

1088.105

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Preparation of Polymer Latices

We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, 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 the preparation of polymer latices which is especially an adhesive and coating applications.

The term "latex" is used herein to designate an aqueous dispersion of a water-insoluble polymer, the polymer being present in the form of very fine particles.

It is known that polymeric latices and solutions for laminating and coating articles made from wood, fabric, plastics, metals, etc., can be made from many different polymers. Latex adhesives and coating compositions are preferred over the solution-type compositions by many laminators, painters and manufacturers of coated articles for reasons well known in the art. For example, the use of water instead of a volatile organic solvent as the liquid phase not only reduces material and equipment costs but also reduces such application problems as toxicity, fire hazard, noxious odors, difficulty of clean up, damage to solvent-sensitive substrates, limited solubility of high molecular weight polymers, and excessive viscosity at high polymer solids content.

Carboxylic polymers are an important class

of polymers used by the adhesive and coating composition industries.

"Carboxylic polymer" herein designates a substantially water-insoluble interpolymer containing pendant carboxylic acid groups ($-\text{COOH}$), or salts thereof (e.g., $-\text{COONH}_4$). The pendant carboxylic acid groups may be attached directly to the polymer carbon-carbon chain or indirectly through other groups such as the group $-\text{CO.O.A}-$, where A is an alkylene group. Interpolymers of this type are the product of polymerising at least one monomer containing both a carboxylic acid group (or equivalent source of carboxyl groups) and olefinic unsaturation with at least one other monomer copolymerizable therewith.

It is frequently preferable to make adhesives and coating compositions from carboxylic polymers in latex form rather than solution form for the reasons listed above and because these polymers are so efficiently produced in latex form by emulsion polymerisation.

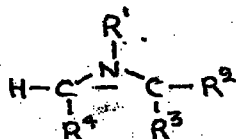
Although many useful coating and laminating compositions for fabrics, paper and man-made leather have been made from carboxylic polymer latices, the dry-film adhesion of these compositions to various substrates is not entirely satisfactory for many applications. Another limitation is the serious loss in adhesion and abrasion resistance of the dried film when the coated or laminated article is subjected to contact with water. This problem can be minimised by using much less than

[Price 4s. 6d.]

useful in/

the normal amount of surfactant in the latex, but only at a sacrifice in latex stability.

We have now found that aminoester latices useful as adhesives can be prepared by reacting a latex of a carboxylic polymer with aziridines and according to the present invention we provide a method of making an aminoester polymer latex, as herein defined, which comprises reacting a latex of a carboxylic polymer, as herein defined, with an aziridine of the formula:—

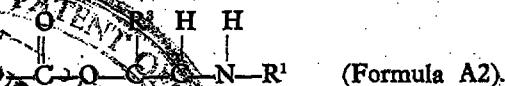
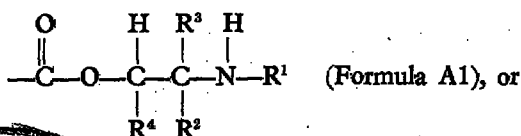


(Formula B)

where R¹ is hydrogen, an alkyl group containing from 1 to 10 carbon atoms or a benzyl group, R² and R³, which may be the same or different, are hydrogen, an alkyl group containing from 1 to 10 carbon atoms, a benzyl group or an aryl group and R⁴ is hydrogen or an alkyl group containing from 1 to 5 carbon atoms, until at least some of the pendant carboxylic acid radicals of the carboxylic polymer have reacted with the aziridine to form pendant amino ester groups.

The term "aminoester polymer latex" is used herein to designate the reaction product of the carboxylic polymer and the aziridine.

The reaction between the carboxylic polymer and the aziridine may be referred to as the "imination reaction" and the aziridine compound is sometimes referred to as an alkylene imine. It is possible for the ring opening of the aziridine to take place in two ways by cleavage of either of the two C—N bonds to give products having pendant groups of the formula:—



However, it is believed that, when neither of R² and R³ is hydrogen, the aminoester group formed in the first one, above having Formula A1.

When the aminoester polymer latex is required to have maximum dry-film adhesion, R¹ should be H or a C₁ or C₂ alkyl radical. Alkyl radicals above C₃ should be unbranched on the alpha carbon atom unless dry-film adhesion is of no great concern.

The carboxylic polymer latex can be pre-

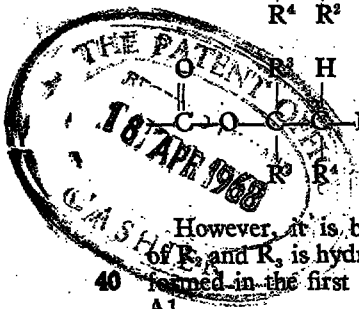
pared by known methods of emulsions polymerization wherein a carboxylic acid monomer is reacted in an aqueous medium with a copolymerizable monomer that is not a carboxylic acid, for example, an alkyl ester of acrylic or methacrylic acid in which the alkyl group contains 1 to 12 carbon atoms, a conjugated diene having 4—10 carbon atoms, acrylonitrile, styrene, alkyl-substituted styrene, vinyl chloride, vinyl acetate, or a blend of two or more such monomers. A non-acid monomer component containing a substantial proportion (over 30% by weight of the total monomers) of an alkyl methacrylate is especially useful when the latex of the invention is to be used for achieving a polyvinyl fluoride layer or in an application requiring good resistance to extended outdoor exposure.

It is usually best to use either methacrylic acid, acrylic acid or mixtures thereof as the monomer containing a carboxylic group for preparing the carboxylic polymer. Also useful, however, are other olefinically-unsaturated carboxylic acids possessing one or more olefinic carbon-to-carbon double bonds and one or more carboxyl groups. Preferably, the carboxylic acid should contain at least one olefinic carbon-to-carbon double bond which readily functions in an addition polymerization. That is, it should preferably contain either (1) a double bond in the alpha-beta position with respect to a carboxyl group (—CH=C—COOH), or (2) a double bond

attached to a terminal methylene grouping (CH₂=C).

The following acid monomers exemplify members of the number (1) group: crotonic acid, angelic acid, cinnamic acid, m-chlorocinnamic acid, p-chlorocinnamic acid, alpha-cyanocinnamic acid, and umbellic acid, sorbic acid, alpha-methyl sorbic acid, alpha-ethyl sorbic acid, alpha-chloro sorbic acid, alpha-methyl-gamma-acid benzal crotonic acid, beta-(2-butenyl) acrylic acid, 2, 4-heptadienoic acid, 2, 4-pentadienoic acid, 2, 4, 6-octatrienoic acid, 1-carboxylic-1-ethyl-4-phenyl butadiene - 1, 3, 5, 9-dimethyl-decatriene (2, 4, 8)-oic acid, 2-isopropenyl-furan-yl-(5)-acetic acid, hydromuconic acid, glutaconic acid, maleic acid, furamic acid, 2-vinyl-maleic acid and muconic acid.

The following acid monomers exemplify members of the number (2) group: acrylic acid, alpha-chloro acrylic acid, methacrylic acid, ethacrylic acid, alpha-isopropenyl acrylic acid, alpha-styryl-acrylic acid (2-carboxy-4-phenyl butadiene - 1, 3), beta-vinyl-acrylic acid (1-carboxybutadiene - 1, 3), alpha-vinyl acrylic acid, beta-acryloxy propionic acid and itaconic acid. We prefer to use a monoolefinic monocarboxylic acid having a terminal olefinic double bond in the alpha-beta position with respect to the



carboxyl group, i.e. a carboxylic acid of groups (1) and (2).

The carboxyl groups can also be introduced into the essential interpolymer from a carboxyl-supplying reagent such as maleic anhydride or monosodium oxalate by the method disclosed in U.S. Patent Specification No. 2,662,874 (e.g. in column 3, line 34 and column 4, line 8), or from a reagent containing groups hydrolyzable to carboxyl groups by the method disclosed in U.S. Patent Specification No. 2,710,292.

Typical of the known methods of making a carboxylic polymer latex useful in the practice of this invention are those described in U.S. Patents Specifications Nos. 2,395,017; 2,724,707, 2,868,752 and 2,868,754 and British Patent Specifications Nos. 761,928 and 832,111, the disclosures of which are incorporated herein by reference. Especially pertinent is the method described in U.S. Patent Specification No. 2,724,707, column 5, line 21 to column 6, line 60.

The emulsion used in preparing the carboxylic polymer latex usually is composed of the mixture of monomers, suitable emulsification and suspension agents (surfactants) buffering agents for pH control and a free radical catalyst, for example, potassium persulfate, a peroxide such as hydrogen peroxide, a diazo compound such as azobisisobutyroamide hydrochloride or a redox catalyst such as sodium persulfate-sodium sulfite, or mixtures of such catalysts. Polymerization can be carried out in the presence of a free radical catalyst in a closed vessel in an inert atmosphere and under autogeneous pressure or under artificially induced pressure or in an open vessel under reflux at atmospheric pressure. The temperatures of the polymerization can be varied from 0° C. or lower to 100° C. or higher, preferably from 20° C. to 90° C., depending to a large degree upon the activity of the monomers and catalyst used and the molecular weight desired in the polymeric product. The carboxylic acid monomer is preferably added to the emulsion reaction mixture in an amount sufficient to result in a carboxylic polymer into which 0.01 to 2% amino-nitrogen (by weight of polymer) can be introduced during the subsequent imination reaction. Generally, the carboxylic polymer should have an acid equivalent of 0.001 to 3.0, preferably 0.1 to 1.0, milliequivalents per gram (dry basis). In the interest of obtaining a substantially water-insoluble carboxylic polymer and a stable latex product, it is usually best to add less than 15% acid monomer based on the total weight of monomer in the reaction mixture.

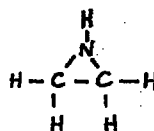
The acid content of the carboxylic polymer can be determined by separating the polymer from the aqueous phase, dissolving it in a solvent and titrating the resulting polymer solution with alcoholic KOH to a

phenolphthalein end-point. The acid content can also be determined by complete chemical analysis of the polymer.

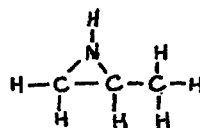
The carboxylic polymer is produced in any molecular weight that fits the intended use of the final product, usually upwards of 100,000 and frequently upwards of a million.

As indicated previously, the aminoester polymer latex is prepared by reacting the carboxylic polymer in latex form with an aziridine compound (alkylene imine) of Formula B above. Ethylenimine (Formula C) and 1,2-propylenimine (Formula D) are particularly preferred aziridines because of their relatively low cost and plentiful supply and because they tend to give the best adhesion characteristics in most final products.

FORMULA C



FORMULA D



The aziridine compound is added to the carboxylic polymer latex in an amount equal to 10 to 200% of the theoretical amount required to esterify all the pendant carboxyl groups of the carboxylic polymer. When the aziridine compound is added as an aqueous solution, the solution should be prepared a very short time before the solution is mixed with the latex; this is to avoid any undue hydrolysis of the aziridine compound prior to the imination reaction. The stability of the aminoester polymer latex that results from the imination reaction (esterification) tends to be enhanced by the presence of unreacted (non-esterified) carboxyl groups. The amount of unreacted carboxyl groups present in the product can be increased by adding proportionately less aziridine compound.

In a typical procedure for carrying out the imination reaction, the aziridine compound is mixed with the carboxylic polymer latex in a reaction vessel at, or near, room temperature (e.g., 18—30° C.) and atmospheric pressure, stirring is continued under the same conditions for about 10 to 60 minutes, the mixture is heated at about 40 to 80° C. until the reaction is completed, (e.g., 1/2 hour at the higher temperatures to about 12 hours at lower temperatures) and finally the reaction product is cooled to room temperature. The upper temperature limit is determined largely

by how much heat the particular latex will withstand without coagulating. The entire reaction can be carried out at room temperature, but heating is generally preferred because of the resulting shorter reaction time.

The product of the imination reaction described above is the aminoester polymer-latex. As shown previously, the aminoester polymer contains pendant amino ester groups. The amino nitrogen content of the aminoester polymer should be preferably from 0.01 to 2.0% by weight, and more preferably from 0.1 to 1.5%.

Various additives or modifiers known to be useful in latex adhesives and coating compositions can be added to the aminoester polymer latex, for example, pigments, other polymers in finely divided form, fillers, anti-freeze agents, plasticizers, stabilizers, odor controlling agents, fungicides, surfactants and flow controlling agents (e.g., thickeners). The surfactant content can vary over a wide range; for example, from 0.05 to 10% by weight based on the polymer solids content covers the most useful range of surfactant content for coating compositions.

The novel process is useful for the production of amino ester polymer latices in which the polymer has a molecular weight of any desired value, for example, upwards of 100,000, or even upwards of a million. Much greater utility is provided with the higher molecular weight polymer latices than is obtainable with these polymers in solution form because the viscosity does not become excessive in the latices as it does in the solutions. In fact, polymers can be used without difficulty in the latex which are extremely difficult to dissolve in ordinary volatile organic solvents. Greater utility is also provided in the lower molecular weight polymer latices than with solutions of these polymers because a higher polymer solids content can be present in the latices without an undue increase in viscosity.

Since the aziridines are known to be very susceptible to hydrolysis, it is quite unexpected that these compounds can be reacted so effectively with carboxylic polymers in aqueous media. It was expected that these imines would hydrolyze before any useful amount of aminoester units could be formed. Also, in view of the known sensitivity of latices, it is surprising that the imination reaction of the present method can be carried out without the latex being coagulated or otherwise destroyed.

The novel method is simple, economical and substantially free of health and fire hazards. Moreover, since many of the preferred carboxylic polymers are most effectively produced by emulsion polymerization, and since the imination reaction of this method is performed within the resulting latex, certain costly steps that would be necessary in a sol-

vent-medium reaction are absent from this method (e.g., separation, drying and dissolving the carboxylic polymer).

The aminoester polymer latices produced in accordance with this invention are useful as interior or exterior coating compositions and adhesives having a high degree of adhesion to a wide variety of materials, for example, wood (bare, primed or coated with an old paint film), plastics, fabrics, paper, and man-made leather, papered, painted or bare plaster walls and ceilings, metals, fabrics, masonry and cement-asbestos sheet materials. The adhesion to most materials is far superior to that obtained with the corresponding carboxylic polymer latex.

Before coating or laminating metal articles with the novel latex, it is usually best to passivate the metal first, for example, in a suitable chromate, phosphate or anodizing bath. Some of the most adhesion-resistant plastics can be strongly laminated to themselves and to other materials with this latex; for example, polyvinyl fluoride film can be laminated to itself and to most conventional construction materials.

In a typical lamination process, a coat of the latex is applied to one or both of the surfaces to be bonded, the coat is dried in a heat zone, the surfaces are integrally united under heat and pressure, and then the bonded assembly is cooled to room temperature. During the pressing cycle the aminoester polymer is heated enough to render it fluid and tacky. When laminating porous materials, such as wood or paper, the adhesive layer can be dried after the layers are united.

The invention provides an adhesive and coating composition characterized not only by improved dry-film adhesion and the other advantages mentioned above, but also by the known cost and application advantages of latices over polymer solutions as previously discussed. Moreover, house paints and latex compositions for coating man-made leather, paper and other articles are obtainable in accordance with this invention which have a unique combination of good latex stability and good retention of adhesive and abrasion resistance of the dried film when an article coated therewith is exposed to water (e.g., by immersion or spraying). Surprisingly enough, the durability after water-soaking is obtainable even when a relatively large proportion of surfactant is present in the latex, for example, from 5 to 10% by weight based on the polymer solids content of the latex. The latex product is also useful as a binder for non-woven fabrics, as a coating for tire cord, as a printing ink (colorants are added) and wherever else that polymers in latex form are known to be useful.

The Examples which follow are given for the purpose of illustrating the invention. All

quantities shown are on a weight basis unless otherwise indicated. The water listed in the formulation is deionized water.

EXAMPLE 1

- 5 An aminoester polymer latex having advantageous utility as an adhesive for laminating a wide variety of materials is prepared by first following Formulation E to make a latex of a carboxylic polymer.

10	Formulation E—Carboxylic Polymer Latex	Parts By Weight
	Portion 1	
	Water	405.0
15	Anionic surfactant (sodium lauryl sulfate)	0.91
	Portion 2	
	Water	18.0
	Potassium persulfate	0.73
20	Portion 3	
	Ethyl acrylate	206.0
	Methyl methacrylate	141.0
	Methacrylic acid	14.5
	Portion 4	
25	Water	71.0
	Anionic surfactant (sodium lauryl sulfate)	6.3
	Portion 5	
	Water	4.5
30	Potassium persulfate	0.4
		868.34

- Each portion is premixed before it is added. Portion 1 is charged into a conventional polymerization vessel equipped with stirrer, thermometer, condenser, and means to introduce nitrogen and reagents. The polymerization reaction to follow is carried out under nitrogen. Portion 1 is heated to 70° C., Portion 2 is added with stirring, and while keeping the contents of the vessel at 70 to 80° C., Portions 3 and 4 are added gradually and simultaneously over a period of 2 hours. Then Portion 5 is added, and the temperature of the mixture is kept at 70 to 80° C. for another 2 hours. After the resulting carboxylic polymer latex is cooled to 25° C., it is filtered through cheese-cloth to remove any coarse coagulum that has formed.

- The completed Formulation E latex has a carboxylic polymer content of about 42%. The polymer is a 57:39:4 interpolymers of ethyl acrylate:methyl methacrylate:methacrylic acid having a molecular weight of over a million.

- 55 A reaction vessel equipped with stirrer, thermometer, condenser and addition funnel is charged with 100 parts of the formulation

E carboxylic polymer latex and propyleneimine is added as a 30% aqueous solution (freshly prepared) in an amount equal to about 110% of the theoretical amount required to esterify all the pendant carboxyl groups of the carboxyl polymer. The propyleneimine (1, 2-propyleneimine or 2-methylaziridine) is added gradually over a period of 10 minutes while stirring at 25° C. Then the mixture is heated to 50° C. over a period of 30 minutes and the 50° C. temperature is maintained for an additional 30 minutes. After the resulting aminoester polymer latex is slowly cooled to 25° C. and the pH is adjusted to 9.5 with dilute ammonia, it is filtered through cheese-cloth to remove any coarse coagulum that has formed. The latex has a viscosity of 9.4 centipoises at 24° C., a preferred viscosity for rapid application of adhesive films.

Analysis of the latex before and after the imination reaction shows that 53.3% of the pendant carboxyl groups have been converted to aminoester groups during the reaction. The completed latex has good storage stability.

The molecular weight of the polymer is over a million. The amino nitrogen content of the aminoester polymer is about 0.8%.

The utility of the aminoester polymer latex as a wood adhesive is demonstrated by first applying a 1/2 inch wide strip of the latex to a lightly sanded surface of a piece of 0.2 inch thick plywood in an amount equal to 0.2 gram of latex per linear inch. A similar piece of plywood is then clamped in superposed contact with the latex-coated surface under a pressure of about 5 p.s.i. and the assembly is heated in a 110° C. oven for one hour. To facilitate subsequent testing of adhesion, the adhesive film is applied to within about 1/2 inch of the end of the substrate. After cooling the laminate to 25° C. and removing the clamps, the bond strength is measured in a conventional manner on an Instron (Trade Mark) Tensile Tester by pulling the pieces of wood apart at 180° angles at a rate of 2 inches per minute. The bond strength is 1187 p.s.i. (pounds per square inch).

When the wood lamination and test procedure described above is repeated except that the aminoester polymer latex is replaced with the Formulation E carboxylic polymer latex, the bond strength is only 632 p.s.i. Thus, the imination reaction almost doubles the wood-to-wood bond strength obtainable with the latex.

The utility of the Example 1 aminoester polymer latex as an adhesive for laminating sheet aluminum to polyvinyl fluoride film is demonstrated by first applying a 10 mils thick 1/2 inch wide strip of the latex to a conventional dichromate passivated surface of a 25 mil thick aluminum sheet, and drying the latex layer in a heat zone. A surface of a 2 mil thick, biaxially oriented, titanium di-

propyleneimine

0-25

oxide pigmented polyvinyl fluoride film is placed in contact with the dried latex layer, and the assembly is heated at 110° C. for 5 minutes between the platens of a press while under a pressure of about 500 p.s.i. After cooling the laminate to 25° C. and removing it from the press, the bond strength is measured by pulling the 2 plies apart at a rate of 2 inches per minute. A pull of over 5 pounds is required to remove the plastic film from the aluminum sheet. The bond is so strong that it is difficult to remove the plastic film without tearing it.

When the test described in the above paragraph is repeated except that the aminoester polymer latex is replaced with the Formulation E carboxylic polymer latex, a pull of only 2.9 pounds is required to remove the plastic film. The film is easily removed without being torn.

EXAMPLE 2

Aminoester polymer latices useful for laminating and coating a wide variety of materials are prepared by individually substituting the aziridines listed in Table I for propylenimine in the imination reaction described in Example 1. The percentage of pendant carboxyl groups converted to aminoester groups during the imination reaction in each latex is shown in Table II as "% Conversion".

TABLE I

Aziridine Compound	% Conversion
Ethylenimine (aziridine)	43.2
N-Butylaziridine	55.7
2,2-Dimethylaziridine	59.1
2-Ethylaziridine	53.4

EXAMPLE 3

Aminoester polymer latices having wide utility in coating and laminating industries are produced by repeating the imination reaction of Example 1 except for individually substituting carboxylic polymers made from the monomers listed in Table II for the carboxylic polymer used in Example 1. The ratio of monomers used, which is also the ratio of polymerized units in the interpolymers, is shown, as well as the percent conversion (as described in Example 2).

TABLE II

Monomers	Ratio	% Conversion
EA/MMA/AA	57/39/4	48.0
EA/MMA/MAA	58/40/2	52.5
EA/MMA/MAA	56/38/6	54.2
EA/MMA/IA	57/39/4	54.8
BMA/MAA	96/4	41.0
B/MMA/MAA	36/60/4	52.0

In Table II, EA is ethyl acrylate, BMA is butyl methacrylate, B is butadiene, MMA is methyl methacrylate, AA is acrylic acid, MAA is methacrylic acid, and IA is itaconic acid.

EXAMPLE 4

An aminoester polymer latex house paint adapted for use on the exterior siding and trim of houses having clapboard or other types of siding is prepared by first following Formulation F to make a latex of a carboxylic polymer.

Formulation F—Carboxylic Polymer Latex

Portion	Parts By Weight	
Portion 1		
Water	455.0	70
Portion 2		
Water	380.0	75
Methyl Methacrylate	346.5	
2-Ethylhexyl acrylate	408.0	
Methacrylic acid	15.5	
Anionic surfactant, 30% aqueous solution of sodium lauryl sulfate	25.6	80
Sodium meta-bisulfite	0.81	
Portion 3		
Potassium persulfate, 10% aqueous solution	16.94	
Portion 4		
Same as Portion 3	4.18	85
Portion 4		
Nonionic surfactant, 50% aqueous solution of "Triton" X-100 (octyl phenyl polyglycol ether)	92.4	90
	1744.93	

"Triton" is a Trade Mark

Portion 1 is charged into a conventional polymerization reaction vessel equipped with stirrer, means to control temperature, and means to introduce nitrogen. The polymerization reaction to follow is carried out under nitrogen. Portion 2 is premixed to emulsify the acrylic monomers; 120 parts of this portion are added to the vessel with stirring and the resulting mixture is heated to 65° C. Portion 3 is then added with stirring, the temperature is raised to 74° C., a reaction mixture temperature of 74 to 78° C. is maintained for 5 minutes, and while continuing to maintain this temperature, the remainder of Portion 2 is added gradually over a period of 140 minutes. Portion 4 is added and the mixture kept at 74 to 78° C. for 90 minutes more. After cooling the resulting interpolymer latex to 25° C., Portion 5 is added with thorough stirring, stirring is continued for 15 minutes, then the latex is filtered through cheesecloth to remove any coarse coagulum that has formed.

The resulting latex has a polymer content of about 47%, the polymer being a 45:53:2



interpolymer of methyl methacrylate:2-ethylhexyl acrylate:methacrylic acid. The average diameter of the polymer particles is about 0.1 to 0.2 micron. The polymer has a molecular weight of over 500,000, a relative viscosity of about 1.20, a tensile strength of over 1000 p.s.i. at 0° F. and an elongation of over 180% at 0° F.

The carboxylic polymer is iminated by charging a reaction vessel equipped with stirrer, thermometer, nitrogen inlet, condenser and addition funnel with 100 parts of the Formulation F latex. The reaction to follow is carried out under nitrogen. 1,2-Propylenimine (non-diluted) is added gradually with stirring at 26° C. in an amount sufficient to esterify 33% of the pendant carboxyl groups of the polymer; the amount actually added is equal to about 100% of the theoretical amount required to esterify all the pendant carboxyl groups. Then the mixture is heated to 58° C. over a period of 30 minutes and the 58° C. temperature is maintained for an additional 60 minutes.

After the resulting aminoester polymer latex is slowly cooled to 25° C. and the pH is adjusted to 9.5 with dilute ammonia, it is filtered through cheesecloth to remove any coarse coagulum that has formed. Analysis shows that 33% of the pendant carboxyl groups have been converted to aminoester groups during the reaction.

Pigment and various modifiers are added to the Formulation F latex in the form of a premixed dispersion prepared according to Formulation G.

Formulation G—Pigment Dispersion

	Parts By Weight
Portion 1	
Talc pigment extender	10.93
Methyl cellulose, "Methocel" HG	0.27
Portion 2	
Water	12.21
Portion 3	
Anti-foam agent, "Nopco" 1497V	0.30
Potassium tripolyphosphate	0.17
Ammonium hydroxide, 28% NH ₃	0.23
Bodying agent, "Acrysol" A-3	0.51
Phenyl mercury oleate, 10% in mineral spirits	3.24
Ethylene glycol	2.59
Portion 4	
Titanium dioxide pigment	35.68
Portion 5	
Nonionic surfactant, "Tween" 40	0.10
Water	6.03
Mica pigment extender	10.93

Portion 6

Ammonium hydroxide, 28% NH ₃	0.17	60
Anti-foam agent, "Nopco" 1497V	0.13	Nopco
Formulation F latex	8.50	

Portion 7

Formulation F latex	8.01	
	100.00	65

"Methocel", "Tween", and "Acrysol" and "Nopco" are trade marks.

In Formula G: "Methocel" HG has a viscosity of 3000 to 5000 centipoise at 20° C., measured on a 2% aqueous solution. "Nopco" 1497V is understood to be composed of 60% anionic sulfated saturated fatty acid, 8% free fatty acid, and 32% inert matter. "Acrysol" A-3 is a 25% aqueous solution of low molecular weight water-soluble polyacrylic acid. The titanium dioxide is an 82:18 blend of rutile and anatase types.

The 7 portions of Formulation G are introduced into a mixing tank in the order shown and uniformly blended and dispersed in accordance with conventional procedure for making pigment dispersions for use in latex paints.

Next, a paint composition is prepared by uniformly blending the components shown in Formulation H.

Formulation H—Acrylic Latex House Paint

	Parts By Weight	
Formulation F latex	459.0	90
Formulation G pigment dispersion	656.7	
Bodying Agent, "Acrysol" ASE-60	5.3	
	1121.0	

"Acrysol" ASE-60 is a 28% aqueous solution of a water-soluble interpolymer of methyl methacrylate, ethyl acrylate, and acrylic acid, the latter making up about 35% of the polymer.

The resulting paint has a pigment volume concentration of about 30%, a pH of about 9, a density of about 11.2 pounds per gallon and a convenient brushing viscosity of about 74 Krebs Units. The paint also has good stability on storage and exposure to temperatures alternating between freezing and ordinary room temperature.

The clapboard siding on the exterior walls of a house is painted with one coat of the completed latex paint, using an ordinary paint brush. The house had been painted four years previously with a conventional oil-base primer and white topcoat. The old weathered paint film is scraped lightly to remove loose paint from cracked and blistered areas, and the bare areas are primed with a conventional oil-base exterior primer and allowed to dry prior to the latex paint application. The paint has excel-

lent application properties on both the primed areas and the weathered film areas. The paint film is allowed to air-dry and age under ordinary atmospheric conditions. The paint film on the house is examined at frequent intervals for a period of several months and is found to have excellent resistance to cracking and blistering and good retention of appearance in general.

Loose pieces of clapboard siding in the same condition as those on the house are painted and dried as described above. The painted pieces are immersed in water for several hours and then tested immediately for paint film adhesion and abrasion resistance by conventional methods. The paint film is found to be much more resistant to removal with pressure-sensitive adhesive tape and to damage by abrasion with a pencil eraser than a carboxylic polymer paint film deposited and tested in the same manner. The latter is deposited from a paint made as described in Example 4 except the imination reaction is omitted.

Considering the amount of surfactant present in the paint of Example 4 and the well known tendency of surfactant-stabilized latex paints to suffer serious reduction in adhesion and abrasion resistance when the painted article is soaked in water, the results obtained are indeed advantageous and unexpected.

EXAMPLE 5

A man-made leather shoe-upper material having a poromeric (porous polymeric) vapor permeable structure is prepared and surface-finished with an aminoester polymer latex in the following manner.

A poromeric man-made leather material is produced in accordance with Example 6 of U.S. Patent 3,000,757. This material is comprised of a nonwoven fabric containing a porous elastomeric binder and surface coated with an adherent and durable layer of microporous elastomeric material.

Next, a carboxylic polymer latex is prepared in accordance with Example 3 of U. S. Patent 2,795,564. The polymer solids content of the latex is adjusted to 42%. The polymer is a 37:61.5:1.5 interpolymers of methyl methacrylate: ethyl acrylate, methacrylic acid.

The carboxylic polymer is iminated by charging a reaction vessel equipped with stirrer, thermometer, condenser and addition funnel with 100 parts of the carboxylic polymer latex. 1,2-Propylenimine is gradually added (as a freshly made 33% aqueous solution) with stirring at 25° C. in an amount sufficient to esterify 50% of the pendant carboxyl groups of the polymer. Then the mixture is heated to 58° C. over a period of 30 minutes and this temperature is maintained for an additional 30 minutes.

After the resulting aminoester polymer latex is slowly cooled to 25° C. and the pH is

adjusted to 9.5 with dilute ammonia, it is filtered through cheesecloth to remove any coarse coagulum that has formed. Analysis shows that 50% of the pendant carboxyl groups have been converted to aminoester groups during the reaction. A brown coating composition is prepared from the latex in accordance with Formulation I.

Formulation I—Latex Coating Composition

	Parts by Weight	
Black dye	2.43	
Brown dye	10.20	
Yellow dye	1.70	
Titanium dioxide, 20% aqueous dispersion	2.43	
Water	58.94	
Nonionic surfactant, 10% aqueous solution	0.05	
Aminoester polymer latex of this example	23.80	
	99.55	

In Formulation I: The 3 dyes are anthraquinone vat dyes in the form of 20% aqueous pastes. The yellow is C. I. 61725, the brown is C.I. 69015 and the black is a 50:50 blend of olive C.I. 69525 and navy blue C.I. 71200. C.I. designates Color Index Number as given in "Colour Index", second edition, Volume 3, copyright 1957 in the U.S. by the American Association of Textile Chemists and Colorants. The titanium dioxide is dry-ground water-dispersible anatase type. The surfactant is the condensation product obtained by reacting 20 moles of ethylene oxide with 1 mole of an aliphatic C-18 alcohol. The ingredients are added and mixed in the order listed in a conventional pigment-dispersion mixer.

The man-made leather material is coated on the microporous surface with a 0.2 mil (dry thickness) layer of the Formulation I composition. The coating is done by spraying a first coat, briefly air drying, and spraying a second coat. Next, the coloured aminoester coating is dried for 3 minutes in a 105° C. heat zone.

A 0.05 mil (dry thickness) coat of clear pyroxylin lacquer of a type commonly used in finishing leather products is applied by spraying over the Formulation I coat. The pyroxylin lacquer has a pyroxylin content of about 5% and a solvent composed of a 70:30 blend of ethanol and toluene. The lacquer also contains about 30% of a plasticizer for pyroxylin (based on the weight of pyroxylin) the plasticizer being a 60:40 blend of tricresyl phosphate and castor oil.

After the pyroxylin coat is dried and the product cooled to room temperature, the coated surface of the shoe-upper material is embossed in a conventional manner with a fine grain pattern that simulates the appearance of leather grain. The pyroxylin coat

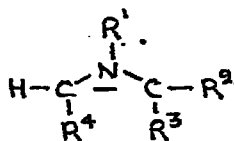
facilitates embossing by preventing the surface from sticking to the hot engraved metal embossing roll.

- 5 The Formulation I coating does not unduly reduce the vapor permeability of the product and it is surprisingly adherent and durable, not only when dry but after the product is soaked for 60 minutes in water. The water-soaked abrasion resistance is measured by wrapping a piece of the water-soaked product around a 1 inch diameter cylinder with the coated surface exposed and rubbing the coated surface against wet #10 cotton duck under a weight of 1 pound per linear inch. The length of each stroke of rubbing is 2 inches. It takes 200 such strokes to damage the coating.

- 20 A control sample made in accordance with Example 5 except that the imination reaction is omitted takes only 40 strokes to damage the coating after the sample is soaked 60 minutes in water. Shoes made with uppers of the control sample material are much less resistant to damage of the finish than shoes made with uppers of the Example 5 product, for example, when overshoes or rubbers are worn after the shoes have become wet.

WHAT WE CLAIM IS:—

- 30 1. A method of making an aminoester polymer latex, as hereinbefore defined, which comprises reacting a latex of a carboxylic polymer, as hereinbefore defined, with an aziridine of the formula:—



- 35 where R¹ is hydrogen, an alkyl group containing from 1 to 10 carbon atoms or a benzyl group, R² and R³, which may be the same or different, are hydrogen, an alkyl group containing from 1 to 10 carbon atoms, a benzyl group or an aryl group and R⁴ is hydrogen or an alkyl group containing from 1 to 5 carbon atoms, until at least some of the pendant carboxylic acid radicals of the carboxylic polymer have reacted with the aziridine to form
- 45 pendant aminoester groups.

2. A method according to claim 1 in which the carboxylic polymer has an acid equivalent of from 0.001 to 3.0 milliequivalents per gram.

3. A method according to claim 1 or 2 in which the latex of the carboxylic polymer is reacted with the aziridine until sufficient pendant carboxylic acid radicals are converted to amino ester radicals to result in an amino-ester polymer having an amino nitrogen content of from 0.01 to 2.0% by weight.

4. A method according to claim 3 in which the resultant aminoester polymer has an amino nitrogen content of from 0.1 to 1.5% by weight.

5. A method according to any of claims 1 to 4 in which the aziridine is ethylene imine.

6. A method according to any of claims 1 to 4 in which the aziridine is 1,2-propylene imine.

7. A method according to any of claims 1 to 4 in which R¹ is an alkyl radical containing from 1 to 4 carbon atoms.

8. A method according to any of claims 1 to 7 in which the carboxylic polymer contains over 30% by weight of structural units derived from an alkyl methacrylate.

9. A method according to any of claims 1 to 8 in which the carboxylic polymer contains structural units derived from methacrylic acid and/or acrylic acid.

10. A method of making an aminoester polymer latex, as hereinbefore defined, substantially as hereindescribed with reference to any of the Examples.

11. An aminoester polymer latex when made by the method claimed in any of the preceding claims.

12. A liquid coating composition comprising the latex claimed in claim 11 and colouring matter dispersed therein.

13. A liquid coating composition according to claim 12 which also contains from 0.05 to 10% by weight surfactant based on the polymer solids content.

14. An article coated with a dried layer of the composition claimed in claim 12 or 13.

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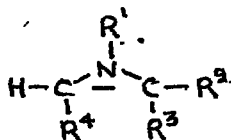
facilitates embossing by preventing the surface from sticking to the hot engraved metal embossing roll.

The Formulation I coating does not unduly reduce the vapor permeability of the product and it is surprisingly adherent and durable, not only when dry but after the product is soaked for 60 minutes in water. The water-soaked abrasion resistance is measured by wrapping a piece of the water-soaked product around a 1 inch diameter cylinder with the coated surface exposed and rubbing the coated surface against wet #10 cotton duck under a weight of 1 pound per linear inch. The length of each stroke of rubbing is 2 inches. It takes 200 such strokes to damage the coating.

A control sample made in accordance with Example 5 except that the imination reaction is omitted takes only 40 strokes to damage the coating after the sample is soaked 60 minutes in water. Shoes made with uppers of the control sample material are much less resistant to damage of the finish than shoes made with uppers of the Example 5 product, for example, when overshoes or rubbers are worn after the shoes have become wet.

WHAT WE CLAIM IS:—

1. A method of making an aminoester polymer latex, as hereinbefore defined, which comprises reacting a latex of a carboxylic polymer, as hereinbefore defined, with an aziridine of the formula:—



where R^1 is hydrogen, an alkyl group containing from 1 to 10 carbon atoms or a benzyl group, R^2 and R^3 , which may be the same or different, are hydrogen, an alkyl group containing from 1 to 10 carbon atoms, a benzyl group or an aryl group and R^4 is hydrogen or an alkyl group containing from 1 to 5 carbon atoms, until at least some of the pendant carboxylic acid radicals of the carboxylic polymer have reacted with the aziridine to form pendant aminoester groups.

2. A method according to claim 1 in which the carboxylic polymer has an acid equivalent of from 0.001 to 3.0 milliequivalents per gram.

3. A method according to claim 1 or 2 in which the latex of the carboxylic polymer is reacted with the aziridine until sufficient pendant carboxylic acid radicals are converted to amino ester radicals to result in an amino-ester polymer having an amino nitrogen content of from 0.01 to 2.0% by weight.

4. A method according to claim 3 in which the resultant aminoester polymer has an amino nitrogen content of from 0.1 to 1.5% by weight.

5. A method according to any of claims 1 to 4 in which the aziridine is ethylene imine.

6. A method according to any of claims 1 to 4 in which the aziridine is 1,2-propylene imine.

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12. A liquid coating composition comprising the latex claimed in claim 11 and colouring matter dispersed therein.

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