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(54) Emulsion polymerisation.

(57) The wet rub resistance of a pigmented wallpaper ground coat is improved by using a polymer emulsion prepared by pressure reaction in the presence of a stabilising surfactant containing a C14 to C20 alkylene moiety and then post reacted with an epoxy silane.

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EMULSION POLYMERISATION

FIELD OF THE INVENTION:

This invention relates to the use of aqueous emulsions in pigmented wallpaper ground coats. These aqueous emulsions are based on vinyl alkanoate copolymers, usually vinyl acetate/ethylene copolymers.

BACKGROUND TO THE INVENTION:

Pigmented wallpaper ground coats are applied on one side of a cellulosic wallpaper substrate. This side is then printed and will form the exposed surface when adhered to a wall. The wet rub resistance of the exposed surface is important because it allows the printed surface to be washed without eroding the decorative appearance.

GENERAL DESCRIPTION OF THE INVENTION:

The invention provides for the use in a wallpaper ground coat of a copolymer emulsion latex having a solids contents of about 20% to about 70% by weight, preferably from about 40% to about 60%, wherein vinyl C1 to C13 alkanoate forms at least about 40% by weight of the monomer charge characterised in that

i) the polymerisation is performed in the presence of an effective amount of a stabilising surfactant having a C14 to C20 alkylene moiety, and

ii) the polymerised emulsion is reacted with an effective amount, preferably about 0.1% to about 3% by weight of the emulsion of an epoxy silane material. The stabilising surfactant is preferably present in an amount of from about 1% to about 10%, preferably 2% to 8%, by weight of the copolymerisable monomers.

Although vinyl acetate is the preferred vinyl alkanoate monomer because of its availability, cost and known reactivity, other vinyl esters within the class defined are usable in particular vinyl formate, propionate, butyrate, isobutyrate, valerate, 2-ethyl hexanoate, isooctanoate, nonanoate, decanoate, pivalate and versatate.

A preferred comonomer is ethylene but other ethylenic hydrocarbons, for example propylene, butylene and isobutene and higher alpha-olefins, are usable. Alkyl (C2 to C8) acrylates, eg. ethyl, butyl and 2-ethyl hexyl acrylate, are also preferred comonomers.

Optionally the copolymer may contain minor monomer components added to provide specific benefits, examples are sodium vinyl sulphonate, acrylic acid, methacrylic acid, acrylamide, hydroxy functional acrylates, vinyl silanes and vinyl halides. A favoured comonomer is a polyethylenically unsaturated compound selected from triallyl cyanurate, triallyl isocyanurate, diallyl maleate, diallyl fumarate, divinyl benzene and diallyl phthalate.

The epoxy silane used is preferably a gamma glycidoxy silane, having the formula $x\text{-}Si(OR)_3$ whre X is an alkyl group containing a reactive expoxy moiety and R, which may be the same or different, is hydrogen, C1 to C4 alkyl radicals with not more than two of the radicals being hydrogen. Examples are gamma glycidoxy propyl trimethoxy silane and gamma glycidoxy propyl methoxy diethoxy silane.

Examples of the stabilising surfactant having an alkylene moeity are oleyl propanol amide sulphosuccinate obtained from Witco of USA under the trade name Emcol 8300 and the potassium salt of the sulphonation product of oleic acid obtainable from Lankro Chemcials of Manchester, England under the trade name Lankropol OPA.

Methods for preparing the copolymer emulsions of the invention are well characterised in the literature. Polymer Synthesis (vols I and III) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Ed) by Sorenson and Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Wey) Band XIV published by George Tieme Verlag Stuttgart (1961) also provides preparative descriptions.

TEST METHOD:

Wet scrub resistance was measured by formulating the aqueous emulsion into the wallpaper ground

coat composition (parts by dry weight).

Emulsion	20 parts
Clay	100 *
Water retention aid	0.5 **
Dispersant	0.3 ***
Sodium hydroxide to give 45% solids	0.15

* Obtainable as SPS clay from English China Clay Ltd of St Austell England.
** Obtainable as Finnfix FF5 from Finn Forest Chemicals of Cheam, England
*** Obtainable as Dispex N40 from Allied Colloids Ltd of Bradford, England.

The coat composition was coated onto a wallpaper at a level of 25g/m^2 and dried for 2 minutes at 120 °C. It was then equilibrated overnight at 20 °C and 65% RH. The coated wallpaper was then callendered twice at 50 to 55 °C under a pressure of 200 lbs/sq in and then allowed to equilibrate overnight at 20 °C and 65% RH before testing.

In method A a Timperley testing machine fitted with a felt pad was used with a soft soap solution and set to operate at 120 ± 10 strokes/minute. All groundcoats were tested to 150 rubs and visually graded for coating abrasion.

In method B a wet abrasion scrub tester (Sheen Instruments Ltd of Teddington England) fitted with a hogs hair brush was used with a soft soap solution. Groundcoats were tested to 500 scrubs and again visually graded for coating abrasion.

VS - very slight, ie. best resistance
S - slight
M - moderate
H - heavy
VH - very heavy, ie. worst resistance

SPECIFIC DESCRIPTION OF THE INVENTION:

Examples of the preparation and use of vinyl acetate copolymer emulsions will now be given to illustrate but not limit the invention.

EXAMPLE I

The components were utilised in the following percentages.

Monomer Phase	% by weight
base monomers: Vinyl acetate	80.00
Ethylene	20.0
functional monomers:	
Acrylic Acid	1.0 pphm
Diallyl Maleate	0.2 pphm
pphm = parts per hundred of base monomer	
Surfactant System	
Emcol K8300	2.3
Aerosol A102	1.3
Initiator System	
Ammonium persulphate	
i) initial charge	0.3
ii) continuous addition	0.4
Finishing off stage	
t-butyl hydroperoxide	0.3
Sodium metabisulphite	0.3
Post-addition	
gamma-glycidoxypropyltrimethoxysilane	1.0

The surfactant solution comprising a 37% aq solution of Emcol K8300 (87.7g), 30% aq solution of Aerosol A102 (61.5g) and ammonium persulphate (4.3g, initial charge) dissolved in deionised water (1038g) was prepared and charged to a 4 litre pressure vessel heated to 38° C. At 38° C the reactor was purged twice with nitrogen, once with ethylene and pressurised with ethylene to 800 psi with stirring. The temperature was adjusted to 75° C while 10% of the monomer phase was pumped to the reactor.

The reaction mass was held at 75° C for 30 minutes then the continuous additions of persulphate solution (5.3g in 300g of deionised water) and the remainder (90%) of the monomer phase were started. The persulphate solution was added over 6.5 hours and the monomer phase over 6.0 hours.

The pressure was maintained at 800 psi until the desired quantity of ethylene has been reacted, this was after 3.5 hours from start of continuous additions.

After completion of all continuous addition the reaction mass was held at 80° C for 30 minutes and the contents of the reactor then cooled to 40° C followed by pumping of finishing off stage (4.6g of each in 50g of deionised water) to the reactor, in separate streams, over 30 minutes. The contents of the reactor then cooled to 25° C and discharged to a degassing tank.

Ammonia solution was used to adjust the pH of the emulsion latex to 8 then post-reacted with 1.0% epoxy silane while stirring. The emulsion had a solids content of 50%.

The product emulsion and post reacted emulsion were each tested for scrub resistance: the results are given in Table I.

Example 2

The procedure of example 1 was repeated but using a base monomer charge of:

vinyl acetate	90%
ethylene	10%

and a functional monomer charge:

acrylic acid	1.0 pphm
diallyl maleate	0.2

Example 3

The procedure of example 1 was repeated but using a base monomer charge of:

vinyl acetate	77%
ethylene	23%

and a functional monomer charge:

acrylic acid	0.5 pphm
diallyl maleate	0.2

Example 4

The procedure of example 1 was repeated but using a base monomer charge of:

vinyl acetate	84%
ethylene	16%

and a functional monomer charge:

acrylic acid	0.5 pphm
diallyl maleate	0.2

In addition the surfactant Aerosol A102 (1.3%) was replaced by Arylan SC15 0.45% (Dodecylbenzene sulphonate ex. Lankro Chemicals, Manchester, England).

Example 5

The procedure of example 1 was repeated but using a base monomer charge of:-

vinyl acetate	93%
ethylene	7%

With no functional monomer charge, in addition the surfactant Aerosol A102 (1.3%) was replaced by Arylan SC15 (0.45%).

Example 1-4, which contain acrylic acid as a functional comonomer, all show an improvement in scrub

resistance on post-addition of epoxy silane. However results for example 5 show an improvement and here the acrylic acid is absent. It is however, regarded as essential that the polymerisation is performed in the presence of an effective amount of stabilising surfactant having a C14 to C20 alkylene moiety.

Example 6

This example described the preparation and use of a copolymer emulsion having the composition by weight of:

vinyl acetate	80%
butyl acrylate	20%

and a functional monomer charge:

acrylic acid	1.0 pphm
diallyl maleate	0.2

A surfactant solution comprising a 37% aqueous solution of Emcol K8300 (15.7g), 31% aqueous solution of Aerosol A102 (11.0g) and ammonium persulphate (0.8g) dissolved in distilled water (180g) was charged to a 1 litre glass reactor, purged twice with nitrogen and heated to 75 °C with stirring. A monomer mix comprising:

vinyl acetate	200 g
butyl acrylate	50 g
acrylic acid	2.5 g
diallyl maleate	0.5 g

had been previously prepared and 10% was added to the reactor when the temperature reached 60 to 65 °C. When the reactor temperature reached 75 °C it was held at that temperature for 45 minutes.

Then an ammonium persulphate solution (persulphate 0.95g in distilled water 30g) was added continuously over a 5 hour period and the remaining 90% of the monomer mix added over 4-5 hours. After completion of all additions the reaction was held at 75 °C for 30 minutes and the contents of the reactor cooled to 40 °C before adding a finishing off stage of oxidising and reducing agent.

Ammonia solution was used to adjust the pH of the emulsion latex to 8 then post-reacted with the epoxy silane of Example I while stirring. The emulsion had a solids content of 50%.

The product emulsion and post reacted emulsion were each tested for scrub resistance, the results are given in Table 1.

Example 7

The procedure of Example 6 was repeated but using a base monomer charge of:

vinyl acetate	80%
butyl acrylate	20%

and a functional monomer charge:

acrylic acid	0.5 pphm
diallyl maleate	0.2 pphm
sodium vinyl sulphonate	1.0 pphm

Example 8

The procedure of example 7 was repeated but omitting the functional monomers and replacing Aerosol A102 (1.3%) with Arylan SC15 (0.28%).

Example 6 and 7, which contain acrylic acid as a functional comonomer, all show an improvement in scrub resistance on post-addition of epoxy silane, (Table 1). However, results for example 8 also shows an improvement and here the acrylic acid is absent. It is however regarded as essential that the polymerisation is performed in the presence of an effective amount of stabilising surfactant having a C14 to C20 alkylene moiety. This is demonstrated in example 9.

Example 9 (comparison)

The procedure of example 7 was repeated but omitting the functional monomers and replacing the Emcol K8300 with further Aerosol A102. Adjustment to pH 8 with ammonia and post-addition of epoxy silane did not show any improvement in the scrub resistance over that of the base emulsion.

The emulsions of the invention gave improved results when incorporated in wallpaper ground coats.

TABLE 1

EXAMPLE	SCRUB RESISTANCE			
	PRODUCT		POST REACTED	
	A	B	A	B
1	H	*	VS	VS
2	*	VH	*	M
3	VH	*	S	*
4	VH	*	S/M	*
5	S/M	S/M	S	S
6	*	VH	*	M
7	VH	*	M	*
8	*	H	*	S/M
9**	M	VH	M	VH

* not measured

** comparison

It is seen that post reacting the product emulsion with epoxy silane improves the scrub resistance..

Claims

1. The use in a wallpaper ground coat of a copolymer emulsion latex having a solids contents of about 20% to about 70% by weight, preferably from about 40% to about 60%, wherein vinyl C1 to C13 alkanoate forms at least about 40% by weight of the monomer charge characterised in that

i) the polymerisation is performed in the presence of an effective amount of a stabilising surfactant having a C14 to C20 alkylene moiety, and

ii) the polymerised emulsion is reacted with an effective amount of an epoxy silane material.

2. A copolymer emulsion latex according to claim 1 wherein the comonomer is a C2 to C4 ethylenic hydrccarbon.

3. A copolymer emulsion latex according to any preceding claim wherein the stabilising surfactant is present in an amount of from about 1% to about 10% by weight, preferably 2% to 8%, relative to the copolymerisable monomers.

4. A copolymer emulsion latex according to any preceding claim wherein the epoxy silane is present at a level of about 0.1% to 3% by weight of emulsion.

5. A copolymer emulsion latex according to any preceding claim wherein the epoxysilane is present in an amount of from about 0.1% to about 3% by weight (dry) relative to the latex.