

PATENT SPECIFICATION

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C3P 4C12A 4C13A 4C13B 4C13C 4C14A 4C14B 4C15
 4C20B 4C20C 4C6A 4C6B 4C8B 4D3B1 4D3B3
 4K4 4K7 4K8 4P1E5 4P2A1 4P2A4 4P2B 4P2X
 4P4X 4P6A 4P6D 4P6G 7C12A 7C13A 7C13B
 7C13C 7C14A 7C14B 7C15 7C20B 7C20C 7C6A
 7C6B 7C8B 7D1A 7D2A1 7K4 7K8 7K9 7P1C
 7P1E2 7P1F 7P2X 7P4C 7P6A 7P6D 7P6G
 8C12A 8C13A 8C13B 8C13C 8C14A 8C14B
 8C15 8C20B 8C20C 8C6A 8C6B 8C8B 8D2A
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 9C8B 9D1A1 9K7 9T2D

C3G 1BX 1C2 2B 2C 3A2 3C4 C

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(54) PROCESS FOR THE PREPARATION OF FILM-FORMING
 LATICES BY EMULSION POLYMERISATION

(71) We, REVERTEX LIMITED, a British Company, of 51—55 Strand, London, W.C.2., 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 film-forming latices of high polymeric substances suitable for use as binders in emulsion paints and other aqueous coating compositions. In particular the invention relates to a process involving the modification of latices prepared by emulsion copolymerisation of (a) a vinyl ester of a saturated aliphatic mono-carboxylic acid containing 2 to 4 carbon atoms, with (b) a vinyl ester of a branched saturated aliphatic mono-carboxylic acid of which the carboxyl groups are attached to tertiary and/or quaternary carbon atoms, and which contain not less than 9 carbon atoms. Hereinafter these acids will be referred to as "branched mono-carboxylic acids" in the interest of brevity.

The preparation of latices by emulsion polymerisation of the vinyl esters of branched mono-carboxylic acids has already been proposed, and copolymers of vinyl acetate with the vinyl esters of branched mono-carboxylic acids are frequently employed as the film forming binders in aqueous coating compositions, such as e.g. emulsion paints. A particular advantage of such copolymer latices is

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their relatively high degree of resistance to hydrolysis and to degradation by natural weathering. These advantages are conferred principally by the vinyl esters of the branched mono-carboxylic acid. However for certain applications, surface coating compositions based on such latices suffer from the disadvantage of exhibiting too high a degree of dirt retention when exposed to exterior weathering. This is particularly evident in emulsion paints or similar aqueous coating compositions containing relatively low amounts only of pigments and/or extenders. Coatings with a low volume concentration of pigments, extenders or fillers are of importance where it is desired that the resulting surface shall exhibit a relatively high degree of gloss. At least one reason for this disadvantageously high degree of dirt retention is that the film forming binder is too soft and/or too tacky at ambient temperatures.

While it is possible to reduce the softness and/or tackiness of copolymers of vinyl acetate and the vinyl ester of a branched mono-carboxylic acid by reducing the proportion of the latter component, this is undesirable in practice, because, in order to achieve a sufficient degree of hardness, the proportion of vinyl ester of branched mono-carboxylic acid would have to be reduced to such an extent that the advantages conferred by this type of monomer would be almost completely lost.

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The purpose of the present invention is to modify the properties of copolymers such as those of vinyl acetate and the vinyl esters of branched mono-carboxylic acids in such a way that excessive dirt retention of coatings based on these copolymers is avoided while gloss retention is enhanced. Nevertheless the advantages of a high resistance to saponification and good exterior durability, conferred by such copolymers, are retained, and may even be enhanced. This desirable modification is achieved by the addition to such a latex of one or more ethylenically unsaturated monomers and the subsequent polymerisation of the added monomer or monomers. Therefore in accordance with the present invention there is provided a process for preparing an aqueous film-forming latex, wherein a pre-formed latex prepared by aqueous emulsion copolymerisation of (a) one or more vinyl esters of saturated unbranched aliphatic mono-carboxylic acids, which acids contain 2 to 4 carbon atoms with (b) one or more vinyl esters of branched saturated aliphatic mono-carboxylic acids of which the carboxyl groups are attached to tertiary and/or quaternary carbon atoms and which acids contain not less than 9 carbon atoms, is subjected to at least one further polymerisation step by mixing the pre-formed latex with an ethylenically unsaturated monomer or mixture of ethylenically unsaturated monomers, the monomer or monomers being different from the monomer precursors of the preformed latex, and subsequently causing the monomer or monomers to polymerise, the or at least one of the admixed monomers being so chosen that if polymerised in the absence of the pre-formed latex but in the presence of any other admixed monomer it yields a homopolymer or copolymer having a glass transition temperature higher than that of polyvinyl acetate.

The types of monomer which are used in the present process are those which, as indicated, yield homopolymers having glass transition temperatures higher than that of polyvinyl acetate, i.e. they are so-called "hardening comonomers". It is a disadvantage of most of the hardening comonomers readily commercially available that they cannot be readily copolymerised with vinyl acetate, except in the presence of at least one other monomer such as the esters of acrylic acid, which are "softening" monomers. The manufacture of vinyl acetate copolymers containing a usefully high proportion of such monomers is therefore not commercially attractive. In particular, vinyl aromatic monomers such as styrene or substituted styrenes and also the esters of methacrylic acid such as methyl methacrylate greatly retard the rate of polymerisation of vinyl esters. Acrylonitrile and methacrylonitrile will not copolymerise readily with vinyl esters in the absence of at least one

further monomer such as acrylic acid or its esters.

In the compositions prepared in accordance with the present invention a pre-formed latex is subjected to at least one process of subsequent polymerisation. The pre-formed latex is obtained by the emulsion copolymerisation of (a) a vinyl ester of an unbranched mono-carboxylic acid containing from 2 to 4 carbon atoms together with (b) a vinyl ester of a branched saturated aliphatic mono-carboxylic acid as hereinbefore defined. The preparation of copolymer latices of this type by emulsion copolymerisation is well known to those skilled in the art. One or more other ethylenically unsaturated monomers may be copolymerised together with the indicated vinyl esters if so desired. Such monomers include alpha-beta unsaturated mono- or di-carboxylic acids such as maleic acid, fumaric acid, itaconic acid and acrylic acid; and the esters of these acids with mono-hydric alcohols containing from 1 to 20 carbon atoms; vinyl chloride; olefins such as ethylene, propylene and isobutylene; and vinyl esters of alkanolic acids.

The modification of the pre-formed latex is carried out by mixing the latex with a monomer or mixture of monomers and subsequently causing the monomer or monomers to polymerise. It is believed that a substantial amount of graft polymerisation on to the polymer of the pre-formed latex occurs, but that the grafting will not proceed to completion, and that some homopolymerisation (when there is one monomer) or copolymerisation (when there is more than one monomer) will also occur. It is a necessary condition of the present invention that at least one of the admixed monomers, if polymerised in the presence of the pre-formed latex should yield a homopolymer having a glass transition temperature higher than that of polyvinyl acetate.

Before, during or after the further polymerisation initiator (catalyst) capable of yield-emulsion stabilisers, solvents, plasticisers, chain transfer agents, electrolytes and other ingredients of the type known in the art of emulsion polymerisation may be added to the said pre-formed latex. It is also envisaged that after substantially complete polymerisation of the monomer or mixture of monomers used in this modifying step, a further step or steps of consecutive polymerisation may be carried out if so desired.

It is envisaged that the monomer or mixture of monomers added to the pre-formed latex will be caused to polymerise by a free radical mechanism and that this polymerisation will be induced e.g. by heat or by the addition to the system of a free radical polymerisation initiator (catalyst) capable of yielding free radicals, which initiator may consist of a redox initiator system. Examples of such initiators include those containing the group-

ings —O—O— or —N—N— i.e. peroxy or azo compounds. Examples of suitable peroxy compounds include hydrogen peroxide, organic hydroperoxides such as tertiary butyl hydroperoxide, di-alkyl peroxides such as di-tertiary butyl peroxide, di-acyl peroxides such as benzoyl peroxide, and the salts of peroxy disulphuric acid. An example of a suitable azo compound is azo di-isobutyronitrile. The polymerisation of the added monomer or mixture of monomers in the presence of the pre-formed latex may be conducted at a temperature in the range 0° C. to 100° C. The decomposition of the initiator into free radicals may be simply the result of thermal decomposition or this decomposition may be activated by the incorporation in the mixture of a reducing agent or other substance. Suitable reducing agents which act as activators for free radical initiators include sulphites, sulphoxylates, ferrous salts, tertiary aromatic amines, sugars and ascorbic acid.

Examples of monomers which may be used in the modifying step and which when polymerised alone or in admixture with each other or other monomers, yield polymers having a glass transition temperature higher than that of polyvinyl acetate, are styrene, alpha-methyl styrene, vinyl toluene, methyl methacrylate, vinylidene chloride, acrylonitrile and vinyl chloride. In addition to these monomers, other ethylenically unsaturated monomers may be added including those indicated above as being optionally copolymerisable with the vinyl ester components (a) and (b).

The total quantity of the ethylenically unsaturated monomer or monomers mixed with the pre-formed latex may vary, but is preferably from 1 part to 50 parts by weight, more preferably from 1 to 25 parts by weight for every 100 parts by weight of the non-aqueous portion of the pre-formed latex.

The present latices are used as film-forming compositions and may be compounded with other ingredients well known to those skilled in the manufacture or practical application of polymer dispersions, such as pigments, extenders, plasticisers, anti-foaming agents, buffers, solvents, colloids, dispersants and wetting agents. The present latices are particularly useful for forming aqueous emulsion paints which have good gloss-retention on weathering.

The examples which follow are intended to illustrate the practice of the present invention. Unless otherwise stated all parts and percentages quoted in the examples are by weight.

EXAMPLE 1

This example describes the preparation of a latex of a simple copolymer of (a) vinyl acetate with (b) the vinyl ester of a branched mono-carboxylic acid sold commercially under

the Registered Trade Mark "Veova" 911 by Shell Chemical Co. Ltd.

	Parts	
Sodium dioctyl sulphosuccinate	0.24	
Hydroxyethyl cellulose*	1.20	
Sodium Bicarbonate	0.16	
Crotonic acid	0.10	70
Water	43.39	
Vinyl acetate	42.80	
"Veova" 911	10.80	
Carbon tetrachloride	0.03	
Ammonium persulphate	0.16	75
Polyethoxylated nonylphenol	1.12	
	100.00	

*supplied under the Registered Trade Mark "Natrosol" 250L by Hercules Powder Co. Ltd.

The polymerisation, using the above ingredients, was carried out by the well-known delayed monomer addition technique at a temperature of 80 to 85° C. The resulting latex had a total solids content of 55%, a viscosity of 1770 cps measured at a shear rate of 12.0 sec⁻¹, and an average particle diameter of 0.53 microns as determined by light-scattering.

EXAMPLE 2

This example illustrates the polymerisation of a monomer, namely styrene, in the presence of the pre-formed latex of Example 1 to yield a product prepared according to the teachings of the present invention.

	Parts	
Pre-formed latex of Example 1	100.0	95
Styrene	5.0	
tert-Butyl hydroperoxide	0.05	
10% aqueous solution of sodium formaldehyde sulphonylate	0.75	100

The pre-formed latex was placed at ambient temperature in a suitable vessel equipped with a mechanical stirrer and the styrene was added over the course of approximately 5 minutes. The tertiary butyl hydroperoxide was then added and the mixture was stirred for 10 minutes. The sodium formaldehyde sulphonylate solution was then stirred in. Stirring was continued for 30 minutes, and the product was then left at ambient temperature for at least 24 hours before use.

EXAMPLE 3

This example illustrates the polymerisation of methyl methacrylate in the presence of the pre-formed latex of Example 1.

	Parts	
Latex of Example 1	100.0	
Methyl methacrylate	5.0	
tert-Butyl hydroperoxide	0.05	
10% aqueous solution of sodium formaldehyde sulphonylate	0.75	120

The procedure was the same as that described in Example 2, except that the tertiary butyl hydroperoxide was dissolved in the methyl methacrylate before the latter was added to the pre-formed latex.

EXAMPLE 4

This example demonstrates the increased indentation resistance which results when the latex of Example 1 is modified as follows:

	Parts
Latex of Example 1	100.0
Styrene	5.0
tert-Butyl hydroperoxide	0.05
10% Aqueous solution of ascorbic acid	1.0

The procedure of Example 2 was followed, except that the sodium formaldehyde sulfoxylate solution was replaced by a solution of ascorbic acid.

A dry film of the copolymer was obtained by allowing a sample of the resulting latex to dry, and the indentation behaviour of this film was examined using a micro-indentometer manufactured by Research Equipment (London) Ltd. The indentation produced by a 5 gm. weight acting on a stylus of 0.032 inch diameter was 0.58 micron. The copolymer of Example 1 gave an indentation of 0.99 micron.

EXAMPLE 5

This example illustrates the conjoint polymerisation of two monomers, styrene and butyl acrylate, in the presence of the pre-formed latex of Example 1. These two monomers are respectively "hardening" and "softening" monomers.

	Parts
Latex of Example 1	100.0
Styrene	7.5
Butyl acrylate	2.5
tert-Butyl hydroperoxide	0.08
10% Aqueous solution of sodium formaldehyde sulfoxylate	1.20

The procedure of Example 2 was used.

EXAMPLE 6

This example compares the properties of semi-gloss emulsion paints based respectively on the products of Examples 1, 2 and 3.

A pigment dispersion was made according to the following formula:

	Parts	
Titanium dioxide	55.0	50
Tetrasodium pyrophosphate	0.1	
"Pluronic" L64*	1.0	
Ammonia solution S.G. 0.910	0.3	
10% Sodium salt of a copolymer of maleic anhydride and an α -olefin	3.0	55
Hydrocarbon oil defoaming agent	0.5	
15% solution of polyacrylic thickener	10.0	
water	10.0	60
	<u>79.9</u>	

*An ethylene oxide-propylene oxide block copolymer marketed by Wyandotte Chemicals Corporation; "Pluronic" is a Registered Trade Mark.

Three paints were then made from this pigment dispersion, according to the following formulation, using the latices of Examples 1, 2 and 3 (all adjusted to 55% total solids content (TSC)).

	Parts	
Pigment dispersion	79.9	
Latex (at 55% TSC)	100.0	
Butoxy-ethanol	2.0	
Propylene Glycol	18.0	75
Hydrocarbon oil defoaming agent	0.5	
	<u>200.4</u>	

In the following table, values are given, for each paint, of the % gloss measured at an angle of 60° C.

Latex used in gloss paint	% gloss reading (60° angle)
Latex of Example 1	40
Latex of Example 2	52
Latex of Example 3	50

After 8 weeks exterior exposure the paint made from the unmodified latex showed much more severe dirt contamination than either of the modified latices.

5 WHAT WE CLAIM IS:—

1. A process for preparing an aqueous film-forming latex, wherein a pre-formed latex prepared by aqueous emulsion copolymerisation of (a) one or more vinyl esters of saturated unbranched aliphatic mono-carboxylic acids, which acids contain 2 to 4 carbon atoms with (b) one or more vinyl esters of branched saturated aliphatic mono-carboxylic acids of which the carboxyl groups are attached to tertiary and/or quaternary carbon atoms and which acids contain not less than 9 carbon atoms, is subjected to at least one further polymerisation step by mixing the pre-formed latex with an ethylenically unsaturated monomer or mixture of ethylenically unsaturated monomers, the monomer or monomers being different from the monomer precursors of the pre-formed latex, and subsequently causing the monomer or monomers to polymerise, the or at least one of the admixed monomers being so chosen that if polymerised in the absence of the pre-formed latex but in the presence of any other admixed monomer it yields a homopolymer or copolymer having a glass transition temperature higher than that of polyvinyl acetate.

2. A process as claimed in Claim 1, wherein component (a) of the pre-formed latex is vinyl acetate.

3. A process as claimed in Claim 1 or 2, wherein the monomer mixed with the pre-formed latex is styrene, methyl methacrylate, acrylonitrile, vinyl chloride, or a mixture of two or more thereof.

4. A process as claimed in any preceding Claim, wherein said mixture of monomers mixed with the pre-formed latex comprises one or more alpha-beta unsaturated mono- or di-carboxylic acids, or the esters of such acids with the mono-hydric alcohols containing from 1 to 20 carbon atoms.

5. A process as claimed in any preceding Claim, wherein said mixture of monomers mixed with the pre-formed latex comprises one or more vinyl esters of alkanolic acids.

6. A process as claimed in any preceding Claim, wherein the total quantity of said monomer or monomers mixed with the pre-formed latex is from 1 part to 50 parts by weight for every 100 parts by weight of the non-aqueous portion of the pre-formed latex.

7. A process as claimed in Claim 6, wherein the total quantity of said monomer or monomers is from 1 to 25 parts by weight for every 100 parts by weight of the non-aqueous portion of the pre-formed latex.

8. A process as claimed in any preceding Claim, wherein the further polymerisation step or steps is or are carried out in the presence of a free-radical polymerisation initiator.

9. A process as claimed in Claim 8, wherein the polymerisation initiator consists of a redox initiator system.

10. A process for preparing an aqueous film-forming latex substantially as hereinbefore described in any one of Examples 2 to 5 of the foregoing Examples.

11. An aqueous film-forming latex produced by the process claimed in any preceding claim.

12. A composition comprising the film-forming latex of Claim 11 compounded with one or more of pigments, extenders, plasticisers, anti-foaming agents, buffers, solvents, colloids, dispersants and wetting agents.

13. A composition as claimed in Claim 12 in the form of an aqueous emulsion paint.

14. An aqueous emulsion paint in accordance with Claim 13 substantially as hereinbefore described in Example 6 of the foregoing Examples.

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2. A process as claimed in Claim 1, wherein component (a) of the pre-formed latex is vinyl acetate.

35 3. A process as claimed in Claim 1 or 2, wherein the monomer mixed with the pre-formed latex is styrene, methyl methacrylate, acrylonitrile, vinyl chloride, or a mixture of two or more thereof.

40 4. A process as claimed in any preceding Claim, wherein said mixture of monomers mixed with the pre-formed latex comprises one or more alpha-beta unsaturated mono- or di-carboxylic acids, or the esters of such acids with the mono-hydric alcohols containing from

45 1 to 20 carbon atoms.

5. A process as claimed in any preceding Claim, wherein said mixture of monomers mixed with the preformed latex comprises one or more vinyl esters of alkanolic acids.

6. A process as claimed in any preceding Claim, wherein the total quantity of said monomer or monomers mixed with the pre-formed latex is from 1 part to 50 parts by weight for every 100 parts by weight of the non-aqueous portion of the pre-formed latex.

7. A process as claimed in Claim 6, wherein the total quantity of said monomer or monomers is from 1 to 25 parts by weight for every 100 parts by weight of the non-aqueous portion of the pre-formed latex.

8. A process as claimed in any preceding Claim, wherein the further polymerisation step or steps is or are carried out in the presence of a free-radical polymerisation initiator.

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10. A process for preparing an aqueous film-forming latex substantially as hereinbefore described in any one of Examples 2 to 5 of the foregoing Examples.

11. An aqueous film-forming latex produced by the process claimed in any preceding claim.

12. A composition comprising the film-forming latex of Claim 11 compounded with one or more of pigments, extenders, plasticisers, anti-foaming agents, buffers, solvents, colloids, dispersants and wetting agents.

13. A composition as claimed in Claim 12 in the form of an aqueous emulsion paint.

14. An aqueous emulsion paint in accordance with Claim 13 substantially as hereinbefore described in Example 6 of the foregoing Examples.

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