

LATEX POLYMER COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to novel latex polymers and aqueous compositions containing the same which are capable of providing exceptionally high water resistance when used in coatings and other applications. The aqueous latex compositions containing the novel polymers are prepared by the emulsion polymerization of ethylenically unsaturated monomers including highly branched neo vinyl esters and ethylenically unsaturated reactive surfactants. Aqueous latex compositions containing these polymers are especially suitable for use in coatings, adhesives, caulks and sealants where excellent water resistance is desirable. Such polymers are also suitable for use as additives, modifiers, inks, binders for dyes and pigments, and textile treatments.

BACKGROUND OF THE INVENTION

Water resistance is an important property for protective compositions used as surface coatings, adhesives, caulks and sealants. Water is known to penetrate porous materials and contribute to their deterioration. Examples of such damage include warping and swelling of wood, cracking and spalling of concrete and masonry caused by freeze/thaw cycles and dissolved salts and the corrosion of reinforcing steel in concrete caused by chloride ions found in deicing salts. Protective compositions containing a variety of polymers have been suggested for use in eliminating or reducing such damage. Many of these compositions require the presence of organic solvents. Because of recognized environmental toxicity and flammability problems, a significant effort is being made to replace these solvent-based systems with water based systems.

Considerable effort has been devoted to the development of water-based polymer systems which have sufficient water resistance to be useful in protective coating compositions. Such water-based polymer compositions are prepared by well known emulsion polymerization techniques which normally require the presence of one or more surfactant, often in combination with water soluble protective colloids, to emulsify the monomer reactants and stabilize the final polymer latex product. Conventional surfactants do not react with the monomers and residual amounts of these surfactants in coating and other protective compositions can have a negative effect on properties such as water resistance.

These surfactants can migrate through the polymer and form aggregates in the polymer matrix. The surfactants can also migrate to the dried polymer surface as well as to the polymer and substrate interface. Surfactants and water soluble protective colloids are water sensitive materials which can cause blushing and whitening as well as swelling of dried latex polymer when in contact with water. Blushing, whitening and swelling of dried latex polymers by water can destroy the integrity of the polymer latex and eventually causing the protective composition to fail. It would be desirable to have a polymer latex made by emulsion polymerization which does not have the water sensitivity resulting from the presence of the conventional surfactants or protective colloids required to emulsify monomers and stabilize the polymer latex during polymerization and post handling.

An improvement in the water resistance of protective compositions containing aqueous polymer latexes has been achieved by substituting a class of compounds known as reactive surfactants for part or all of the conventional surfactants used in the preparation of the polymer latexes. The reactive surfactants are covalently bonded to the latex polymer and thus are not subject to migration and other

problems associated with conventional surfactants. The reactive surfactants are similar to conventional surfactants with surface activity imparted by the hydrophilic and hydrophobic moieties in the molecules. The hydrophilic moiety can be either ionic or nonionic in nature. Reactive surfactants also contain ethylenically unsaturated double bonds for free radical reaction with other monomers during polymerization. U.S. Pat. No. 4,224,455 describes the preparation of reactive surfactants that are comprised of ring sulfonated half esters of maleic anhydride with alkoxyated alkyl arylols and their applications to impart stability to polymers made by emulsion polymerization. U.S. Pat. No. 4,075,411, 5,563,214, 5,296,627, 5,332,854, 4,939,283, 5,324,862, 4,814,514 are examples describing other representative types of reactive surfactants and their use as emulsifiers in emulsion polymerization.

In an article presented at Eurocoat 95, titled "A New Class of Latex Binders for Water-Borne Wood Coatings", M. Slinckx and S. Spanhove, International Congress Eurocoat, Lyon, pp. 19-21, highly branched neo vinyl esters such as vinyl neodecanoate and vinyl neononanoate are described as providing improved water resistance when incorporated into acrylic polymers. This article discloses such neo vinyl esters polymerized with methyl methacrylate and 2-ethylhexyl acrylate. These monomers are emulsion polymerized in the presence of conventional surfactants. While such compositions exhibit an improved water resistance, they are not as good as solvent based systems and the neo vinyl esters are recognized as being difficult to polymerize with certain monomers. Accordingly, the protective compositions industry is still seeking an aqueous polymer system which offers the exceptional water resistance and exterior durability provided by solvent based systems.

SUMMARY OF THE INVENTION

This invention relates to novel latex polymers having excellent water resistance comprising:

- (a) at least one neo vinyl ester,
- (b) at least one reactive surfactant,
- (c) optionally, at least one ethylenically unsaturated monomer which is different from (a) or (b), and
- (d) optionally, at least one ethylenically unsaturated monomer which is different from (a), (b) or (c).

The novel latex polymers are prepared by emulsion polymerization of the ethylenically unsaturated monomers. The aqueous compositions containing the novel latex polymers are useful to impart superior water resistance to architectural coatings and in other applications where protection against water is desirable.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to novel latex polymers and aqueous compositions containing the same made by emulsion polymerization which exhibit exceptionally high water and alkali resistance. The novel latex polymers of this invention comprise (a) about 5 to about 99.9 percent by weight of highly branched neo vinyl esters; (b) 0 to about 94.9 weight percent of one or more alkyl esters of acrylic or methacrylic acid; (c) 0 to about 50 weight percent of other ethylenically unsaturated monomers; and (d) about 0.1 to 10.0 weight percent of one or more ethylenically unsaturated reactive surfactants.

The highly branched neo vinyl esters useful in this invention typically contain from 8 to 18 carbon atoms and are prepared from suitable highly branched carboxylic acids by methods well known in the art. Commercially available neo vinyl ester products are normally

a mixture containing a predominance of one species. Suitable neo vinyl ester compositions for use in the present invention include, but are not limited to, vinyl neononanoate (VeoVa 9), vinyl neodecanoate (VeoVa 10), and vinyl esters of mixed branched carboxylic acids (VeoVa 11), sold by Shell Chemical Company, and vinyl esters of mixed C10-C13 branched carboxylic acid, (EXXAR Neo-12) sold by Exxon Chemical Corp., and the like.

The aqueous polymer compositions of the present invention may contain as little as about 5% by weight of the highly branched neo vinyl esters to as much as about 99.9% by weight. When polymerized with other comonomers such as acrylates, the neo vinyl esters are present preferably in an amount of from about 10% to about 80%, and most preferably from about 15% to about 70% by weight, based on the weight of all monomers. Useful polymers have been prepared containing about 98.7% by weight of neo vinyl esters and 1.3% by weight of one or more reactive surfactants.

The reactive surfactants useful in the novel latex polymers of the present invention may be any compound which contains ethylenically unsaturated double bonds for free radical reaction with the neo vinyl esters and other monomers during polymerization while also containing hydrophilic and hydrophobic moieties similar to conventional surfactants which impart surface activity. Example of compounds which are useful as reactive surfactants in the novel latex polymers of the present invention include the compounds prepared by reacting sulfonated half esters of maleic anhydride with alkoxylated alkyl arylols described in U.S. Pat. No. 4,224,455; nonyl phenoxy(ethyleneoxy)₁₀₋₄₀ ethyl acrylate, nonyl phenoxy(ethyleneoxy)₁₀₋₄₀ ethyl methacrylate and nonyl phenoxy(ethyleneoxy)₁₀₋₄₀ crotonate which are disclosed in U.S. Pat. No. 4,075,411; the compounds based on N-acryloyl-piperazine disclosed in U.S. Pat. No. 5,563,214; the

compounds having a hydrophobic portion having terminal ethylenic unsaturation and a hydrophilic portion containing a poly(alkyleneoxy) segment and an ionic segment described in U.S. Pat. No. 5,296,627; the compounds containing nonylphenoxy propenyl moieties described in U.S. Pat. No. 5,332,854 and U.S. Pat. No. 5,324,862; the compounds containing allylic unsaturation described in U.S. Pat. No. 4,939,283 and U.S. Pat. No. 4,814,514; the disclosure of all of the above patents being incorporated herein by reference, and sodium dodecyl allyl sulfosuccinate (Trem LF-40) sold by Henkel Corporation.

Generally, the amount of ethylenically unsaturated reactive surfactants incorporated into the latex polymers of the present invention will range from about 0.1% to about 10% by weight based on the total weight of the polymer, and preferably from about 0.5% to about 8% by weight.

Reactive surfactants with nonylphenoxy propenyl groups or other groups structurally similar to styryl groups, behave similarly to styrene in copolymerization with highly branched neo vinyl esters, i.e. polymerization of the neo vinyl ester monomer is severely retarded in the presence of these compounds. It has been noted that the presence of certain other monomers such as the alkyl esters of acrylic and methacrylic acid appear to function as bridge between the branched neo vinyl esters and the reactive surfactants containing groups structurally similar to styryl groups allowing stable latexes to be made. Other reactive surfactants with ethylenically unsaturated moieties not similar to styryl groups generally react well in or show less retardation toward the polymerization of highly branched neo vinyl esters. Copolymers of highly branched neo vinyl esters with other ethylenically unsaturated monomers and all vinyl ester polymers and copolymers can be made with these reactive surfactants. Conventional non-reactive surfactants may also be present in the novel latex

polymers of the present invention, but minimal use of such surfactants is preferred to achieve the best results in the practice of this invention.

Comonomers which may be copolymerized with the highly branched neo vinyl esters and reactive surfactants include those ethylenically unsaturated addition monomers readily recognized by one skilled in the art as useful in the preparation of latex polymers. Particularly useful monomers include ethylenically unsaturated alkyl esters of acrylic and methacrylic acid, such as, but not limited to, one or more of the following: n-butyl acrylate, isobutyl acrylate, isopropyl acrylate, ethyl acrylate, methyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isooctyl acrylate, nonyl acrylate, oleyl acrylate, dodecyl acrylate, stearyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, nonyl methacrylate, lauryl methacrylate, isobutyl methacrylate, isobornyl methacrylate, isobornyl acrylate, pentyl acrylate, and mixtures thereof. Generally, the amount of ethylenically unsaturated alkyl esters of acrylic and methacrylic acid present in the novel latex polymers of the present invention ranges from about 0% to about 95% by weight based on the total weight of the polymer. Particularly good results are obtained when such monomers are present in an amount of from about 20% to about 90% by weight, preferably from about 30% to about 80% by weight, based on the total weight of the polymer.

The inventors have found that highly branched neo vinyl esters react slower when copolymerized with alkyl esters of acrylic and methacrylic acid due to the differences in monomer reactivity ratios. The alkyl esters of acrylic and methacrylic acid are nearly completely reacted shortly after monomer addition has been completed during polymerization, while there typically will be substantial measurable amounts of highly branched neo vinyl esters which remain unreacted. The inventors have found that the substantial measurable amounts of

unreacted highly branched neo vinyl esters which remain can be driven towards completion by adding additional initiators and continuing the polymerization. By following this procedure, structured latex particles or core/shell latex particles may be obtained with highly branched neo vinyl esters deposited on the outer layers or shell layers of latex particles. Thus another feature of this invention is a chemical means to prepare structured latex particles with an outer shell layers or layers which have very low oxygen content and low water permeability.

Other ethylenically unsaturated monomers which may be used in the preparation of the latex polymers of the present invention include, but are not limited to: vinyl esters, for example, vinyl acetate, vinyl propionate, vinyl formate, vinyl n-butyrate, vinyl laurate, vinyl stearate, vinyl pivalate, vinyl 2-ethylhexanoate, and the like; vinyl ethers, for example, methylvinyl ether, ethylvinyl ether, butylvinyl ether, and the like; allyl monomers, for example, allyl acetate, allyl propionate, allyl lactate, allyl amines, and the like; olefins, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, and the like. Other vinyl monomers, functional monomers, and crosslinking monomers, for example, acrylic acid, methacrylic acid, acrylonitrile, styrene, p-methyl styrene, vinyl and vinylidene halides such as vinyl chloride and vinylidene chloride, sodium vinyl sulfonate, sodium styrene sulfonate, sodium allyl ether sulfate, acrylamide, methacrylamide, sodium 2-acrylamide-2-methyl-propane sulfonate (AMPS), diacetone acrylamide, N-methylol acrylamide, N-methylol methacrylamide, 2-sulfoethyl methacrylate, 2-sulfopropyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, 2,2,4-trimethyl-1,3-pentanediol monomethacrylate, 2-cyanoethyl acrylate, diethylaminoethyl acrylate, dimethylaminoethyl methacrylate, glycidyl acrylate, glycidyl methacrylate, acetoacetoxyethyl methacrylate, allylacetoacetamide,

allyl methacrylate, trimethylol propane trimethacrylate, trifluoroethyl methacrylate, triallyl cyanurate, triallyl isocyanurate, sodium methallyl sulfonate, ethyl imidazolidone methacrylate, methoxy ethyl acrylate, methacrylamidoethylethyleneurea, allylic derivatives of aminoethylethyleneurea (Sipomer WAM), cyclic imides derivatives of urea/ureido monomers (Cylink WAM; WO 97/49676), β -carboxyethyl acrylate, dicyclopentenyl acrylate, dicyclopentenyl methacrylate, trimethylolpropane trimethacrylate, pentaerythritol triacrylate, vinyltrimethoxysilane, vinyl-tris(2-methoxyethoxysilane), gamma-methacryloxypropyltrimethoxysilane, vinylpyrrolidone, ethylene methacrylate phosphate, maleic acid, fumaric acid, itaconic acid, dimethyl maleate, di-n-butyl maleate, diethyl maleate, diethylhexyl maleate, diethyl fumarate, butadiene, chloroprene, isoprene, polybutene and poly(isobutylene-co-butene) oligomers containing ethylenically unsaturated double bonds (Indopol series from Amoco Chemical Company), 1,4-butanediol dimethacrylate, diallyl maleate, divinyl adipate, crotonic acid, mixtures thereof, and the like. Typically, these additional ethylenically unsaturated monomers are present in an amount of from about 0% to about 50% by weight, based on the total weight of the polymer, and more typically up to about 30% by weight.

Any known method of emulsion polymerization may be used to prepare the novel latex polymers of the present invention including semi-batch, staged feed, power feed, full batch, continuous, seeded emulsion polymerization or any other suitable procedure. Any suitable polymerization conditions may be used. Typically, the reaction temperature will range from about 0 °C to about 100 °C, and preferably from about 40 °C to about 90 °C. The polymerization normally will be conducted using polymerization initiators. Suitable polymerization initiators include, but are not limited to: water-soluble persulfates and peroxides capable of generating free radicals such as ammonium

persulfate, sodium persulfate, potassium persulfate, hydrogen peroxide, t-butyl hydroperoxide, di-t-butyl peroxide, peracetic acid, perbenzoic acid, diacetyl peroxide, t-butyl peracetate, t-butyl perbenzoate, and the like, azo initiators, such as 2,2-azobisisobutyronitrile, and the like, and other radiation and transition metal compounds capable of generating free radicals. The amount of such free radical initiators used generally ranges from about 0.05% to about 6% by weight based on the weight of all monomers present. Alternatively, redox initiators may be used, especially when polymerization is carried out at lower temperatures. For example, reducing agents may be used in addition to the persulfate and peroxide initiators mentioned above. Typical reducing agents include, but are not limited to: alkali metal salts of hydrosulfites, sulfoxylates, thiosulfates, sulfites, bisulfites, reducing sugar such as glucose, sorbose, ascorbic acid, erythorbic acid, and the like. In general, the reducing agents are used at levels from about 0.01% to about 6% by weight.

Various additives can be added before, during or after polymerization. These include conventional surfactants, buffering agents, neutralizing agents, defoamers, chain-transfer agents, plasticizers and polymeric stabilizers. Suitable conventional surfactants include, but are not limited to, one or more: alkyl and/or aryl sulfates, sulfonates, phosphates, or carboxylates such as sodium lauryl sulfate, sodium salt of alkylaryl polyether sulfates, linear alcohol ethoxylate phosphates, alkylphenol ethoxylate phosphates, and the like; oxyalkylated fatty amines, fatty acid amides and/or monoalkylphenols such as oxyethylated lauryl alcohol, oxyethylated oleyl alcohol, oxyethylated stearyl alcohol, oxyethylated p-isooctylphenol, oxyethylated p-n-nonylphenol, oxyethylated p-n-dodecylphenol, and the like; fluorocarbon-based surfactants, such as

ammonium perfluoroalkyl sulfonates, potassium perfluoroalkyl sulfonates, amine perfluoroalkyl sulfonates, ammonium perfluoro alkyl carboxylates, potassium fluorinated alkyl carboxylates, fluorinated alkyl polyoxyethylene ethanols, fluorinated alkyl alkoxyates, fluorinated alkyl esters, and the like. The amount of conventional surfactants may range from about 0% to about 5% by weight, and preferably from about 0% to about 2% by weight. Any polymeric stabilizers capable of stabilizing latex particles may be used, these include, but not limited to, cellulose ethers such as hydroxyethylcellulose, alkyl modified hydroxyethylcellulose, aryl alkyl modified hydroxyethylcellulose, carboxymethylcellulose, alginate, starch, poly(vinyl alcohol), polyacrylates, polymethacrylates, styrene-maleic anhydride copolymers, polyvinylpyrrolidones, polyacrylamides, polyethers, and the like. The amount of polymeric stabilizers may range from about 0% to about 5% by weight, and preferably from about 0% to about 2% by weight.

The latex polymers of the present invention are normally obtained as an aqueous composition by emulsion polymerization. Techniques well known to the skilled artisan may be employed to obtain a latex polymer of the present invention having the desired physical characteristics required for a particular application. Useful aqueous composition containing the latex polymers of the present invention will typically have a solids content of from about 10% to about 70% by weight based on the total weight of the composition. The latex polymers of the present invention may be tailored to obtain any desired molecular weight and viscosity. Typically, the latex polymers of the present invention will have a viscosity in the range of about 10 to about 5000 cps. The pH of an aqueous composition containing the latex polymer of the present invention will normally be within the range of

about 2 to about 12, while the particle size of the latex polymer will normally be in the range of from about 0.02 to about 2.0 microns.

The novel latex polymers of the present invention can be tailored for use in many applications. Representative examples including architectural coatings for wood including paints, varnishes, stains and clear sealers; architectural coatings for other substrates such as plaster, concrete, brick and metal; appliance finishes, automotive finishes, coil coatings, can coatings, marine coatings, aircraft finishes, paper coatings and various adhesives including pressure sensitive adhesives. Other potential uses for the novel latex polymers include caulks and sealants, additives and modifiers, binders for dyes and pigments, cement modifiers, waterproofing agents, overprint varnishes, flexographic inks and polishes for shoes, floors and furniture.

EXAMPLES

The following examples are offered to illustrate the novel aqueous polymer compositions of this invention and are not intended to be limiting in scope. All of the parts, percentages and proportions referred to herein are by weight unless otherwise indicated .

EXAMPLE 1

This example illustrates the preparation of an aqueous latex polymer composition with alkyl esters of acrylic and methacrylic acid in the presence of conventional surfactants. A reaction kettle was equipped with an agitator, thermocouple, reflux condenser, nitrogen inlet, water jacket, and suitable addition ports. A monomer preemulsion was prepared by mixing together 60.1 parts of deionized water, the conventional surfactants 0.37 part of a sodium lauryl sulfate (Rhodapon UB supplied by Rhodia Company) and an ethoxylated

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nonylphenol (Tergitol NP-15 supplied by Union Carbide Corp.), 46.52 parts of n-butyl acrylate, 52.13 parts of methyl methacrylate, and 1.34 parts of methacrylic acid. The reaction kettle was charged with 72.1 parts of deionized water, 1.12 parts of Rhodapon UB and 2.26 parts of Tergitol NP-15, 2.75% of the above prepared monomer preemulsion, and 0.05 part of an ammonium persulfate in 1.22 parts of deionized water. The kettle was heated to 80°C with continued agitation and nitrogen purge. Twenty minutes later, the rest of monomer preemulsion along with 0.55 part of an ammonium persulfate in 6.09 parts of deionized water in separate feed stream were added to the reaction kettle over a three hour period. The temperature was maintained at 80°C for 30 minutes more after all additions. 0.29 part of t-butyl hydroperoxide in 2.44 parts of deionized water and 0.12 part of sodium formaldehyde sulfoxylate in 2.52 parts of deionized water were added to the reaction kettle over a one hour period. The latex was then cooled to room temperature. The properties of the latex obtained are presented in Table 1.

EXAMPLE 2

This example describes the preparation of an aqueous latex polymer composition with alkyl esters of acrylic and methacrylic acid in the presence types of conventional surfactants which are different from those used in Example 1. The equipment, procedure and ingredients described in Example 1 were used, except that the conventional surfactants employed to prepare the monomer preemulsion were 0.24 part of an ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol (ABEX EP-110 supplied by Rhodia Company) and 0.57 part of a nonylphenoxy poly(ethyleneoxy) ethanol (Igepal CO-630 supplied by Rhodia Company). 1.12 parts of ABEX EP-110 and 2.26 parts of Igepal CO-630 were charged to the

reaction kettle initially. The properties of the latex obtained are presented in Table 1.

EXAMPLE 3

This example describes the preparation of an aqueous latex polymer composition with alkyl ester of acrylic and methacrylic acid in the presence of ethylenically unsaturated reactive surfactants. The equipment, procedure and ingredients described in Example 1 were used, except that in place of the conventional surfactants, the following ethylenically unsaturated reactive surfactants were employed to prepare the monomer preemulsion. 0.07 part of a nonylphenoxy propenyl polyethoxylate sulfate (Hitenol BC-10 supplied by DKS International, Inc.) and 0.57 part of a nonylphenoxy propenyl polyethoxylated alcohol (Noigen RN-10 supplied by DKS International, Inc.). 0.34 part of Hitenol BC-10 and 2.26 parts of Noigen RN-10 were charged to the reaction kettle initially. The properties of the latex obtained are presented in Table 1.

EXAMPLE 4

This example describes the preparation of an aqueous latex polymer of a highly branched neo vinyl ester with alkyl esters of acrylic and methacrylic acid in the presence of conventional surfactants. The equipment and procedure described in Example 1 were used. A monomer preemulsion was prepared by mixing together 58.38 parts of deionized water, 0.58 part of an ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol (ABEX EP-110 supplied by Rhodia Company) and 1.13 parts of a nonylphenoxy poly(ethyleneoxy) ethanol (Igepal CO-630 supplied by Rhodia Company) which are conventional surfactants, 37.52 parts of vinyl neodecanoate (VeoVa 10 supplied by Shell Chemical Company), 25.82 parts of n-butyl acrylate,

35.32 parts of methyl methacrylate, and 1.34 parts of methacrylic acid. The reaction kettle was charged with 72.1 parts of deionized water, 0.88 part of ABEX EP-110 and 1.70 parts of Igepal CO-630, 2.75 percent of the above prepared monomer preemulsion, and 0.05 part of ammonium persulfate in 1.22 parts of deionized water. The kettle was heated to 80°C with continued agitation and nitrogen purge. Twenty minutes later, the rest of monomer preemulsion along with 0.55 part of ammonium persulfate in 6.09 parts of deionized water in separate feed stream were added to the reaction kettle over a three hour period. The free VeoVa 10 at the end of addition was found to be about 5.5 percent. The free methyl methacrylate was found to be about 0.13 percent and n-butyl acrylate was not detectable. The temperature of the reaction kettle was maintained at 80°C for 30 minutes more and 0.29 part of t-butyl hydroperoxide in 2.44 parts of deionized water and 0.12 part of sodium formaldehyde sulfoxylate in 2.52 parts of deionized water were then added over one hour period. The residual methyl methacrylate was 0.02 percent while VeoVa 10 and n-butyl acrylate were not detectable at the end of additional initiator addition. Thus the additional initiator was capable of driving the VeoVa 10 reaction towards completion. It was possible that structured latex particles or core/shell latex particles were obtained with highly branched neo vinyl esters deposited on the outer layers or shell layers of the latex particles. The properties of the latex obtained are presented in Table 1.

EXAMPLE 5

This example illustrates the novel latex polymers of the present invention. It describes the preparation of an aqueous latex polymer of a highly branched neo vinyl ester polymerized with alkyl esters of acrylic and methacrylic acid in the presence of ethylenically unsaturated reactive surfactants containing nonylphenoxy propenyl groups. The

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equipment, procedure and ingredients described in Example 4 were used, except that the following ethylenically unsaturated reactive surfactants were employed in place of the conventional surfactants to prepare the monomer preemulsion; 0.15 part of a nonylphenoxy propenyl polyethoxylate sulfate (Hitenol BC-10 supplied by DKS International, Inc.) and 1.13 part of a nonylphenoxy propenyl polyethoxylated alcohol (Noigen RN-10 supplied by DKS International, Inc.). 0.26 part of Hitenol BC-10 and 1.70 parts of Noigen RN-10 were charged to the reaction kettle initially. At the end of monomer preemulsion and initiator additions, the free VeoVa 10 was found to be 3.5 percent, while free methyl methacrylate and n-butyl acrylate were 0.03 and 0.02 percent, respectively. The temperature of the reaction kettle was maintained at 80°C for 30 minutes more and 0.29 part of t-butyl hydroperoxide in 2.44 parts of deionized water and 0.12 part of sodium formaldehyde sulfoxylate in 2.52 parts of deionized water were then added over one hour period. The residual VeoVa 10 was found to be about 0.07 percent while methyl methacrylate was 0.02 percent and n-butyl acrylate was not detectable. In this example, structured latex particles or core/shell particles may be made with highly branched neo vinyl esters deposited on the outer layers or shell layers of the latex particles. Surprisingly, VeoVa 10 polymerization was not retarded in the presence of reactive surfactants containing nonylphenoxy propenyl groups as one skilled in the art might have expected. The properties of the latex obtained are presented in Table 1.

Table 1: Latex Compositions and Properties

	Example 1	Example 2	Example 3	Example 4	Example 5
n-Butyl acrylate	46.52	46.52	46.52	25.82	25.82
Methyl methacrylate	52.13	52.13	52.13	35.32	35.32
Veova 10 (a)				37.52	37.52
Methacrylic acid	1.34	1.34	1.34	1.34	1.34
Rhodapon UB (b)	1.49				
Tergitol NP-15 (c)	2.83				
ABEX EP-110 (d)		1.36		1.46	
Igepal CO-630 (e)		2.83		2.83	
Hitenol BC-10 (f)			0.41		0.41
Noigen RN-10 (g)			2.83		2.83
Latex solids content, wt%	41.02	42.27	39.24	41.39	41.19
pH	2.12	2.11	2.13	2.18	2.18
Particle size, micron	0.12	0.16	0.19	0.14	0.13
Brookfield viscosity, cps	20	20	20	20	20

(a) Vinyl neodecanoate supplied by Shell Chemical Company.

(b) Sodium lauryl sulfate (30% in aqueous solution) conventional surfactant supplied by Rhodia Company.

(c) Ethoxylated nonylphenol conventional surfactant supplied by Union Carbide Corp.

(d) Ammonium salt of sulfated nonylphenoxy poly(ethyleneoxy) ethanol (30% in aqueous solution) conventional surfactant supplied by Rhodia Company.

(e) Nonylphenoxy poly(ethyleneoxy) ethanol conventional surfactant supplied by Rhodia Company.

(f) Nonylphenoxy propenyl polyethoxylate sulfate reactive surfactant supplied by DKS International, Inc.

(g) Nonylphenoxy propenyl polyethoxylated alcohol reactive surfactant supplied by DKS International, Inc.

Test formulations were prepared to examine the water repellent effectiveness of each latex shown in Table 1. Each test formulation contained 100 parts of the latex to be tested, 106.5 parts of deionized water and 4.5 parts of diethylene glycol monobutyl ether. Each test formulation was equilibrated for 24 hours before testing.

The water repellent effectiveness of each latex was measured gravimetrically. Water absorption was tested using matching 1 by 2 by 0.25 inch Southern Yellow Pine boards. Four boards were treated with each latex formulation by immersing the boards in the latex formulation for three minutes. The boards were then allowed to dry for three days in a room maintained at constant temperature and humidity (72°F and 50% humidity). Four untreated boards were used as a control. All of the treated and untreated boards were weighed, immersed in deionized water for 30 minutes, and weighed again. The difference in weight represents the amount of water absorbed. The water repellent effectiveness (WRE) of each latex is determined by subtracting the weight of water absorbed by the board treated with the latex from the weight of the water absorbed by the untreated board, dividing that by the weight of water absorbed by the untreated board and multiplied by 100, as shown in the equation below.

$$\text{WRE} = \frac{(\text{water absorbed by untreated control} - \text{water absorbed by treated board})}{(\text{water absorbed by untreated control})} \times 100$$

The average of the water repellent effectiveness of the four boards treated with each latex of the examples is shown in Table 2. The results show that the water resistance of the novel aqueous polymer

compositions of the present invention represented by Example 5 are significantly better than the water resistance of the prior art compositions.

Table 2: Water Repellent Effectiveness

<u>Example</u>	<u>Water Repellent Effectiveness</u>
1	43.69
2	46.69
3	57.41
4	72.75
5	81.28

The following recipes are examples of typical architectural coating formulations employing the novel latex polymer of Example 5:

Clear Sealer for Wood or Concrete

<u>Ingredients</u>	<u>Gallons</u>
Water	43.59
Glycol	3.95
Ammonia	0.11
Wax Additive	2.89
CoSolvent	1.09
Antioxidant	0.25
Mildewcide	0.87
Preservative	0.17
Latex of Example 5	47.05

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Wetting Agent	0.02
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Total	100
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% Weight Solids	20
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White Paint/Stain for Wood and Concrete

<u>Ingredients</u>	<u>Gallons</u>
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Water	42.00
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Preservative	0.40
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Glycol	4.00
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Rheology Modifier	0.40
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Dispersant	1.50
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Defoamer	0.20
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Surfactant	0.20
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Prime Pigment	5.00
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Extender Pigment	10.00
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Latex of Example 5	34.00
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CoSolvent	1.50
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Mildewcide	0.76
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Total	100
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% Weight Solids	47
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We claim:

1. A latex polymer comprising:
 - (a) at least one highly branched neo vinyl ester, and
 - (b) at least one reactive surfactant.
2. The polymer of claim 1 which further contains:
 - (c) at least one ethylenically unsaturated monomer which is different from (a) or (b).
3. The polymer of claim 2 wherein (c) is at least one alkyl ester of acrylic or methacrylic acid.
4. The polymer of claim 3 which further contains:
 - (d) at least one ethylenically unsaturated monomer which is different from (a), (b) or (c).
5. The polymer of claim 1 wherein the reactive surfactant of (b) contains ethylenic unsaturation and hydrophilic and hydrophobic moieties.
6. The polymer of claim 1 wherein (a) is a neo vinyl ester containing from 8 to eighteen carbon atoms.
7. The polymer of claim 6 wherein the neo vinyl ester is selected from vinyl neononanoate, vinyl neodecanoate, vinyl esters of mixtures of C₈ to C₁₃ branched carboxylic acids, or mixtures thereof.



8. The polymer of claim 7 wherein the neo vinyl ester is present in an amount of 5% to about 99.9% by weight based on the total weight of the polymer.
9. The polymer of claim 5 wherein the reactive surfactant is present in an amount of from 0.1% to 10% by weight based on the total weight of the polymer.
10. A latex polymer comprising:
- (a) from about 15% to about 70% by weight, based on the total weight of the polymer of a highly branched neo vinyl ester selected from vinyl neononanoate, vinyl neodecanoate, vinyl esters of mixtures of C₈ to C₁₃ branched carboxylic acids, or mixtures thereof,
 - (b) from about 0.5% to about 8 % by weight of at least one reactive surfactant having ethylenic unsaturation and containing hydrophilic and hydrophobic moieties, and
 - (c) from about 30% to about 80% of at least one alkyl ester of acrylic or methacrylic acid.
11. An architectural coating composition comprising water and the latex polymer of claim 1.
12. A water resistant coating containing the latex polymer of claim 1.
13. A method of enhancing the water resistance of a coating composition by adding thereto an effective amount of the latex polymer of claim 1.