during polymerisation or subsequently to neutralize free acid groups on the copolymer, thus converting the dispersant to the operable salt. As is well known, catalyst fragments such as derived from a persulfate may appear as part of the polymer.

The method of this invention, is particularly applicable to the dispersion of solid pigments into coating compositions comprising an aqueous latex of a film-forming polymer, which method comprises dispersing the pigment therein with the aid of from 0.01 to 5%, based on weight of the pigment, preferably 0.1 to 2%, of the aforescribed copolymer salt. An additional embodiment of the invention involves such an aqueous emulsion coating composition modified for higher gloss by the addition thereto of from 0.1 to 2 pounds, preferably 0.5 to 1.3 lbs., of alkylene glycol per U.S. gallon of the coating composition. The alkylene glycol, for example, ethylene glycol, propylene glycol, which is preferred, and hexylene

glycol, functions to slow the drying rate of the paint, increasing the wet-edge time, and to improve leveling, as well as generally causing the development of higher gloss than with an all aqueous system.

5 Suitable latexes for paints are aqueous addition polymer dispersions, generally obtained most conveniently by direct emulsion polymerization. The most important of these dispersions used in making water-based paints are polymers including homopolymers and copolymers of: (1) vinyl esters of an aliphatic acid having 1 to 18 carbon atoms, especially vinyl acetate; (2) acrylic acid esters and methacrylic acid esters of an alcohol having 1 to 18 carbon atoms, especially methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate and butyl methacrylate; and (3) mono- and di-ethylenically unsaturated hydrocarbons, such as ethylene, isobutylene, styrene, and aliphatic dienes, such as butadiene, isoprene, and chloroprene. 5 10

15 Poly(vinyl acetate) and copolymers of vinyl acetate with one or more of the following monomers; vinyl chloride, vinylidene chloride, styrene, vinyltoluene, acrylonitrile, methacrylonitrile, one or two of the acrylic and methacrylic acid esters mentioned above are well known as the film-forming component of aqueous base paints. Similarly copolymers of one or more of the acrylic or methacrylic acid esters mentioned above with one or more of the following monomers: vinyl acetate, vinyl chloride, vinylidene chloride, styrene, vinyltoluene, acrylonitrile, and methacrylonitrile are also more or less conventionally employed in aqueous base paints. Homopolymers of ethylene, isobutylene, and styrene, and copolymers of one or more of these hydrocarbons with one or more esters, nitriles or amides of acrylic acid or of methacrylic acid or with vinyl esters, such as vinyl acetate and vinyl chloride, or with vinylidene chloride are also used. The diene polymers are generally used in aqueous base paints in the form of copolymers with one or more monomers following: styrene, vinyltoluene, acrylonitrile, methacrylonitrile, and the abovementioned esters of acrylic acid or methacrylic acid. It is also quite common to include a small amount, such as 1/2 to 2.5% by weight, of an acid monomer in the monomer mixture used for making the copolymers for all three general types mentioned above by emulsion polymerization. Acids used include acrylic, methacrylic, itaconic, aconitic, citraconic, crotonic, maleic, fumaric, the dimer of acrylic acid, and so on. 15 20 25 30

35 These aqueous dispersions as the emulsion polymer in the paint may be made using one or more emulsifiers of anionic, cationic, or non-ionic type. Mixtures of two or more emulsifiers regardless of type may be used, except that it is generally undesirable to mix a cationic with an anionic type in any appreciable amounts since they tend to neutralize each other. The amount of emulsifier may range from 0.1 to 6% by weight or sometimes even more, based on the weight of the total monomer charge. When using a persulfate type of initiator, the addition of emulsifiers is often unnecessary and this omission or the use of only a small amount, e.g., less than 0.5%, of emulsifier, may sometimes be desirable from the cost standpoint (elimination of expensive emulsifier), and less sensitivity of the dried coating or impregnation to moisture, and hence less liability of the coated substrate to be affected by moisture, which, for instance, would produce coatings less liable to swelling or softening, particularly when subjected to humid atmospheres. The average particule size or diameter of these dispersed polymers may be from 0.03 to 3 microns or even larger. The particle size, whenever referred to herein, is the "weight average diameter". This number, expressed in microns, is determined using the ultra-centrifuge. A description of the method can be found in the Journal of Colloid Science 15, pp. 563—572, 1960 (J. Brodnyan). In general, the molecular weights of these emulsion polymers are high, e.g., from 100,000 to 10,000,000 viscosity average, most commonly above 500,000. 35 40 45 50

55 In general, a gallon of emulsion paint is comprised of 0.5 to 3 lbs. of film-forming resin and 0.2 to 5 lbs. of finely-divided pigment. Typical pigments are titanium dioxide and other titanium pigments, white lead, zinc oxide, zinc sulfide, barium sulfate, calcium carbonate, lithopone, silica, talc, mica, clays, iron oxide, carbon black, cadmium sulfide, toluidene red, chrome orange, chrome yellow, chrome green, and others known in the art. Typical latices of film-forming resins are those of the alkyl acrylates and methacrylates, vinyl acetate, styrene-butadiene, and others known in the art. Minor amounts of other coatings additives may be included in the paint formulations, for example, antifoams, mildewcides, thickeners, wetting agents, bacteriostats, etc. 55 60

65 Another aspect of the invention is the provision of dispersions of pigments as fluid pastes of high solids content and low aqueous media content (said aqueous 65

media comprising water and optionally an alkylene glycol as aforementioned) containing in admixture a relatively minor amount of the described water-soluble salt of the copolymer of ethylenically unsaturated acid and the hydroxyalkyl ester thereof as dispersant. The amount of the salt of the copolymer effecting dispersion of solids and fluidity of the pigment paste will usually not be over three percent of the weight of pigment and may be as low as 0.05%.

For the preparation of these pigment pastes, it is generally most convenient to prepare an aqueous solution of copolymer in salt form. Concentrations of 5 to 40% may be used, although those of 10 to 20% are usually preferred. Pigment, water (including an alkylene glycol), and solutions are mixed. If desired, the paste or suspension may be ground in a mill—a pebble mill, roll mill, colloid mill, or high speed stone mill, or in some instances a high shear mixer being suitable. Sufficient copolymer is used to ensure good dispersion and fluidity of the paste. The optimum amount of copolymer will depend upon the specific pigment or pigments and upon the state of subdivision thereof; In general, the finer the particle size the more dispersant should be used. Concentrated pastes can be extended to give dilute pastes, when the latter are needed. The pigment pastes are a suitable and convenient composition for addition to aqueous resin latexes or dispersions, as previously discussed, to form emulsion paints. Moreover, fluid pastes of certain pigments have diverse uses, for example, such high solids content slurries of calcium hydroxide are useful for coatings as white-wash, field markings, or the like, or as concentrated alkaline reagents in chemical manufacturing; dispersions of carbon blacks in aqueous media are useful in the fields of paper, cement, water-base paints, coating compositions, inks, rayons, and rubber. The pigments may be present in the foregoing pastes in an amount up to 85% by weight of the paste.

In the representative examples next presented, the following abbreviations are used for the sake of brevity:

MAA: methacrylic acid

AA: acrylic acid

HEMA: 2-hydroxyethyl methacrylate

HPMA: 2-hydroxypropyl methacrylate

DHPMA: 2,3-dihydroxypropyl methacrylate

BMA: N-butyl methacrylate

Various illustrative processes for preparing the copolymer dispersants used in the invention are as follows:

#### Process A

A two-liter, four-necked, round bottomed flask fitted with stirrer, reflux condenser, heating mantle, two addition funnels and nitrogen inlet, is charged with 348 g. isopropanol which is heated to reflux under nitrogen. A monomer mixture of 143 g. HEMA and 94.6 g. glacial MAA is added simultaneously over a one hour period with the addition of a solution of 18.8 g. "Lupersol 11", Registered Trade Mark, (57% t-butyl peroxyvalate) in 94 g. isopropanol while maintaining the reactor contents at reflux (84°C.). Reflux is maintained for another hour. The resulting polymer solution (36.3% solids, viscosity = 1825 centipoise, Brookfield LV #2, 12 rpm) is added gradually along with addition of equivalent amounts of 50% NaOH solution (to maintain homogeneity) to 300 g. water heated to reflux in a similar reaction vessel fitted with a distillation head. Isopropanol and water are distilled off until the vapor temperature reaches 100°C. The pH of the clear colorless product is adjusted to 9.6 with additional caustic solution, and solids concentration is diluted to 25% (solution viscosity = 39.5 cps., LV #2, 60 rpm). The dissolved copolymer is composed of HEMA/MAA in a 60/40 weight ratio.

#### Process B

A reaction flask as described above is charged with 300 g. propylene glycol which is heated to 150°C. under nitrogen blanket. A solution of 210 g. HEMA, 90 g. MAA, 3 g. mercaptoethanol and 12 g. "Lupersol 70" (75% t-butyl peracetate) is

added over a five hour period while maintaining temperature at 150°C. Addition of 1.2 g. more of "Lupersol 70" without exotherm indicates completion of reaction; however, heating is continued for 30—45 minutes.

Vacuum is applied and about 160 g. propylene glycol is removed at 120° C./30 mm. Hg. The contents are cooled to 50°C., and 50% aqueous NaOH is added gradually until the pH of the solution is 9.2. The copolymer solution, adjusted to 50% solids concentration by water addition, contains 19% propylene glycol. Its appearance is light amber, viscosity = 1,000 cps. (LV #2, 6 rpm); adjusted to 25% solids, viscosity = 16 cps. The dissolved copolymer is composed of HEMA/MAA in a 70/30 weight ratio.

#### *Process C*

A five-liter flask equipped as those described above is charged with 1955 g. water and 567.3 g. propylene glycol and the solution heated to 90°C. while sparging with nitrogen. 45% of a catalyst solution of 62.5 g. ammonium persulfate in 312.5 g. water is added, and then the remainder of the catalyst solution and 480.75 g. MAA and 1121.75 g. HEMA are added simultaneously over a 1.5 hours period. The reaction mixture is held at 92—95°C. for an additional hour. The viscosity of the mixture is 82.5 cps. (LV #2, 60 rpm).

The mixture is cooled and 430 g. of 50% aqueous NaOH are added gradually to give a pH of 9.6. The propylene glycol content of the solution is 11.2%, dissolved solids content is 42%, viscosity 360 cps. (LV #2, 30 rpm); when diluted to 25% solids, viscosity is 23 centipoise. The dissolved copolymer is composed of HEMA/MAA in a 70/30 weight ratio.

Various copolymer compositions are thus prepared according to one of the above processes, as summarized in Table I below.

TABLE I

Example No.	Monomers in Copolymer, and Weight Ratios	Process Polymerization	Product Solution (Na <sup>+</sup> Salt)		
			pH	% Solids	Viscosity Cps.
1 (control)	MAA	C	9.7	25	40
2	HEMA/MAA, 30/70	A	9.7	25	36
3	Do., 50/50	B	9.5	25	20
4	Do., 50/50	C	9.5	25	31
5	Do., 60/40	A	9.6	25	40
6	Do., 60/40	B	9.1	25	13
7	Do., 60/40	C	9.2	25	30
8	Do., 70/30	B	9.2	25	16
9	Do., 70/30	C	9.6	25	23
10	Do., 70/30	C	9.5	25	27
11	Do., 75/25	C	9.3	25	27
12	Do., 80/20	A	9.1	25	28
13	HPMA/MAA, 70/30	B	9.2	25	12
14	HEMA/AA, 60/40	A	9.7	35	28
15	Do., 80/20	A	9.5	26	25
16	* DHPMA/MAA, 30/70	C	9.5	35	856
17	Do., 50/50	C	9.5	35	498
18	Do., 70/30	C	9.8	35	210
19	BMA/HEMA/MAA, 32/29/39	A	9.1	35	125

\* DHPMA introduced as isopropylidene glycerol methacrylate and allowed to hydrolyze to DHPMA *in situ*.

*Evaluation of Polymers as Pigment Dispersants*

The above described polymers, along with an additional prior art control (U.S. 2,930,775), are evaluated as pigment dispersants to produce semigloss latex paints in accordance with the general formulation given below. All components are maintained in equal proportion with the exception of pigment dispersant level which is specified in Table II as a percentage based on total pigment weight.

The following ingredients in parts by weight are charged to a suitable steel vessel and ground in a Cowles (Registered Trade Mark) dissolver (high speed dispersing mill) at about 4,000 peripheral feet per minute for 20 minutes to prepare a pigment paste.

5				5
10				10
	Propylene glycol	60.0		
	Polymeric dispersant in water	9.2		
	Water	5.1		
	Zinc Oxide	25.0		
15	Rutile Titanium Dioxide	250.0		15
	Nopco (Registered Trade Mark) "NXZ" antifoaming agent	1.0		
	Octylphenoxy polyethoxyethanol (OPE) <sub>9-10</sub> (surfactant)	2.5		
20	Tert-butylaminoethanol (wetting agent)	3.7		20
	The dispersions are then "let down" at a lower speed with:			
	Water	30.0		
	Propylene glycol	38.0		
25	Eastman "Texanol" coalescing aid (pentanediol monoisobutyrate)	25.0		25
	Nopco "NXZ" antifoaming agent	1.0		
	2-N-octyl-4-isothiazolin-3-one, 45% active ingredient (mildewcide)	2.0		
30	Hercules "Natrosol (Registered Trade Mark) 250 MR" hydroxyethyl cellulose thickener, 3% active ingredient in water	72.7		30
35	Acrylic copolymer latex (50.7% methyl methacrylate, 1.3% methyl acrylate, 48% butyl acrylate, 46% solids, pH 9.5)	546.7		35

The paint formulations are evaluated for the critical properties of specular gloss, viscosity at high and low shear rate, and stability thereof when subjected to elevated temperature and to freeze-thaw cycling in accordance with the following procedures.

40	Specular gloss:	ASTM D523—67 (reapproved 1972)	40
	Low Shear Viscosity:	Stormer viscosity (KU), ASTM D562—55 (reapproved 1972)	

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	High Shear Viscosity:	ICI Cone and Plate (poise), Research Equipment (London), Ltd.	
	Stability Conditions:	(Closed paint cans)	
	Equilibrated:	240 hours at room temperature	
5	Heat Aged:	250 hours at 140°F.	5
	Freeze thaw:	5 cycles wherein one cycle is 16 hours at -10°C., followed by 8 hours at room temperature.	
10	All formulations are sheared by shaking for 15 minutes on a Red Devil (Registered Trade Mark) paint mixer prior to measuring viscosity. Test results are summarized in Table II, below.		10



TABLE II

Formulation No.	Dispersant (of example)	% Dispersant (on pigment)	60° Gloss Heat aged sample	Init.	Stormer Viscosity (Low Shear, KU)			Brushing Viscosity (High Shear, ICI)		
					equili-brated	Heat aged	freeze-thaw	equili-brated	Heat aged	freeze-thaw
a	1 (control)	1.0	25	71	70	67	80	1.1	1.1	1.1
b	Control *	1.0	55 (Initial)	75	70-gel (var.results)	gel	gel	~2+	gel	gel
c	2	1.0	43	72	72	69	72	1.2	1.0	1.2
		1.1	36	72	72	63	72	1.2	1.1	1.1
d	3	1.0	48	70	72	72	79	1.3	1.1	1.4
		1.8	43	70	72	72	77	1.0	1.0	1.1
e	4	1.0	54	72	67	67	67	1.0	1.0	1.1
f	5	1.0	56	72	74	67	72	1.3	1.1	1.2
		1.7	51	72	76	69	72	1.2	1.1	1.2
g	6	1.0	52	72	72	77	79	1.0	1.1	1.1
		2.2	45	72	72	72	79	1.1	1.0	1.2
h	7	1.0	59	74	67	67	72	1.1	1.1	1.1
i	8	1.0	64	70	72	77	87	1.2	1.3	1.3
		2.7	60	70	72	67	79	1.1	1.1	1.1
j	9	1.0	67	83	82	82	77	1.2	1.2	1.3
		1.5	62	72	72	77	82	1.1	1.1	1.1
		2.0	55	72	72	67	77	1.2	1.1	1.1
		2.5	53	72	72	67	72	1.1	1.1	1.1
k	10	2.5	43	-	77	72	77	1.2	1.1	1.2
m	11	1.0	66	86	82	82	89	1.3	1.3	1.4

TABLE II (Continued)

Formulation No.	Dispersant (of example)	% Dispersant (on pigment)	60° Gloss Heated aged sample	Stormer Viscosity (Low Shear, KU)			Brushing Viscosity (High Shear, ICI)			
				Init.	equili- brated	Heat aged	freeze- thaw	equili- brated	Heat aged	freeze- thaw
n	12	1.0	56	95	72	69	82	1.4	1.3	1.4
		2.5	64	89	69	67	72	1.0	1.1	1.1
o	13	2.4	70	75	82	77	82	1.2	1.3	1.3
	14	1.0	57	72	79	67	86	1.3	2.5	1.2
p		1.7	52	72	77	72	76	1.2	1.1	1.2
	15	1.0	45	89	79	86	> 141	1.5	1.8	2.0
q		3.0	59	89	82	67	88	1.3	1.3	1.6
	16	1.0	47	74	67	67	67	1.1	1.0	1.0
s	17	1.0	57	77	67	67	72	1.1	1.0	0.9
	18	1.0	67	86	86	82	82	1.2	1.2	1.2
u	19	1.0	58	82	82	77	84	1.3	1.2	1.3

\* This control is the sodium salt of diisobutylene-maleic anhydride copolymer (1:1 mole ratio) described by Fordyce et al, U.S. 2,930,775.

All paints with the present dispersants exhibit excellent viscosity stability. A steady improvement in specular gloss with increasing nonionic comonomer content is observed; however, excessive nonionic comonomer content leads to poor stability if used at inadequate levels (Formulation q). Very poor gloss is found with the methacrylic acid control dispersant (Formulation a). Very poor stability is found with the other control dispersant (Formulation b).

In all cases except Formulation b, adhesion of the test paints to a glossy oil based alkyl paint (duPont Outside Trim and Shutter Gloss Enamel, Code 801C Light Green) is excellent.

In a test for foaming tendency, dispersant samples are diluted to 5 weight percent solids with water and shaken vigorously in jars. With the exception of the control dispersant used in Formulation b, all of the materials confer little or no foaming tendency.

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## WHAT WE CLAIM IS:—

1. A coating composition comprising an aqueous latex of a film-forming emulsion homopolymer or copolymer having a pigment dispersed therein with the aid of a dispersing agent, wherein the dispersing agent is a water-soluble alkali metal, ammonium or amine salt of a copolymer of:
- 5 a) from 25—90% by weight, based on the weight of the copolymer, of units derived from one or more  $C_2$ — $C_6$  hydroxyalkyl esters of acrylic or methacrylic acid;
- 10 b) from 10—75% by weight, based on the weight of the copolymer, of units derived from one or more of acrylic acid, methacrylic acid, itaconic acid, or a half ester or half amide of itaconic acid; and
- 15 c) from 0—35% by weight, based on the weight of the copolymer, of units derived from one or more other ethylenically unsaturated comonomers; said dispersing agent having a number average molecular weight in the range 500 to 15,000 and being present in said composition in an amount of from 0.01 to 5% by weight, based on the weight of the pigment.
2. A composition according to claim 1, wherein the copolymeric dispersing agent has a number average molecular weight in the range 1,000 to 10,000.
3. A composition according to claim 1 or 2, wherein component a) of the copolymeric dispersing agent is constituted by units derived from one or more  $C_2$ — $C_3$  hydroxyalkyl acrylates or methacrylates.
- 20 4. A composition according to any one of the preceding claims, wherein the copolymeric dispersing agent is a copolymer consisting of from 45—90% by weight of said hydroxyalkyl acrylate or methacrylate units and from 10 to 55% by weight of said acid units.
- 25 5. A composition according to claim 4, wherein the said copolymer contains from 55—80% by weight of said hydroxyalkyl acrylate or methacrylate units and from 20—45% by weight of said acid units.
- 30 6. A composition according to claim 5, wherein the copolymer contains from 60—75% by weight of said hydroxyalkyl acrylate or methacrylate units and from 25—40% by weight of said acid units.
- 35 7. A composition according to claim 4, 5 or 6, wherein the copolymer is a copolymer of 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate or 2,3-dihydroxypropyl acrylate and either methacrylic acid or acrylic acid.
8. A composition according to any one of the preceding claims, wherein the dispersing agent is a sodium or ammonium salt of said copolymer.
9. A composition according to any one of the preceding claims, wherein said copolymeric dispersing agent is present in an amount of from 0.1 to 2% by weight, based on the weight of the pigment.
- 40 10. A composition according to any one of the preceding claims, which additionally contains from 0.1 to 2 lbs per U.S. gallon of an alkylene glycol.
11. A composition according to claim 10, wherein the alkylene glycol is present in an amount of from 0.5 to 1.3 lbs per U.S. gallon.
- 45 12. A composition according to claim 10 or 11, wherein the alkylene glycol is ethylene glycol, propylene glycol or hexylene glycol.
13. A composition according to any one of the preceding claims, wherein the film-forming polymer is a homopolymer or copolymer of a vinyl ester of a  $C_1$ — $C_{18}$  aliphatic carboxylic acid, a  $C_1$ — $C_{18}$  alkyl ester of acrylic or methacrylic acid, or a mono- or diethylenically unsaturated hydrocarbon.
- 50 14. A composition according to claim 13, wherein the film-forming polymer is poly(vinyl acetate) or a copolymer of vinyl acetate with one or more of the following: vinyl chloride, vinylidene chloride, styrene, vinyl toluene, acrylonitrile, methacrylonitrile or a  $C_1$ — $C_{18}$  alkyl acrylate or methacrylate.
- 55 15. A composition according to claim 1, having a formulation substantially as hereinbefore identified under any one of reference letters 'c' to 'u'.
16. A method of dispersing a solid pigment in an aqueous medium wherein the aqueous medium contains as a dispersant for the pigment from 0.01 to 5% by weight, based on the weight of the pigment, of a water-soluble alkali metal, ammonium or amine salt of a co-polymer as defined in claim 1.
- 60 17. A method according to claim 16, as applied to the preparation of a composition as defined in any one of claims 1—14.
18. A method of dispersing a solid pigment in water to obtain a paste containing up to 85% by weight of pigment, which comprises dispersing the pigment in said water with the aid of a dispersing agent, said dispersing agent being
- 65

used in an amount of from 0.05 to 5% by weight based on the weight of the pigment and being a water-soluble alkali metal, ammonium or amine salt of a copolymer of:

- 5 a) from 25—90% by weight, based on the weight of the copolymer, of units derived from one or more C<sub>2</sub>—C<sub>6</sub> hydroxyalkyl esters of acrylic or methacrylic acid; 5
- b) from 10—75% by weight, based on the weight of the copolymer, of units derived from one or more of acrylic acid, methacrylic acid, itaconic acid, or a half ester or half amide of itaconic acid; and
- 10 c) from 0—35% by weight, based on the weight of the copolymer, of units derived from one or more other ethylenically unsaturated comonomers; said copolymer having a number average molecular weight in the range 500 to 15,000. 10
19. A method according to claim 18, which comprises adding the pigment to an aqueous solution containing from 5—40% by weight of said dispersing agent based on the weight of the solution.
- 15 20. A method according to claim 18 or 19, wherein there is present in the aqueous phase an alkylene glycol. 15
21. A method according to any one of claims 18—20, wherein the dispersing agent is a salt as required by any one of claims 2—8.
- 20 22. A paste comprising an aqueous vehicle and up to 85% by weight of pigment dispersed therein, when prepared by a method claimed in any one of claims 18—21. 20

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