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<p>(21) International Application Number: PCT/US90/04664 (22) International Filing Date: 17 August 1990 (17.08.90) (30) Priority data: 396,854 21 August 1989 (21.08.89) US (71) Applicant: UNION OIL COMPANY OF CALIFORNIA [US/US]; 1201 West 5th Street, Los Angeles, CA 90017 (US). (72) Inventor: BIALE, John ; 530 S. Scout Trail, Anaheim, CA 92807 (US). (74) Agent: HACKLER, Walter, A.; 2372 S.E. Bristol, Suite B, Santa Ana Heights, CA 92797 (US).</p>	<p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: WATER-BASED VARNISHES</p>		
<p>(57) Abstract</p> <p>A polymeric emulsion comprising a (i) polymer, (ii) water, and (iii) a surfactant is useful as a binder for a water-based varnish that is resistant to water, 50 % ethanol, and alkali. The polymer comprises about 20 to about 40 weight percent of a soft monomer whose homopolymer has a T_g of less than about -20°C and about 60 to about 80 weight percent of a mixture of hard monomers each of whose homopolymer has a T_g of greater than about 30°C. As part of the hard monomer component of the polymer, the polymer comprises about 5 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent of an olefinic carboxylic acid. Typically, the polymer comprises less than about 1 weight percent surfactant and has a calculated T_g of about 25° to about 60°C, an actual T_g of about 30° to about 70°C, and an average particle size of less than about 250 nm. The emulsion generally comprises at least about 40 weight percent solids and has a surface tension of at least about 45 dynes/cm.</p>		

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BACKGROUND

The present invention relates to polymeric emulsions and to varnishes.

Due to increasingly more stringent regulations limiting the volatile organic content (VOC) of coatings, e.g., paints and varnishes, and the ease of handling water-based materials, the coating industry is continuously reformulating solvent-based coatings to meet VOC specifications and, wherever possible, replacing solvent-based products with water-based materials.

However, varnishes, which are required to possess block resistance, good gloss, and exceptional resistance to (a) water, (b) 50 weight percent (wt %) aqueous ethanol solution, and (c) mild alkali, e.g., 1 wt % aqueous trisodium polyphosphate (TSP) solution, have remained predominantly the exclusive area of solvent-based formulations.

SUMMARY OF THE INVENTION

The present invention provides water-based polymeric emulsions that are useful as a binder for water-based varnishes. The water-based varnishes exhibit block resistance, good gloss, and exceptional resistance to (a) water, (b) 50 wt % ethanol, and (c) mild alkali. The polymeric emulsions contain at least

about 40 percent solids and comprise a (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization. Usually, the emulsion comprises less than about 1 weight percent surfactant based on the total monomer weight in the polymer. The polymer comprises about 20 to about 40 weight percent soft monomer and about 60 to about 80 weight percent hard monomer. A portion of the hard monomer component of the polymer is composed of acrylonitrile and an olefinic carboxylic acid monomer. Typically, the polymer comprises about 2 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent olefinic carboxylic acid monomer. As used in the specification and claims, the term "soft monomer" means a monomer whose homopolymer has a T_g of less than about -20°C ; the term "hard monomer" means a monomer whose homopolymer has a T_g of greater than about 30°C ; and the terms "weight percent hard monomer," "weight percent soft monomer," "weight percent olefinic carboxylic acid monomer," and "weight percent acrylonitrile" each mean the total dry weight of the respective constituent ingredient employed in making the polymer divided by the total weight of the monomers employed in making the polymer, this quotient being multiplied by 100%. Generally, the emulsions have a surface tension of at least about 45 dynes/cm and the polymers have an average particle size of less than 250 nm. When the emulsion is employed as the binder component of a varnish, the resulting water-based varnish, when applied to a surface and dried, forms a film that is resistant to, inter alia, water, 50% ethanol, and alkali.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, each polymeric emulsion comprises a (i) polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization. Generally, the emulsion comprises less than about 1 weight percent surfactant. As used in the specification and the claims, "weight percent surfactant" is defined as the total dry weight of the surfactant(s) employed in making the polymer divided by the total weight of the monomers employed in making the polymer, this quotient being multiplied by 100%. Preferably the emulsion comprises less than about 0.5 weight percent surfactant.

In general, when all other parameters are held constant, the lower the surfactant content of the polymer, the more insensitive the polymer is to water and the higher the surface tension of the emulsion. Typically, the emulsion has a surface tension of at least about 45 dynes/cm, and preferably about 45 to about 65 dynes/cm.

The surfactant is normally a copolymerizable surfactant, an anionic surfactant, a nonionic surfactant, or a mixture of two or more of these surfactants. Exemplary copolymerizable surfactants include, but are not limited to, sulfoethylmethacrylate, vinylsulfonate salts, sulfopropylmethacrylate, styrene sulfonate salts, 2-acrylamido-2-methylpropanesulfonic acid salts, and mixtures thereof. Anionic surfactants include, but are not limited to, alkylphenoethoxylate sulfates and

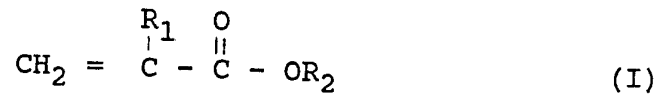
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sulfonates, alkylsulfates and sulfonates, and mixtures thereof. Nonionic surfactants include, but are not limited to, alkylarylpolyether alcohols, alkylphenolet-hoxylates, alkylethoxylates, ethyleneoxide/propylene oxide block copolymers, and mixtures thereof.

The polymer generally comprises about 20 to about 40 weight percent of a soft monomer and about 60 to about 80 weight percent of a plurality of hard monomers. Preferably, the polymer comprises about 25 to about 35 weight percent soft monomer and about 65 to about 75 weight percent hard monomer. The soft and hard monomers together typically constitute at least about 95 weight percent of the polymer, and preferably at least about 98 weight percent of the polymer.

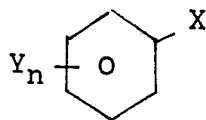
The soft monomer, which is a monomer whose homopolymer has a T_g of less than about -20°C , is typically selected from the group consisting of non-functional acrylic monomers, ethylene, and mixtures thereof. As used in the specification and claims, the term "non-functional monomer" means a monomer that is devoid of any group, e.g., hydroxyl, carboxyl, amide, and amine, that can undergo further reaction after polymerization of the monomer. Non-functional acrylic monomers are the preferred soft monomers.

The non-functional acrylic monomers have the formula I



wherein R₁ is selected from the group consisting of hydrogen and methyl, and R₂ is an alkyl group, preferably having up to about 15 carbon atoms. As used in the specification and claims, the term "alkyl" means cyclic and acyclic saturated hydrocarbon groups that can be either branched or unbranched. Exemplary soft, non-functional acrylic monomers include, but are not limited to, butyl acrylate, isobutyl acrylate, ethylhexyl acrylate, isodecyl methacrylate, lauryl methacrylate, tridecylmethacrylate. 2-ethylhexyl acrylate is the preferred soft, non-functional monomer.

With respect to the hard monomer (whose homopolymer has a T_g of greater than about 30° C), hard monomers include, but are not limited to, vinyl halides, acrylonitrile, methacrylamide, alkyene aromatic monomers and non-functional methacrylic monomers. As used in the specification and claims, "alkenyl aromatic monomers" are defined as any organic compound containing at least one aromatic ring and at least one aliphatic-containing moiety having alkenyl unsaturation. Preferred alkenyl aromatic monomers are represented by the formula II



(II)

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wherein X is an aliphatic radical containing at least one alkenyl bond, Y is a substituent on the aromatic ring, and n is the number of Y substituents on the ring, n being an integer from 0 to 5. Generally, X comprises at least 2 carbon atoms, but usually no more than about 6, and preferably no more than about 3 carbon atoms. X is preferably a substituted or unsubstituted alkenyl group. Preferred substituents on the alkenyl group are halogen radicals, e.g., chloride. However, the most preferred alkenyl group is unsubstituted, i.e., a hydrocarbon, and contains only one olefinic unsaturation. Ethylene is the most preferred X.

Y is an organic or inorganic radical. As used throughout the specification and claims, the term "organic radical" means any group containing at least one carbon atom, and the term "inorganic radical" means any group devoid of carbon atoms. When n is 2 or more, Y can be the same or different. If organic, Y generally contains from 1 to about 15 carbon atoms and, preferably, is an aliphatic radical. Even more preferably, Y is a saturated aliphatic radical. If inorganic, Y is preferably a halogen. Exemplary Y substituents include halo and cyano radicals and substituted and unsubstituted alkyl radicals of 1 to about 10 carbon atoms. Preferred Y substituents are chloride and unsubstituted alkyl groups of 1 to about 6 carbon atoms. Y is more preferably a chloride radical and C₁ to about C₄ unsubstituted alkyl radicals.

Illustrative alkenyl aromatic monomers include styrene, p-methyl styrene, methyl styrene, o,p-dimethyl styrene, o,p-diethyl styrene, p-chlorostyrene, isopropyl styrene, t-butyl styrene, o-methyl-p-isopropyl styrene, o,p-dichlorostyrene, and mixture thereof. Due to its commercial availability and low cost, styrene is the preferred alkenyl aromatic monomers.

With respect to non-functional methacrylic monomers, exemplary non-functional methacrylic monomers have the formula III



wherein R_3 is an alkyl group that preferably contains up to about 6 carbon atoms. Typical non-functional methacrylic monomers include methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, isobornyl methacrylate, and mixtures thereof.

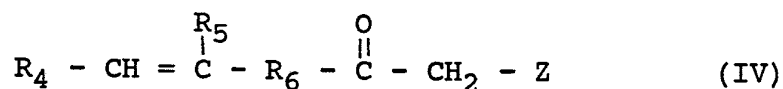
The halide moiety of the vinyl halide monomers is preferably either chloride or bromide, with chloride being the most preferred halide moiety.

An important aspect of the present invention is that acrylonitrile and one or more olefinic carboxylic acid monomers constitute a portion of the hard monomer portion of the polymer. Typically, the polymer comprises about 5 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent olefinic carboxylic acid. Preferably, the polymer comprises

about 8 to about 15 weight percent acrylonitrile and about 2 to about 4 weight percent olefinic carboxylic acid.

Olefinic carboxylic acid monomers include both mono-olefinic carboxylic acid monomers and di-olefinic carboxylic acid monomers. Exemplary mono-olefinic carboxylic acids include, but are not limited to, acrylic acid, methacrylic acid, and acrylamido glycolic acid. An exemplary di-olefinic carboxylic acid is itaconic acid. The preferred olefinic carboxylic acid monomer is methacrylic acid. However, mixtures of olefinic carboxylic acids can also be used.

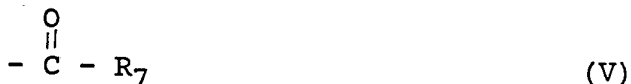
The polymer optionally comprises a cross-linking agent. Typical cross-linking agents include, but are not limited to, N-methylol acrylamide, N-methylol methacrylamide, diacrylates, dimethacrylates, triallyl cyanurate, diallyl maleate, methyl acrylamidoglycolate methyl ether, olefinically unsaturated monomers having the formula IV



and mixtures thereof, wherein R_4 is selected from the group consisting of hydrogen and halogen, R_5 is selected from the group consisting of hydrogen, halo, thio, and monovalent organic radicals, R_6 is a divalent radical, and Z is selected from the group consisting of organoacyl and cyano. Preferably, R_4 is hydrogen, R_5

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is hydrogen or an alkyl radical having up to about 10 carbon atoms, R_6 is a cyclic or acyclic organic radical containing up to about 40 carbon atoms, and Z is an organoacyl having the formula V



wherein R_7 is selected from the group consisting of hydrogen and monovalent organic radicals. More preferably, R_6 is an acyclic radical containing up to about 20 atoms in length, with any and all side groups each being up to about 6 atoms in length, and R_7 is hydrogen or an alkyl group containing up to about 7 carbon atoms. R_6 is most preferably an alkylene group containing up to about 10 carbon atoms, and R_7 is most preferably methyl. Due to its commercial availability, the preferred cross-linking agent of formula IV is acetoacetoxyethyl methacrylate. However, the most preferred cross-linking agent is N-methylol acrylamide.

When employed, the polymer generally contains about 0.2 to about 5 weight percent cross-linking agent, but preferably about 1 to about 3 weight percent cross-linking agent. As used in the specification and claims, the term "weight percent cross-linking agent" means the total dry weight of the cross-linking agent employed in making the polymer divided by the total weight of the monomers employed in making the polymer, this quotient being multiplied by 100%.

The polymer preferably has an average parti-

cle size (i.e., an average maximum cross-sectional dimension) of less than about 250 nm. In general, for the polymer of the invention, the smaller the average particle size, the more water-resistant the polymer. Accordingly, it is preferred that the average particle size of the polymer be from about 85 to about 200 nm, more preferably from about 90 to about 190 nm, and most preferably from about 100 to about 150 nm.

The polymeric emulsion optionally comprises one or more other ingredients. For example, the polymer can comprise one or more ureido-containing monomers. Exemplary ureido-containing monomers include, but are not limited to, 2-ureido-ethyl acrylate, 2-ureido-methyl acrylate, 2-ureido-ethyl acrylamide, 2-ureido-ethyl methacrylamide, and 1-[2-(3-allyloxy-2-hydroxypropylamino)ethyl]imidazolidin-2-one. The preferred ureido-containing monomer is 1-[2-(3-allyloxy-2-hydroxypropylamino)ethyl]imidazolidin-2-one, commercially known as Sipomer WAM brand monomer and available from Alcolac. The ureido-containing monomers are generally used in a concentration sufficient to enhance the wet adhesion strength of the emulsion, e.g., from about 0.25 to about 1 weight percent of the polymer.

A seed is another optional ingredient present in the polymer. The seed acts as a locus for polymerization and generally has an average particle size of less than about 80 nm, and preferably within the range of about 25 to about 60 nm. Exemplary seeds are comprised of a surfactant and a monomer, e.g., alkenyl

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aromatic monomers, acrylate monomers, and mixtures thereof. Usually, styrene and/or butyl acrylate monomers are employed in manufacturing the seed.

The polymers of the present invention demonstrate an actual T_g of about 30° to about 70° C, preferably about 40° to about 60° C, and most preferably about 45° to about 60° C. There are several ways of determining the actual T_g of the polymers. For purposes of the present specification and claims, the actual T_g is determined by differential scanning calorimetry (DSC).

Interestingly, some of the polymers possess a different calculated T_g . The calculated T_g of each polymer is derived by multiplying the weight percent of each constituent monomer by the T_g of a homopolymer made from that monomer and adding all the resulting numerical products. Typically, the calculated T_g of polymers is between about 25° and about 60° C.

The emulsions of the present invention are made, for example, by a delayed addition polymerization process. Typically, the delay-addition polymerization process comprises forming a monomer mixture containing about 20 to about 40 weight percent soft monomer and about 60 to about 80 weight percent hard monomer. As hard monomer constituents, the monomer mixture specifically comprises about 5 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent olefinic carboxylic acid monomer.

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Water is added to a reactor and heated, generally to about 150° to about 190° F., while preferably purging the reactor with an inert gas, such as nitrogen, to remove substantially all oxygen from the reactor. A catalyst is then added to the reactor. Preferably, a locus for polymerization (e.g., a surfactant and/or a surfactant-containing seed) is added to the reactor before, simultaneously with, or after the catalyst addition to form a reactor charge. After the addition of the catalyst and locus for polymerization, the delay-addition of the monomer mixture is then commenced. The ensuing reaction forms the emulsion of the present invention. The addition of the monomer mixture typically takes up to about 3 hours. During the delay-addition of the monomer mixture, additional catalyst is typically also added to the reactor.

In an alternative synthesis procedure, a portion, for example up to about 1/2 of the monomer mixture, is added to the reactor at the beginning of the reaction along with the addition of the initial catalyst and/or seed and/or surfactant.

In order to stabilize the emulsion, toward the end of the monomer mixture addition, the pH of the emulsion is typically adjusted. Generally, the pH of the emulsion is adjusted to at least about 6, preferably to about 6 to about 10, and most preferably to about 6 to about 8. Adjusting the pH to within these ranges substantially neutralizes all olefinic carboxylic acid groups on the polymer.

Usually the pH of the emulsion is adjusted from about 30 minutes before to about 30 minutes after terminating the addition of the monomer mixture. Preferably, the pH adjustment occurs within about 15 minutes after terminating the monomer mixture addition.

After finishing the monomer mixture addition, further catalyst is commonly added while maintaining the emulsion at the elevated reaction temperature to ensure that substantially all of the monomers polymerize. The same catalyst can be used whenever one is employed. Exemplary catalysts include, but are not limited to, t-butyl hydroperoxide, sodium persulfate, hydrogen peroxide, and mixtures thereof.

The emulsion is allowed to cool to ambient or room temperature after all the monomer mixture and catalyst have been added. Usually, the pH of the cooled emulsion is adjusted, if necessary, to about 8 to about 10. Typically, a base is employed in each instance where the pH of the emulsion is adjusted. Exemplary bases are selected from the group consisting of amine-containing bases, hydroxide-containing bases, and mixtures thereof. Dimethylamine, diethylamine, aminopropanol, ammonium hydroxide, and sodium hydroxide are typical bases, with volatile bases being preferred, and ammonium hydroxide being the most preferred.

The polymerization process yields the polymeric emulsion of the present invention. The solids content of the emulsion is generally at least about 40 weight percent, preferably within the range of about 45

to about 60 weight percent, and more preferably within the range of about 45 to about 55 weight percent.

The emulsion is used as a binder in a water-based varnish. A typical varnish comprises a coalescing aid, a defoamer, a biocide, and the binder. A rheology modifier, a mar-resistant agent (e.g., a wax emulsion), and a flattening agent (e.g., silica) are also sometimes used in water-based varnishes. Generally a varnish is clear and, in these instances, is usually devoid of a pigment or coloring agent. However, some varnishes are colored with a color-imparting agent, e.g., pigments, stains, and dyes. Coalescing aids, rheology modifiers, mar-resistant agents, flattening agents, color-imparting agents, defoamers, and biocides suitable for use in water-based varnishes are well known to those skilled in the art.

In use, the varnish is applied to at least a portion of a surface of a substrate. Upon drying, the emulsion forms a film or coating that is resistant to, inter alia, water, 50 wt % ethanol, and mild alkali. More particularly, the film produced by the emulsions of the present invention do not exhibit spotting or physical degradation upon visual inspection when exposed, at room temperature and for at least about 17 hours, to a cotton swab moistened with either water or 50 wt % ethanol or 1 wt % TSP. Accordingly, the emulsion of the instant invention is a suitable binder for use in water-based varnishes.

EXAMPLES

The following examples demonstrate the preparation of exemplary polymeric emulsions within the scope of the present invention as well as the resistance to water, 50% ethanol, and alkali exhibited by films formed with water-based varnishes employing these emulsions as their binder component. However, the invention is not limited to the examples, but is defined by the claims.

EXAMPLES 1-4Preparation of Polymeric Emulsions

Monomer mixtures having the compositions set forth in the following Table I were prepared:

TABLE I

<u>Example</u>	<u>Monomer, g</u>					
	<u>ST</u> ^a	<u>2EHA</u> ^b	<u>MAA</u> ^c	<u>BA</u> ^d	<u>AN</u> ^e	<u>MMA</u> ^f
1	285	-	15	240	30	-
2	315	60	15	120	60	-
3	315	210	15	-	60	30
4	350	60	15	120	60	-

- a. ST denotes styrene.
- b. 2EHA denotes 2-ethylhexyl acrylate.
- c. MAA denotes methacrylic acid.
- d. BA denotes butyl acrylate.
- e. AN denotes acrylonitrile.
- f. MMA denotes methyl methacrylate.

In each of Examples 1-4, water (about 550 g) was added to a reactor and heated while purging the reactor with nitrogen. When the water reached a temperature of about 180° F, the ingredients listed in Table II, infra, were individually added to the reactor.

TABLE II

<u>Example</u>	<u>Ingredients, g</u>		
	<u>Sodium Persulfate</u>	<u>50S^g</u>	<u>30S^h</u>
1	0.9	36	-
2	0.9	-	18
3	0.9	-	18
4	0.9	36	-

g. 50S denotes a 30 weight percent total solids emulsion containing a styrene/butyl acrylate (50:50 weight percent) seed having an average particle size of about 50 nm.

h. 30S denotes a 30 weight percent total solids emulsion containing a styrene seed having an average particle size of about 30 nm.

Next, the monomer mixture shown in the above Table I and a catalyst solution described in Table III were separately, but simultaneously, added to the contents of the reactor over a period of about 3 hours while maintaining the temperature within the reactor at about 185° F.

TABLE III

<u>Example</u>	<u>Ingredients, g</u>		
	<u>Sodium Persulfate</u>	<u>Water</u>	<u>2AIⁱ</u>
1	0.9	27	3.3
2	0.9	27	-
3	0.9	27	-
4	0.9	27	-

i. 2AI denotes Dowfax 2AI brand anionic surfactant (45% active).

In Examples 1-4, immediately after finishing the addition of the catalyst solution and the monomer mixture, a solution containing about 6 ml ammonium hydroxide and about 20 ml water was added to the emulsion. After the emulsion cooled to room temperature, a 10% ammonium hydroxide solution was added in a sufficient amount to raise the pH of the emulsion to about 8.5. The total solid content of the emulsions and the average particle size of the polymers (measured with a Nonsizer N4 brand particle sizer available from Coulter Electronics) are given in Table IV, infra.

TABLE IV

<u>Example</u>	<u>Particle Size, nm</u>	<u>Total Solids, wt. %</u>
1	177	48.6
2	113	50.1
3	125	49.9
4	178	51.0

The polymer component of the emulsion of Examples 2 and 3 had the actual and calculated T_g 's shown in Table V.

TABLE V

<u>Example</u>	<u>Actual T_g, °C</u>	<u>Calculated T_g, °C</u>
2	55	31
3	46	29

EXAMPLE 5

Preparation of Polymeric Emulsion

A monomer mixture and an aqueous solution were prepared. The monomer mixture comprised about 260 g styrene, about 270 g 2-ethylhexyl acrylate, about 12 g acrylic acid, and about 60 g acrylonitrile. The aqueous solution contained about 50 g water and about 6 g acrylamido glycolic acid.

Next, water (about 500 g) was added to a reactor and heated while purging the reactor with nitrogen. When the water reached a temperature of about 180° F, about 0.9 g sodium persulfate and about 18 g of a 30 weight percent total solids emulsion containing a styrene seed having an average particle size of about 30 nm were individually added to the reactor.

The monomer mixture and a catalyst solution

comprising about 0.9 g sodium persulfate and about 27 g water were then separately added to the contents of the reactor over a period of about 3 hours while maintaining the temperature within the reactor at about 185° F. Immediately after finishing the addition of the catalyst solution and the monomer mixture, a solution containing about 10 ml ammonium hydroxide and about 20 ml water was added to the emulsion.

After the emulsion cooled to room temperature, a 10% ammonium hydroxide solution was added in a sufficient amount to raise the pH of the emulsion to about 8.6. The total solid content of the emulsion was about 49.0 weight percent and the average particle size of the polymer was about 122 nm.

EXAMPLE 6

Preparation of Polymeric Emulsion

A monomer mixture and a cross-linking solution were prepared. The monomer mixture comprised about 300 g styrene, about 224 g 2-ethylhexyl acrylate, about 60 g acrylonitrile, and about 12 g acrylic acid. The cross-linking solution contained about 50 g water and about 25 g N-methylol acrylamide.

Next, water (about 550 g) was added to a reactor and heated while purging the reactor with nitrogen. When the water reached a temperature of about 180° F, about 0.9 g sodium persulfate and about 18 g of a 30 weight percent total solids emulsion

containing a styrene seed having an average particle size of about 30 nm were individually added to the reactor.

The monomer mixture and a catalyst solution comprising about 0.9 g sodium persulfate and about 27 g water were then separately added to the contents of the reactor over a period of about 3 hours while maintaining the temperature within the reactor at about 185° F. Immediately after finishing the addition of the catalyst solution and the monomer mixture, a solution containing about 6 ml ammonium hydroxide and about 20 ml water was added to the emulsion.

After the emulsion cooled to room temperature, a 10% ammonium hydroxide solution was added in a sufficient amount to raise the pH of the emulsion to about 8.5. The total solid content of the emulsion was about 47.0 weight percent and the average particle size of the polymer was about 121 nm.

EXAMPLES 7-12

Formulation Of Varnishes

About 0.34 g Colloids 681F brand defoamer (available from Colloids, Inc.) was combined with a sufficient amount of one of the emulsions of Examples 1-6 to yield a composition containing about 106 g (at about 50 weight percent solids) of the respective emulsion. A premixture of butyl cellosolve (about 18.6 g) and sufficient water to reduce the viscosity of the

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resulting varnish to less than about 500 cps was added to the composition with stirring. Finally, about 5.6 g of MichemLUBE 156 brand wax emulsion was added, while stirring, to the composition.

EXAMPLES 13-18

RESISTANCE TESTS

Oak panels were coated with the varnishes of Examples 7-12. The coating process entailed the step of coating a panel with a varnish, drying the coated panel at room temperature, and sanding the coated panel with fine sandpaper. This step was repeated two additional times with the sole modification that the coated panel was not sanded after the third drying procedure.

A plain cotton swab soaked with one of the three test liquids (i.e., water, 50 wt % aqueous ethanol, or 1 wt % aqueous TSP) was placed on the coated panel, covered with a glass dome-shaped lid to reduce evaporation, and allowed to sit there for about 17 hours at room temperature. After 17 hours, the wet cotton swab was removed and the coated panel was visually examined. The visual observations are noted in Table VI, infra.

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TABLE VI

<u>Example</u>	<u>Varnish Containing Emulsion of</u>	<u>Water Test</u>	<u>50% Ethanol Test</u>	<u>1% TSP Test</u>
13	Example 1	OK ^j	Spot ^k	NT ^l
14	Example 2	OK	OK	OK
15	Example 3	OK	OK	OK
16	Example 4	OK	Spot	OK
17	Example 5	NT	OK	NT
18	Example 6	OK	OK	OK

j. OK denotes that coating did not exhibit any discoloration or physical degradation when the test swab was removed.

k. Spot denotes that the coating appeared slightly whitish when the test swab was removed but returned to a clear color after a period of time and did not exhibit any physical degradation.

l. NT denotes not tested.

The data provided in Table VI indicate that the water-based varnishes of the present invention (prepared using the above described polymeric emulsions as their binder component) form coatings that are resistant to water, 50% ethanol, and alkali.

Although the present invention has been described in considerable detail with reference to certain preferred versions thereof, other versions are possible. For example, the varnishes can include one or more ingredients that enhance other film and/or varnish properties. Therefore, the spirit and scope of

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the appended claims should not necessarily be limited to the description of the preferred embodiments contained herein.

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What is claimed is:

1. A polymeric emulsion comprising (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization, wherein the emulsion comprises less than about 1 weight percent surfactant and at least about 40 percent total solids, and the polymer comprises:

(a) about 20 to about 40 weight percent of a soft monomer whose homopolymer has a T_g of less than about -20°C ; and

(b) about 60 to about 80 weight percent of a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30°C , wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer, the polymer comprising about 5 to about 20 weight percent acrylonitrile and 1 to about 5 weight percent olefinic carboxylic acid monomer.

2. The emulsion of claim 1 comprising less than about 0.5 weight percent surfactant.

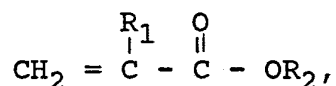
3. The emulsion of claim 1 wherein the polymer comprises about 25 to about 35 weight percent soft monomer and about 65 to about 75 weight percent hard monomer.

4. The emulsion of claim 1 wherein the polymer has a calculated T_g of about 25° to about 60°C .

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5. The emulsion of claim 1 wherein the polymer has an actual T_g of about 30° to about 70° C.
6. The emulsion of claim 1 wherein the polymer has an actual T_g of about 40° to about 60° C.
7. The emulsion of claim 1 wherein the polymer has an average particle size of less than about 250 nm.
8. The emulsion of claim 1 wherein the polymer has an average particle size of about 85 to about 200 nm.
9. The emulsion of claim 1 wherein the polymer has an average particle size of about 90 to about 190 nm.
10. The emulsion of claim 1 wherein the polymer has an average particle size of about 100 to about 150 nm.
11. The emulsion of claim 1 wherein the soft monomer is selected from the group consisting of non-functional acrylic monomers, ethylene, and mixtures thereof.

12. The emulsion of claim 1 wherein the soft monomer is a non-functional acrylic monomer having the formula



wherein R_1 is selected from the group consisting of hydrogen and methyl, and R_2 is an alkyl group.

13. The emulsion of claim 14 wherein R_2 contains up to about 15 carbon atoms.

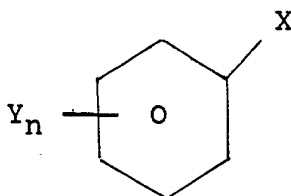
14. The emulsion of claim 1 wherein the soft monomer is selected from the group consisting of butyl acrylate, isobutyl acrylate, ethylhexyl acrylate, isodecyl methacrylate, lauryl methacrylate, tridecyl methacrylate, and mixtures thereof.

15. The emulsion of claim 1 wherein the soft monomer is selected from the group consisting of 2-ethylhexyl acrylate, butyl acrylate, isobutyl acrylate, and mixtures thereof.

16. The emulsion of claim 1 wherein the hard monomer is selected from the group consisting of vinyl halide, acrylonitrile, methacrylamide, alkenyl aromatic monomers, non-functional methacrylic monomers, and mixtures thereof.

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17. The emulsion of claim 1 wherein the hard monomer is an alkenyl aromatic monomer having the formula

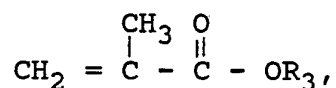


wherein X is an aliphatic radical containing at least one alkenyl bond, Y is a substituent on the aromatic ring, and n is an integer from 0 to 5.

18. The emulsion of claim 17 wherein the alkenyl aromatic monomer is selected from the group consisting of styrene, p-methyl styrene, methyl styrene, o,p-dimethyl styrene, o,p-diethyl styrene, p-chlorostyrene, isopropyl styrene, t-butyl styrene, o-methyl-p-isopropyl styrene, o,p-dichlorostyrene, and mixtures thereof.

19. The emulsion of claim 1 wherein the hard monomer is styrene.

20. The emulsion of claim 1 wherein the hard monomer is a non-functional methacrylic monomer having the formula



wherein R₃ is an alkyl group.

2^o

21. The emulsion of claim 20 wherein R₃ contains up to about 6 carbon atoms.

22. The emulsion of claim 1 wherein the hard monomer is selected from the group consisting of methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, isobornyl methacrylate, and mixtures thereof.

23. The emulsion of claim 1 wherein the olefinic carboxylic acid monomer is selected from the group consisting of mono- and di-olefinic carboxylic acids, and mixtures thereof.

24. The emulsion of claim 1 wherein the olefinic carboxylic acid monomer selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamido glycolic acid, and mixtures thereof.

25. The emulsion of claim 1 wherein the olefinic carboxylic acid monomer is methacrylic acid.

26. The emulsion of claim 1 wherein the polymer comprises about 2 to about 4 weight percent olefinic carboxylic acid monomer.

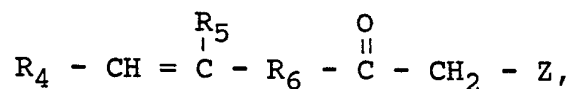
27. The emulsion of claim 1 wherein the polymer comprises about 8 to about 15 weight percent acrylonitrile.

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28. The emulsion of claim 1 wherein the polymer further comprises a cross-linking agent.

29. The emulsion of claim 1 wherein the polymer further comprise about 0.2 to about 5 weight percent of a cross-linking agent.

30. The emulsion of claim 1 wherein the polymer further comprises about 0.2 to about 5 weight percent of a cross-linking agent selected from the group consisting of N-methylol acrylamide, N-methylol methacrylamide, diacrylates, dimethacrylates, triallyl cyanurate, diallyl maleate, methyl acrylamidoglycolate methyl ether, olefinically unsaturated monomers having the formula



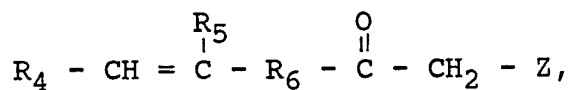
and mixtures thereof, wherein R_4 is selected from the group consisting of hydrogen and halogen, R_5 is selected from the group consisting of hydrogen, halo, thio, and monovalent organic radicals, R_6 is a divalent radical, and Z is selected from the group consisting of organoacyl and cyano.

31. The emulsion of claim 1 wherein the polymer further comprises about 0.2 to about 5 weight percent N-methylol acrylamide.

32. The emulsion of claim 1 wherein the polymer further comprises about 1 to about 3 weight percent cross-linking monomer.

33. The emulsion of claim 1 wherein the emulsion comprises less than about 0.5 weight percent surfactant, and the polymer comprises about 25 to about 35 weight percent soft monomer and about 65 to about 75 weight percent hard monomer, and has (i) a calculated T_g of about 25° to about 60° C, (ii) an actual T_g of about 30° to about 70° C, and (iii) an average particle size of less than about 250 nm; the soft monomer is selected from the group consisting of non-functional acrylic monomers, ethylene, and mixtures thereof; the hard monomer is selected from the group consisting of vinyl halide, acrylonitrile, methacrylamide, alkenyl aromatic monomers, non-functional methacrylic monomers, olefinic carboxylic acid monomers, and mixtures thereof, the polymer comprising about 8 to about 15 weight percent acrylonitrile and about 2 to about 4 weight percent olefinic carboxylic acid monomer; the olefinic carboxylic acid monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamido glycolic acid, and mixtures thereof; and the polymer further comprises a cross-linking monomer selected from the group consisting of N-methylol acrylamide, N-methylol methacrylamide, diacrylates, dimethacrylates, triallyl cyanurate, diallyl maleate, methyl acrylamidoglycolate methyl ether, olefinically unsaturated monomers having the formula

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and mixtures thereof, wherein R_4 is selected from the group consisting of hydrogen and halogen, R_5 is selected from the group consisting of hydrogen, halo, thio, and monovalent organic radicals, R_6 is a divalent radical, and Z is selected from the group consisting of organoacyl and cyano.

34. The emulsion of claim 1 wherein the surfactant-containing locus for polymerization is a seed.

35. The emulsion of claim 1 wherein the surfactant-containing locus for polymerization is a seed having an average particle size of less than about 80 nm.

36. The emulsion of claim 1 wherein the surfactant-containing locus for polymerization is a seed having an average particle size of about 25 to about 60 nm.

37. The emulsion of claim 1 wherein the surfactant-containing locus for polymerization is a seed that comprises a monomer selected from the group consisting of alkenyl aromatic monomers, acrylate monomers, and mixtures thereof.

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38. A polymeric emulsion comprising (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization, the emulsion comprising less than about 1 weight percent surfactant and at least about 40 weight percent total solids, and the polymer having an actual T_g of about 30° to about 70° C and comprising:

(a) a soft monomer whose homopolymer has a T_g of less than about -20° C; and

(b) a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30° C, wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer, the polymer comprising about 5 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent olefinic carboxylic acid monomer.

39. A polymeric emulsion comprising (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization, the emulsion comprising at least about 40 weight percent solids and having a surface tension greater than about 45 dynes/cm, and the polymer comprising:

(a) a soft monomer whose homopolymer has a T_g of less than about -20° C; and

(b) a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30° C, wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer, the polymer comprising about 5 to about 25 weight percent acrylonitrile and about 1 to

about 5 weight percent olefinic carboxylic acid monomer.

40. The emulsion of claim 39 wherein the emulsion has a surface tension of about 45 to about 55 dynes/cm.

41. The emulsion of claim 39 wherein the polymer has an actual T_g of about 30° to about 70° C.

42. The emulsion of claim 39 wherein the emulsion comprises less than about 1 weight percent surfactant.

43. The emulsion of claim 39 further comprising less than about 1 weight percent surfactant, and wherein the polymer has an actual T_g of about 30° to about 70° C.

44. A formulation comprising a coalescing aid and a binder, wherein the binder is the emulsion of claim 1.

45. A film formed by drying the formulation of claim 44.

46. An article comprising a substrate having a surface, wherein at least a portion of the surface is coated with the film of claim 45.

47. The emulsion of claim 1 comprising about 45 to about 55 weight percent total solids.

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48. A polymeric emulsion comprising (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization, wherein the emulsion comprises less than about 1 weight percent surfactant and at least about 40 percent total solids, and the polymer consists essentially of:

(a) about 20 to about 40 weight percent of a soft monomer whose homopolymer has a T_g of less than about -20°C ;

(b) about 60 to about 80 weight percent of a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30°C , wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer, the polymer comprising about 5 to about 25 weight percent acrylonitrile and about 1 to about 5 weight percent olefinic carboxylic acid monomer;

(c) the surfactant; and optionally

(d) a wet adhesion promoter.

49. The emulsion of claim 48 wherein the polymer consists essentially of the soft monomer, the hard monomer, and the surfactant.

50. A polymeric emulsion comprising (i) a polymer, (ii) water, and (iii) a surfactant-containing locus for polymerization, wherein the emulsion, has a surface tension greater than about 45 dynes/cm and comprises less than about 1 weight percent surfactant and at least about 40 percent total solids, and the polymer has an actual T_g of about 30° to about 70° C

and comprises:

(a) about 20 to about 40 weight percent of a soft monomer whose homopolymer has a T_g of less than about -20°C ; and

(b) about 60 to about 80 weight percent of a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30°C , wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer, the polymer comprising about 5 to about 20 weight percent acrylonitrile and 1 to about 5 weight percent olefinic carboxylic acid monomer.

51. A polymer comprising:

(a) about 20 to about 40 weight percent of a soft monomer whose homopolymer has a T_g of less than about -20°C ; and

(b) about 60 to about 80 weight percent of a plurality of hard monomers, each of whose homopolymers has a T_g of greater than about 30°C , wherein acrylonitrile and an olefinic carboxylic acid monomer constitute a portion of the hard monomer component of the polymer and the polymer comprises about 5 to about 20 weight percent acrylonitrile and 1 to about 5 weight percent olefinic carboxylic acid monomer.

52. The polymer of claim 51 comprising about 25 to about 35 weight percent soft monomer and about 65 to about 75 weight percent hard monomer.

53. The polymer of claim 51 having an actual T_g of about 30° to about 70° c.

54. The polymer of claim 51 having an average particle size of less than about 250 nm.

55. The polymer of claim 51 wherein the soft monomer is selected from the group consisting of non-functional acrylic monomers, ethylene, and mixtures thereof.

56. The polymer of claim 51 wherein the hard monomer is selected from the group consisting of vinyl halide, acrylonitrile, methacrylamide, alkenyl aromatic monomers, non-functional methacrylic monomers, and mixtures thereof.

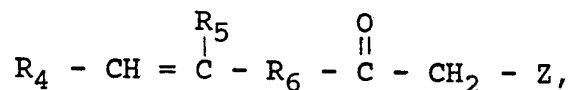
57. The polymer of claim 51 comprising about 2 to about 4 weight percent olefinic carboxylic acid monomer.

58. The polymer of claim 51 comprising about 8 to about 15 weight percent acrylonitrile.

59. The polymer of claim 51 wherein further comprises a cross-linking agent.

60. The polymer of claim 51 further comprising about 0.2 to about 5 weight percent of a cross-linking agent selected from the group consisting of N-methylol acrylamide, N-methylol methacrylamide, diacrylates, dimethacrylates, triallyl cyanurate, diallyl maleate, methyl acrylamidoglycolate methyl ether,

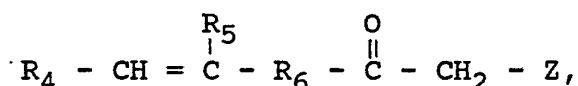
olefinically unsaturated monomers having the formula



and mixtures thereof, wherein R_4 is selected from the group consisting of hydrogen and halogen, R_5 is selected from the group consisting of hydrogen, halo, thio, and monovalent organic radicals, R_6 is a divalent radical, and Z is selected from the group consisting of organoacyl and cyano.

61. The polymer of claim 51 comprising about 25 to about 35 weight percent soft monomer and about 65 to about 75 weight percent hard monomer, and has (i) a calculated T_g of about 25° to about 60° C, (ii) an actual T_g of about 30° to about 70° C, and (ii) an average particle size of less than about 250 nm; the soft monomer is selected from the group consisting of non-functional acrylic monomers, ethylene, and mixtures thereof; the hard monomer is selected from the group consisting of vinyl halide, acrylonitrile, methacrylamide, alkenyl aromatic monomers, non-functional methacrylic monomers, olefinic carboxylic acid monomers, and mixtures thereof, the polymer comprising about 8 to about 15 weight percent acrylonitrile and about 2 to about 4 weight percent olefinic carboxylic acid monomer; the olefinic carboxylic acid monomer is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, acrylamido glycolic acid, and mixtures thereof; and the polymer further comprises a cross-linking monomer selected from the group consist-

ing of N-methylol acrylamide, N-methylol methacrylamide, diacrylates, dimethacrylates, triallyl cyanurate, diallyl maleate, methyl acrylamidoglycolate methyl ether, olefinically unsaturated monomers having the formula



and mixtures thereof, wherein R_4 is selected from the group consisting of hydrogen and halogen, R_5 is selected from the group consisting of hydrogen, halo, thio, and monovalent organic radicals, R_6 is a divalent radical, and Z is selected from the group consisting of organoacyl and cyano.

62. The polymer of claim 51 wherein the soft and hard monomers together comprise at least about 95 weight percent of the polymer.

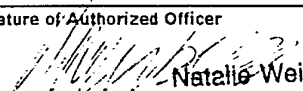
63. The polymer of claim 51 wherein the soft and hard monomers together comprise at least about 98 weight percent of the polymer.

64. The emulsion of claim 1 wherein the soft and hard monomers together comprise at least about 95 weight percent of the polymer.

65. The emulsion of claim 1 wherein the soft and hard monomers together comprise at least about 98 weight percent of the polymer.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/04664

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 09 D 5/02, C 09 D 133/00				
II. FIELDS SEARCHED Minimum Documentation Searched ⁷				
Classification System	Classification Symbols			
IPC5	C 09 D			
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸				
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹				
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³		
X	EP, A2, 0269059 (E.I. DU PONT DE NEMOURS AND COMPANY) 1 June 1988, see claims 1-4 and the description --	1,3-19, 23-27, 44-51, 54-59, 62-65		
X	DE, A1, 3418524 (BASF AG) 21 November 1985, see the whole document --	1-2,11- 25,51, 55-56, 62-65		
X	US, A, 3634298 (ROBERT ALAN WAMSLEY ET AL) 11 January 1972, see the whole document --	1-5,11- 19,23- 27,51- 53,55- 58,62- 65		
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </td> <td style="width: 50%; border: none; vertical-align: top;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </td> </tr> </table>			<p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>
<p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>			
IV. CERTIFICATION				
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report			
17th December 1990	16. 01. 91			
International Searching Authority	Signature of Authorized Officer			
EUROPEAN PATENT OFFICE	 Natalie Weinberg			

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
X	US, A, 4025037 (SHIBAYAMA ET AL) 24 May 1977, see the whole document	1-3,11- 13,16, 23-27, 51-52, 55-58, 62-65
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X	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 86-017886/03, Furukawa Electric Co: "Solderable insulated wire comprises electroconductive core wire has electroconductive core wire acrylonitrile methacrylate-methacrylic acid layer and acrylonitrile-acrylate methacrylic acid coating", JP 60241606, A, 851130, 8603 (Basic)	1,11-13, 16,20, 23-27, 51,55- 58
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A	Dialog Information Services, File 350, World Patent Index 63-80, Dialog accession no. 80-595510/34, Dainippon Ink Chem KK: "Water repellent resin coating compsn. - contains aq. dispersion of copolymer and waxes; POLYACRYLATE POLYVINYL ACETATE POLYACRYLONITRILE", JP 55090562, A, 800709, 8034 (Basic)	1,11-15, 51,55
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A	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 82-36474E/18, Lion Corp: "Emulsifier for emulsion polymerisation contains polyvalent metal salt of alpha-olefin sulphonic acid and opt. nonionic surfactant: MAGNESIUM CALCIUM BARIUM ALUMINIUM ZINC TIN LEAD POLYOXYETHYLENE", JP 57053504, A, 820330, 8218 (Basic)	1,11-15, 51,55
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A	Dialog Information Services, File 351, World Patent Index 81-90, Dialog accession no. 84-143597/23, Daicel Chem Ind KK: "Porous base material coating agent prepd. by dispersing opd. high permeates base and plasticiser in acrylic polymer emulsion", JP 59075959, A, 840428, 8423 (Basic)	1,28-33, 51,59- 65
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28/11/90

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/04664

SA 40288

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 28/11/90. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A2- 0269059	01/06/88	AU-D- 8322387	16/06/88
		JP-T- 1501485	25/05/89
		WO-A- 88/03933	02/06/88

DE-A1- 3418524	21/11/85	NONE	

US-A- 3634298	11/01/72	BE-A- 748763	12/10/70
		DE-A- 2017323	15/10/70
		FR-A- 2043027	12/02/71
		GB-A- 1286384	23/08/72
		NL-A- 7005167	13/10/70
		SE-B-C- 376448	26/05/75

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		FR-A-B- 2251084	06/06/75
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		JP-C- 864447	13/06/77
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