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(54) Title: WATER-DISPERSABLE POLYURETHANE/ACRYLIC POLYMER COMPOSITIONS

(57) Abstract
The present invention provides for aqueous polymer dispersions characterized by a water-dispersible polyurethane/ acrylic support resin/ acrylic polymer, with the acrylic polymer being polymerized from monomers in the presence of the water-dispersible polyurethane and acrylic support resin. The dispersions can be prepared having balanced properties such as toughness, durability, hardness, abrasion and detergent resistance, and depth and retention of gloss. The compositions are particularly suitable in floor coatings.
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WATER-DISPERSABLE POLYURETHANE/ACRYLIC POLYMER COMPOSITIONS

This invention relates to polyurethane/ acrylic polymer aqueous dispersions which, when applied as a coating, will air dry to a hard, abrasion-resistant film having excellent toughness, durability, and gloss. More particularly, the invention relates to aqueous polymer dispersions characterized by an acrylic polymer formed by polymerizing acrylic and styrene type monomers in the presence of a water-dispersible polyurethane and a vinyl support resin. "Acrylic" as used herein to define a monomer or polymer embraces acrylic acid and methacrylic acid, and derivatives thereof such as the esters.

Polyurethanes are well known in, inter alia, the protective coating industry to be materials having exceptional hardness, abrasion resistance, toughness, flexibility, and, when aliphatic in nature, UV stability. These materials have been extensively developed in order to build into the polyurethane specific properties so that the polyurethane can be used in specialized areas.

One area of development has been the modification of the polyurethanes with components having ethylenic unsaturation. Thus,

-Guagliardo et al, U.S. Patent No. 4,317,895; and Guagliardo, U.S. Patent No. 4,318,833 disclose coating compositions based on a thermoplastic copolymer prepared by polymerizing one or more ethylenically unsaturated monomers in the presence of a fully reacted polyurethane. The resulting copolymers are stated to be particularly useful in
automotive finishes.

- Tideswell et al, U.S. Patent No. 4,107,229 discloses vinyl terminated, fully reacted urethane compositions comprising the reaction product of a polyisocyanate, an hydroxyalkylated novolac, and an ethylenically unsaturated alcohol. The vinyl terminated compositions are then copolymerized with ethylenically unsaturated monomers to produce thermoset polymers useful in the manufacture of molded articles, laminates, and in the formulation of marine coatings.

- Suling et al, U.S. Patent No. 4,233,424; and Suling et al, U.S. Patent No. 4,300,886 disclose polymers useful in making dental appliances obtained by bead polymerization of from about 88 to 99.5% by weight of a polymer of methacrylic acid esters, with from 0.5 to 12% by weight of a polyurethane.

- Niederhauser et al, U.S. Patent No. 3,641,199 discloses urethane elastomer impact modifiers wherein ethylenically unsaturated monomers are polymerized in the presence of a polyurethane. The modified polymers are stated to offer an improved balance of physical properties, including impact strength, clarity, and weather resistance.


Although the prior art establishes that the polyurethanes have been extensively modified with the acrylcs, in most all instances the modifications have been for the purpose of providing polyurethane compositions having specific properties for a particular application. There is still a need for modified polyurethanes dispersed in or dispersible in water which, while retaining the advantageous properties of the polyurethanes, will also have the beneficial characteristics of resin systems such as the acrylcs. Moreover, it is particularly desirable to have the ability to modify the polyurethanes in a manner which will permit the obtaining of a variation in the physical characteristics of the polymeric compositions, such as the ability to prepare the compositions to have either low, high, or intermediate glass transition temperatures (Tg), and a balancing of flexibility, durability, hardness, toughness, and gloss in coatings prepared from the polymer compositions without need for the addition of large amounts of modifying components.
Accordingly, it is a primary object of the present invention to provide for polyurethane/ acrylic polymer aqueous dispersions which can be tailored in composition to provide coatings based on the dispersions with varying physical characteristics, which may vary widely to satisfy widely varying applications.

In addition, the polyurethane/acrylic polymer aqueous dispersions are tailored to have balanced properties in coatings prepared from the dispersions with respect to abrasion and detergent resistance, depth and retention of gloss, and recoatability which causes the aqueous dispersions to be particularly suitable for use in floor care compositions.

Specifically, the present invention provides for a water-dispersible polymer composition characterized by water-dispersible polyurethane, an acrylic support resin, and an acrylic polymer; said acrylic polymer being formed from acrylic monomers polymerized in the presence of a mixture of said water-dispersible polyurethane and acrylic support resin to provide the water-dispersible polymer composition.

The components of the final aqueous dispersion will comprise from 3 to 85% by weight water-dispersible polyurethane, 5 to 40% by weight acrylic support resin, and 15 to 85% by weight of the acrylic polymer formed in situ by polymerizing the acrylic monomers. Preferably, the components of the final aqueous dispersion will comprise from 3 to 65% by weight polyurethane, 5 to 30% by weight acrylic support resin, and 25 to 92% by weight of the acrylic polymer formed in situ. More preferably, the final aqueous dispersion will comprise from 5 to 40% by weight polyurethane, 5 to 25% by weight acrylic support
resin, and 35 to 90% by weight of the acrylic polymer formed \textit{in situ}. Most preferably, the final aqueous dispersion will comprise from 10 to 25% by weight polyurethane, 8 to 15% by weight acrylic support resin, and 60 to 82% by weight acrylic polymer formed \textit{in situ}.

By polymerizing the acrylic monomers in the presence of the polyurethane and support resin, it is possible to control the properties of the aqueous dispersion to obtain the favorable properties of the polyurethane such as
UV stability (if aliphatic in nature), hardness, abrasion resistance, toughness, and resistance to salt and organic chemicals; and also in general the favorable properties of acrylic systems which can show excellent UV stability, good depth and retention of gloss, and recoatability. Moreover, it is possible by the judicious selection of the three components of the system to obtain a variety of properties including a glass transition temperature which varies from a high glass transition temperature to a low glass transition temperature to provide a hard resin or a soft resin; and to vary the properties of the dispersions to provide coatings based on the dispersions having a balancing of properties such as hardness, abrasion resistance, toughness, resistance to chemicals such as detergents, and depth and retention of gloss so as to permit the formation of compositions which can be used in such diverse applications as floor coatings, graphic arts inks, paint binders, plastics additives, pigment-dispersant, resins, adhesives, and the like without need for the addition of large amounts of modifying components such as surfactants.

The Water-Dispersible Polyurethanes Used According To The Invention

The water-dispersible polyurethanes which can be used in the compositions of the present invention are pref-
erably the low molecular weight linear polyurethanes. These materials will generally have a number average molecular weight between about 5,000 and 50,000, and preferably from about 15,000 to 40,000. These polyurethanes generally comprise low molecular weight polyols reacted with polyisocyanates. A typical scheme for preparing aqueous urethane dispersions comprises the preparation of an isocyanate terminated prepolymer containing free acid groups. This is achieved by combining a polyether or polyester polyol with a diol acid such as dimethanol propionic acid (DMPA) with an excess of diisocyanate. The acid groups of the isocyanate prepolymer are then neutralized with a tertiary amine, dispersed in water and chain extended with a diamine.

The polyisocyanates used herein preferably are the linear diisocyanates such as 1,6-hexamethylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,4-cyclohexylene diisocyanate, 1-methyl-2,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate, or IPDI), 2,4'-diisocyanato-dicyclohexylmethane, 4,4'-diisocyanato-dicyclohexylmethane, and meta- and para-tetramethylxylenediisocyanate. In addition to the above diisocyanates, the urethane oligomers obtained by isocyanurate or diurethane formation can be employed. It is
preferable to use isocyanates and polyisocyanates containing aliphatic and/or cycloaliphatic bound isocyanate groups in order to obtain good light stability. The polyol employed is generally a linear polyol of the type derived from polyleylene ether glycols, polyester polyols including dihydroxy polyesters, dihydroxy polyester amides, polyester polycarbonate polyols, polyhydroxy polyacetals, polycarbonate polyols, and the like.

More preferably the water-dispersible polyurethanes will have anionic characteristics obtained, for example, by including acid groups which can be neutralized by base materials. However, any of the water-dispersible polyurethanes have application according to the present invention, including those prepared from the aromatic isocyanates such as 2,4-tolylene diisocyanate, m-phenylene diisocyanate, 4-chloro-1,3-phenylene diisocyanate, 4,4'-biphenylene diisocyanate, 1,5-naphthylene diisocyanate, and the like, with any polyol component which can be a polyester having reactive hydroxyl groups such as the alkyd resin polyesters of the type formed by the reaction between glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, neopentyl glycol, pentamethylene glycol, hexamethylene glycol, decamethylene glycol and the like.
with dibasic acids such as maleic, succinic, glutaric, adipic, phthalic, terephthalic, hexahydroterephthalic and para-phenylenediacetic acids. Other alkyd resins formed using glycerine or other polyhydroxy compounds with dibasic acids, as well as to esters of polyhydric alcohols and hydroxy fatty acids, such as glycercyl ricinoleate and castor oil can be used. The polyurethanes useful herein can also include modifiers such as amines and the like.

As will be more fully apparent hereinafter, it is essential to select the components for the polyurethane in order that the polyurethane will have water-dispersible characteristics and which provides the specific characteristics for a tailored end application. Water-dispersible polyurethanes particularly useful herein are commercially available, for example the Spensol Series such as Spensol L-50, L-51, L-52, L-53, L-54, L-55, and L-56 marketed by N. L. Industries, Buffalo, New York. Other suitable, commercially available water-dispersible polyurethanes are marketed by Witco Chemical Corporation, New York, New York, under the tradename Witcobond W-232, W-234, W-240, and W-290H. Still other water-dispersible polyurethanes are commercially available from Mobay Chemical Corporation, Pittsburgh, Pennsylvania, under the tradename Baybond XW 121,
Impranil DLH, and Impranil DLN; from Sanncor, Leominster, Massachusetts, under the tradename Sancure 895, 896, 899, 1815, 1817, and 815; from Hauthaway & Sons Company, Linn, Massachusetts, under the tradename Hauthane HD-2007; and from Polyvinyl Chemical, Inc., Wilmington, Massachusetts, under the tradename Neorez R-960, R-966, and R-940.

The Acrylic Support Resin

The acrylic support resin is a fully formed acrylic addition polymer such as is disclosed in commonly assigned U.S. Patent Nos. 4,414,370; 4,529,787, and 4,546,160, the disclosures thereof being incorporated herein by reference. More particularly,

- the '370 patent discloses styrene and acrylic acid co-polymers made by bulk thermal initiation which have a low weight average molecular weight and having a relatively high number average molecular weight. The process produces resins having relatively high aromatic content, making the resins particularly suitable for use in high solids coatings.

- the '787 patent discloses aromatic/acrylate polymers manufactured in a bulk initiated process wherein the process utilizes a polymerization initiator in the presence of low solvent levels to produce polymers having a narrow molecular
weight distribution and a low chromophore content. These polymers have a number average molecular weight of from about 500 to 6000, a polydispersity of less than about 2.5, and a dispersion index of less than about 4.5. The polymers, because of their low chromophore content, are particularly useful in protective coatings of the type herein contemplated, including floor polishes.

- the '160 patent discloses a continuous bulk polymerization process for producing polymers having a number average molecular weight of about 1000 to about 2500, a polydispersity of less than about 3, a dispersion index of up to about 5, and a low chromophore content.

Whereas the aforesaid commonly assigned patents disclose polymers having particularly desirable characteristics for use as the support resin according to the present invention, other acrylic polymers can be used as the support resin according to this invention. For example, resins made by a solution process are suitable for use herein. Vasanth R. Kamath and James D. Sargent, Sr., Pennwalt Corporation, in a paper entitled "High Solids Acrylic Coatings: Resin Synthesis With T-Amyl Peroxides," presented at the Water-Borne and High-Solids Coatings Symposium on February 5-7, 1986, in New Orleans, Louisiana, disclose low solution vis-
cosity and narrow MWS resins made by polymerizing monomers in a solvent using t-amyl peroxide. Examples of solution prepared resins are also disclosed in patents such as U.S. Patent Nos. 2,556,488; 3,673,168; 3,753,958; 3,879,357, and 3,968,059 noted in the above-referenced U.S. Patent No. 4,414,370.

The polymers useful as the support resin herein, made by bulk or solution processes, include homo- and co-polymers of monomers having only one reactive site of ethylenic unsaturation per molecule including 2-hydroxyethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxybutyl acrylate, 6-hydroxyhexyl acrylate, 2-hydroxymethyl methacrylate, 2-hydroxypropyl methacrylate, 6-hydroxyhexyl methacrylate, 5,6-dihydroxyhexyl methacrylate, methyl methacrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, isopropyl (meth)acrylate, isobutyl (meth)-acrylate, n-amyl (meth)acrylate, n-hexyl (meth)acrylate, isoamyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, N,N-dimethyl-aminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate, 2-sulfoethyl (meth)acrylate, trifluoroethyl (meth)acrylate, benzyl (meth)acrylate, 2-n-butoxyethyl (meth)acrylate, 2-chloroethyl (meth)acrylate,
sec-butyl (meth)acrylate, tert-butyl (meth)acrylate, 1-ethylbutyl (meth)acrylate, cinnamyl (meth)acrylate, cyclo-
hexyl (meth)acrylate, cyclopentyl (meth)acrylate, 2-ethoxy-
ethyl (meth)acrylate, furfuryl (meth)acrylate, hexafluoro-
isopropyl (meth)acrylate, 3-methoxybutyl (meth)acrylate,
2-methoxybutyl (meth)acrylate, 2-nitro-2-methylpropyl
(meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl
(meth)acrylate, 2-phenoxyethyl (meth)acrylate, 2-phenylethyl
(meth)acrylate, phenyl (meth)acrylate, propargyl (meth)acry-
late, tetrahydrofurfuryl (meth)acrylate, tetrahydropyranyl
(meth)acrylate, and (meth)acrylic acid. As used herein,
"meth" in parentheses before acrylic or acrylate is used to
designate either the methacrylic or acrylic compound. Other
monomers which can be used in forming the support resin in-
clude ethylenic monomers such as vinyl acetate, vinyl pyri-
dine, vinyl pyrrolidone, methyl crotonate, maleic anhydride,
styrene, alpha-methylstyrene and the like, preferably in
combination with an acrylic monomer.

Preferred support resins for use herein are those
prepared from a mixture of monomers. It has been found that
the support resin preferably will have a glass transition
temperature (Tg) within the range of from about -40 to 135°C,
and an acid value within a range of 50 to 260. Within these
ranges it is possible to provide water-dispersible polyurethane/acrylic polymer compositions which are hard resins having a high glass transition temperature or water-dispersible polyurethane/acrylic polymer compositions which are soft resins with a low glass transition temperature, with modification between the extreme ranges.

The Acrylic Monomers.

The acrylic monomers which can be polymerized in the presence of the water-dispersible polyurethane and support resin are largely the same monomers which can be used in the formation of the acrylic support resin and as such include the monomers acrylic acid and methacrylic acid and monomers derived from acrylic acid and methacrylic acid such as: the esters of acrylic acid and methacrylic acid including methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, n-butyl (meth)acrylate, isopropyl (meth)acrylate, isobutyl (meth)acrylate, n-amyl (meth)acrylate, n-hexyl (meth)acrylate, isoamyl (meth)acrylate, trifluoroethyl (meth)acrylate, benzyl (meth)acrylate, 2-n-butoxyethyl (meth)acrylate, 2-chloroethyl (meth)acrylate, sec-butyl-(meth)-acrylate, tert-butyl (meth)acrylate, 2-ethylbutyl (meth)acrylate, cinnamyl (meth)acrylate, cyclohexyl (meth)-acrylate, cyclopentyl (meth)acrylate, 2-ethoxyethyl (meth)-
acrylate, furfuryl (meth)acrylate, hexafluoroisopropyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-methoxybutyl (meth)acrylate, 2-nitro-2-methylpropyl (meth)acrylate, n-octyl-(meth)acrylate, 2-ethylhexyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, 2-phenylethyl (meth)acrylate, phenyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, and tetrahydropyranyl (meth)acrylate; monomers containing hydroxyl functionality such as 2-hydroxyethyl acrylate, 3-chloro-2-hydroxypropyl acrylate, 2-hydroxy-butyl acrylate, 6-hydroxy-hexyl acrylate, 2-hydroxymethyl methacrylate, 2-hydroxypropyl methacrylate, 6-hydroxyhexyl methacrylate, 5,6-dihydroxyhexyl methacrylate and the like; and monomers which include aromatic content derived from -C=C- containing aromatic compounds such as styrene, alpha-methylstyrene, vinyl toluene, p-methylstyrene, tertiary-butylstyrene, and the like. Other modifiers which can be used include ethylenically unsaturated monomers such as vinyl acetate, methyl crotonate, and the like. It has been found that particularly advantageous water-dispersible polyurethane/acrylic polymer compositions are obtained when the acrylic monomers selected for polymerizing in the presence of the support resin and water-dispersible urethane, when polymerized in the absence of the support resin and water-dispersible polyurethane according to the solution polymer method described
in Kamath and Sargent, supra, will provide a Tg value of between -40 to 135°C.

Polymerization Reaction Of Monomers In Presence Of Water-Dispersible Polyurethane And Support Resin

The reaction of the monomer component in the presence of the water-dispersible polyurethane and support resin is carried out in bulk at temperatures of from about 50 to 120°C, and preferably at temperatures of from about 75 to 90°C. Alternatively, the polymerization can be conducted using a continuous monomer feed process at temperatures of from about 50 to 120°C, and preferably at temperatures of from about 75 to 90°C.

The bulk polymerization process can be conducted substantially similar to the bulk polymerization process defined in the aforementioned commonly assigned U.S. Patent Nos. 4,414,370; 4,529,787, and 4,546,160. In the bulk polymerization process, the water-dispersible polyurethane dispersed in deionized water, and the support resin are mixed and transferred into a suitable reaction vessel such as a three-neck flask equipped with overhead stirrer, condenser, thermometer, addition funnel, and purged with nitrogen. The acrylic monomers are mixed and added to the reaction vessel. An initiator, such as ammonium persulfate (APS) which can be
dissolved in deionized water is conventionally added, and the reaction mixture heated to effect polymerization. The reaction is normally completed within from about one to four hours. It may be desirable to add a second charge of initiator prior to the reaction completion.

In the continuous monomer feed process, the water-dispersible polyurethane, deionized water, and the support resin are mixed and transferred into a suitable reaction vessel such as a three-neck or four-neck flask again equipped with overhead stirrer, condenser, thermometer, addition funnel, and purged with nitrogen. The monomers and initiator are added to the reaction flask, and the reaction continued until the monomers are completely reacted. Again the reaction is normally completed within from about one to four hours. Again it may be desirable to add a second charge of initiator prior to the end of the reaction. In this process it can be advantageous to first charge a small portion of the monomers, i.e., 10% of the total, and then after an initial heating add the remaining monomer content over time.

It is also possible in preparing the urethane-acrylic emulsions of this invention to add the support resin and/or water-dispersible urethane at different stages of the
polymerization process. For example, in a first step an acidic emulsion can be made, followed by neutralization to a pH above 7. In a second step the support resin and water-dispersible urethane can be added. In a third step the reactive monomers can be added.

In the alternative processes, an aqueous dispersion of the polymer composition is recovered comprising the polyurethane, the support resin, and acrylic polymer polymerized in situ. As set forth hereinbefore, the physical characteristics of the aqueous dispersion can be modified by judicious selection of the water-dispersible polyurethane, the support resin, and the polymer composition within the ranges set forth above.

**Uses Of The Aqueous Dispersion Of Polyurethane/Support Resin/Polymerized Monomers**

The compositions of the present invention are aqueous dispersions having physical characteristics including molecular weight, hardness, and curing characteristics which are controlled based on the selection of the starting polyurethane, support resin and monomer content, as well as on the ratios of components to each other to provide compositions having varying characteristics. If the dispersions are prepared in bulk, they can be used as such without
adjustment. If the materials are prepared by a continuous monomer feed process, it may be desirable to adjust the solids content and the like as is conventional in the art. The products can be used in various applications, including as floor polish ingredients, graphic arts inks, plastics, additives, paint binders, adhesives, coatings, and the like. The products can be tailored to a particular need, particularly with respect to protective coatings on floors, to obtain the desired hardness, toughness, durability, abrasion and detergent resistance, and gloss characteristics essential to such compositions.

Possible Additives

In the formulation of the compositions containing the water-dispersible polymer compositions, it is possible to include either during preparation of the water-dispersible composition or as a post-additive a surfactant to provide improved wettability and the like, or a film fortifier such as a natural or synthetic wax, levelling agents, plasticizers and coalescing agents, depending on the ultimate use of the dispersions. A unique characteristic of the water-dispersible polymer compositions of the present invention, however, is that excellent film-forming characteristics of the dispersions can be maximized with minimum amount of
additives such as surfactants, levelling agents, plasticizers, or coalescing agents.

DETAILED DESCRIPTION OF PRESENTLY PREFERRED EMBODIMENTS

Having described the invention in general terms, the following detailed examples are set forth to further illustrate the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

In this example the water-dispersible polyurethane at 30% by weight solids is a commercially available material marketed by N. L. Industries under the designation Spensol L-51. Spensol L-51 is an anionic aqueous dispersion of the reaction product of isophorone diisocyanate, a low molecular weight polyester polyl, based on polyalkylene glycol, and dimethanol propionic acid. The acrylic support resin which is an acid functional styrene/acrylic resin is manufactured and sold by S. C. Johnson & Son, Inc. under the tradename Joncryl 678. The support resin is made using the bulk polymerization process as described in U.S. Patent No. 4,546,160. The monomers reacted in the presence of the water-dispersible polyurethane and support resin comprised a mixture of methyl
methacrylate and 2-hydroxyethyl methacrylate. The weight percentages are as follows: 47.73% by weight Spensol L-51 as an aqueous dispersion (14.32 non-volatile); 29.68% by weight deionized water; 14.80% by weight of a 20% aqueous dispersion of the support resin (2.96 non-volatile); 6.56% by weight methyl methacrylate monomer (6.56 non-volatile); 1.16% by weight 2-hydroxyethyl methacrylate monomer (1.16 non-volatile); 0.05% by weight ammonium persulfate initiator, and 0.02% by weight t-butyl peroctoate initiator.

Procedure

(A) All of the components were charged to a four-neck round bottom flask, except for 90% of the monomers and the t-butyl peroctoate. The center neck of the flask is fitted with an agitator, one side neck is fitted with a nitrogen gas inlet, and one side neck is fitted with a thermometer. The final side neck is fitted with an addition funnel. The mixture was heated to 80°C. Thereafter, the remaining 90% of the monomers was added over a period of one to one and one-half hours. After all of the monomer was added, the t-butyl peroctoate was added and the reaction charge held at 80°C for an additional hour. After forced cooling, the resultant dispersion was filtered.

(B) A floor coating composition was prepared based on
the polymer dispersion of (A) above comprising 74.12% by weight of the aqueous dispersion; 19.66% by weight water; 1.0% by weight Carbitol; 3.10% by weight Ninate 411 which is a liquid amine aryl sulfonate anionic emulsifier at 92% non-volatile, marketed by Stepan Chemical Company; 0.66% by weight KP-140 which is a tributoxyethyl phosphate plasticizer marketed by the FMC Corporation; and 0.16% by weight BYK-344, a silicone surfactant and levelling agent marketed by BYK Chemie.

(C) The floor composition (B) above when applied to a floor as an air-dry coating had durability, toughness, abrasion and detergent resistance, and hardness superior to a commercial air-dry acrylic floor coating, and had equivalent depth and retention of gloss.

EXAMPLE 2

A procedure as set forth in Example 1 is repeated except that a soft support resin comprising styrene, methyl methacrylate, butylacrylate and acrylic acid, and having the following characteristics is used:

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The weight percentages of the components are as follows:
30.23% by weight polyurethane, Spensol L-51 as an aqueous dispersion (9.07 non-volatile); 41.62% by weight deionized water; 14.83% by weight of a 20% aqueous dispersion of the soft support resin (2.97 non-volatile) as above described; 11.22% by weight methyl methacrylate monomer (11.22 non-volatile); 1.98% by weight 2-hydroxyethyl methacrylate monomer (1.98 non-volatile); and 0.12% by weight ammonium persulfate initiator.

To the emulsion obtained was added 5% of Jonwax 26 which is an emulsified polyethylene wax and a solvent. When used in a non-skid overprint application, the results obtained are as follows:

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<th>60 Degree Gloss</th>
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<tr>
<td>Black Leneta</td>
<td>64</td>
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<tr>
<td>White Leneta</td>
<td>44</td>
</tr>
<tr>
<td>White Clay Coat</td>
<td>45</td>
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</table>

<table>
<thead>
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<th>Slide Angle Degree</th>
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<tbody>
<tr>
<td>Static</td>
<td>25</td>
</tr>
<tr>
<td>Kinetic</td>
<td>14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Rub Resistance Sutherland w/4 lb. wt.</th>
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<tbody>
<tr>
<td>200 Cycles</td>
<td>Excellent</td>
</tr>
<tr>
<td>400 Cycles</td>
<td>Excellent</td>
</tr>
<tr>
<td>600 Cycles</td>
<td>Excellent</td>
</tr>
<tr>
<td>800 Cycles</td>
<td>Very Good</td>
</tr>
<tr>
<td>1000 Cycles</td>
<td>Very Good</td>
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</table>

<table>
<thead>
<tr>
<th>Water Resistance</th>
<th></th>
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<tbody>
<tr>
<td>Excellent</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Block Resistance 140°F/40 psi/16 hours</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Dry</td>
<td>Excellent</td>
</tr>
<tr>
<td>Wet Back</td>
<td>Good</td>
</tr>
<tr>
<td>Wet Face</td>
<td>Fair</td>
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EXAMPLE 3

A similar procedure as outlined in Example 1 is used. The weight percentages of components are as follow:
15.77% by weight Spensol L-52 as an aqueous dispersion (4.73 non-volatile); 35.30% by weight deionized water; 17.50% by weight of a 20% aqueous dispersion of the support resin used in Example 1 (3.50 non-volatile); 0.22% by weight of a 30% aqueous solution of the ammonium salt of tridecyl ether sulfate; 0.74% by weight Triton X-100 sold by Rohm & Haas; 10.71% by weight styrene monomer (10.71 non-volatile); 13.39% by weight 2-ethylhexyl acrylate monomer (13.39 non-volatile); 2.68% by weight butyl acrylate monomer (2.68 non-volatile); 0.13% by weight ammonium persulfate initiator; 0.06% by weight t-butyl peroctoate initiator, and 3.50% by weight diethylene glycol ethyl ether.

The above composition as a blisterpack adhesive is drawn down with a #8 RDS rod onto a styrene-butadiene saturated (SBS) stock board. The film had properties as follows:
Gloss 60/Degree SBS Stock .......... 30
Surface Tack ...................... None

Block Resistance 120°F/4 psi/24 hours
Face/Back ......................... 2
Face/Face ........................ 0

Seal Conditions
250°F/Hot ......................... 9
250°F/Cold ......................... 7
275°F/Hot ......................... 10
275°F/Cold ......................... 8
300°F/Hot ......................... 10
300°F/Cold ......................... 10

Rated from 1-10 (10 = best)

EXAMPLE 4

A similar procedure as outlined in Example 1 is used. The weight percentages for the emulsion are as follows: 17.52% by weight of Spensol L-51 as an aqueous dispersion (5.26 non-volatile); 23.69% by weight of a 20% aqueous solution of a support resin as used in Example 2 (4.74 non-volatile); 28.68% by weight deionized water; 12.72% by weight styrene monomer (12.72 non-volatile); 12.72% by weight butyl acrylate monomer (12.72 non-volatile); 4.49% by weight 2-hydroxyethyl methacrylate monomer (4.49 non-volatile); and 0.18% by weight of ammonium persulfate initiator.
Exxate 600 which is an acetate ester of hexanol and butyl cellosolve were added to the finished emulsion. Samples were drawn down as a non-pigmented overprint for packaging on black/white and clay coated stock with a #6 RDS rod and dried for ten minutes at 140°F. The film properties obtained are as follows:

Gloss  
- Black .................. 65  
- White .................. 55  
- Clay Coat ............... 55

Water Resistance (30 min) .... Excellent  
Static Slide Angle ........... 30°  
Kinetic Slide Angle .......... 27°

The sample as above prepared was mixed with Jonwax 26 which is an emulsified polyethylene wax and Joncryl 52 which is an aqueous ammonia solution of Joncryl 678 in the proportions listed below. Each sample was drawn down on black/white and clay coated stock with a #6 RDS rod, dried at room temperature overnight, and evaluated as listed below.
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<th>B</th>
<th>C</th>
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<tr>
<td>Example #4 Emulsion.....</td>
<td>85</td>
<td>75</td>
<td>65</td>
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<tr>
<td>Jonwax 26................</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Joncryl 52................</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Gloss - 60 Degree</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Black...................</td>
<td>66</td>
<td>69</td>
<td>80</td>
</tr>
<tr>
<td>White....................</td>
<td>43</td>
<td>52</td>
<td>65</td>
</tr>
<tr>
<td>Clay Coat White..........</td>
<td>44</td>
<td>54</td>
<td>65</td>
</tr>
<tr>
<td>Slide Angle Degree</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static..................</td>
<td>30</td>
<td>30</td>
<td>37</td>
</tr>
<tr>
<td>Kinetic..................</td>
<td>17</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Rub (1000 cycles).........</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Water Resistance &lt;30 Min..</td>
<td>Excellent</td>
<td>Excellent</td>
<td>Good</td>
</tr>
</tbody>
</table>

**EXAMPLE 5**

Using a similar procedure as in Example 1, an emulsion was prepared using Spensol DV-4854 and a soft support resin based on styrene, butylacrylate, and acrylic acid.

The resin had the following characteristics:

- **Tg Calc**: -37
- **Acid Number**: 177
- **Number Average Molecular Weight (Mn)**: 3100
- **Weight Average Molecular Weight (Mw)**: 12700
- **Sedimentation Average Molecular Weight (Mz)**: 41810
- **Mz/Mw**: 3.29
- **Mw/Mn**: 4.10

The weight percentages of the components are as follows:

- 26.47% by weight of an aqueous dispersion of Spensol DV-4854 (8.58 non-volatile);
- 27.65% by weight deionized water;
17.24% by weight of a 20% aqueous solution of the resin described above (4.74 non-volatile); 2.00% by weight diethylene glycol monoethyl ether; 11.24% by weight of styrene monomer (11.24 non-volatile); 11.24% by weight butyl acrylate monomer (11.24 non-volatile); 3.97% by weight 2-hydroxyethyl methacrylate monomer (3.97 non-volatile), and 0.19% by weight ammonium persulfate initiator.

The above aqueous dispersion is then ground with a white pigment concentrate composed of TiO₂ pigment, resin solution, and water. The mixture is printed onto polypropylene with a flexohand printer and dried for 10 seconds at 150°F.

Grind Film Properties
Adhesion.................. Poor
Wetting..................... Good
Dry Crinkle............... Good

Other procedures can be used for preparing the urethane/acrylic emulsions whereby the support resin and/or water-dispersible urethane is added at different stages of the polymerization process. This modification can include making an acidic emulsion in the first stage, followed by neutralization to a pH above 7.0. In a second stage, support resin and/or water-dispersible urethane are added. The third stage is the addition of reactive monomers.
EXAMPLE 6

The following emulsion was prepared:

A: Deionized Water ........................................... 253.1 g
    Ethoxylated Octylphenol
    (10 moles ethylene oxide) (Triton X-100) ........ 2.2 g
    Ammonium Salt of Tridecylether Sulfate
    (30% aqueous solution) .......................... 7.4 g

B: Deionized Water ......................................... 15.0 g
    Ammonium Persulfate ................................. 1.58 g

C: Methyl Methacrylate .................................. 98.0 g
    Styrene ............................................ 9.7 g
    Butyl Acrylate .................................... 20.8 g
    Methacrylic Acid .................................. 10.0 g

D: Spensol L-51 ........................................... 197.8 g
    Primacor 4983 (ethylene/acrylic acid)
    (25% solids cut in D.I. water and NH₃) ....... 237.3 g
    Resin described in Example 5
    (27.5% aqueous solution) ......................... 70.5 g

E: Methyl Methacrylate ................................ 102.5 g
    Styrene ............................................ 9.7 g
    Butyl Acrylate .................................... 20.8 g
    2-Hydroxyethyl Methacrylate .................... 5.5 g

Component A is added to the reaction and heated to
80°C under a nitrogen atmosphere. 10% of weight of compo-

nent C is added to the reactor and stirred for three min-
utes. Component B is added and the reaction is held for
five minutes. The rest of component C is added over a 35-40
minute period. After holding for ten minutes, ammonium
hydroxide (10 g) is added. Component D is added dropwise
over 40 minutes. Once half of component D has been charged
(20 minutes), component E is added simultaneously over 40 minutes. Once component E is added, the reaction is held at 80°C for 45 minutes, cooled, and filtered.

The emulsion is evaluated in a floor polish formulation similar to Example 1. The formulation has good water and detergent resistance, and a three-coat 60 degree gloss of 67% on vinyl asbestos tiles.

In the above examples the polyurethane can be replaced with other water-dispersible polyurethanes to provide compositions with modified characteristics. The critical feature is that the polyurethane be water-dispersible and be compatible with the support resin and the acrylic polymer which is formed in situ. The support resin utilized in the examples can also be replaced with other support resins so as to provide varying characteristics in the final composition. For example, if a hard, high glass transition temperature resin is desired, the monomers used in forming the support resin can include aromatic content. The hardness or softness of the final composition can be varied by varying the monomers employed in the support resin and/or by varying the amount of support resin utilized. The monomers selected for polymerization in the presence of the water-dispersible and support resin can be changed to provide controlled characteristics to the final polymer dispersions.
Additionally, in the preparation of a floor coating composition based on the aqueous polymer dispersions of this invention, the components of the floor coating composition can be varied whereby the aqueous polymer dispersion will comprise from about 40 to 85 weight percent of the composition, based on the aqueous dispersion as prepared, Carbitol will comprise from about 0 to 10 weight percent of the composition, a wax will comprise from about 0 to 10 weight percent of the composition, an emulsifier will comprise from about 0 to 6 weight percent of the composition, and plasticizers and levelling agents will comprise from about 0 to 2.5 weight percent of the composition, with the balance of the composition being water. An important advantage in using the aqueous polymer dispersions of the present invention in a floor coating composition is in the ability to formulate the compositions utilizing only low levels of additives. Compositions falling within the aforesaid ranges will provide air-dried films having excellent gloss, durability, and resistance to spotting.

As will be apparent to one skilled in the art, various modifications can be made within the scope of the aforesaid description. Such modifications being within the ability of one skilled in the art form a part of the present invention and are embraced by the appended claims.
1. A water-dispersible polymer composition characterized by a water-dispersible polyurethane, an acrylic support resin, and an acrylic polymer; said acrylic polymer being formed from acrylic monomers polymerized in the presence of a mixture of said water-dispersible polyurethane and acrylic support resin to provide the water-dispersible polymer composition.

2. The composition of claim 1 characterized in that said acrylic support resin has a $T_g$ between about -40 and 135°C and an acid value between about 50 to 260, and the monomers polymerized in the presence of the water-dispersible polyurethane and acrylic support resin are selected whereby when copolymerized in the absence of the support resin and water-dispersible polyurethane will provide a polymer having a $T_g$ value of between -40 and 135°C.

3. The composition of claim 1 or 2 characterized in that said water-dispersible polyurethane is a reaction product of an aliphatic diisocyanate, or an aromatic diisocyanate, and a low molecular weight linear polyol.

4. The composition of claim 3 characterized in that said water-dispersible polyurethane is anionic.

5. The composition of claims 1, 2, 3 or 4 characterized in that the monomers forming the acrylic polymer include unsaturated aromatic monomers, preferably styrene or alpha-methylstyrene.

6. The composition of any of claims 1-5 characterized in that said water-dispersible polyurethane is present at from about 10 to 65% by weight, said acrylic support resin is present at from about 5 to 25% by weight, and said acrylic polymer which is formed from said acrylic monomers in the presence of said water-dispersible polyurethane and acrylic support resin is present at from about 25 to 75% by weight.
7. The composition of any of claims 1-5 characterized in that said water-dispersible polyurethane is present at from about 5 to 65% by weight, said acrylic support resin is present at from about 5 to 35% by weight, and said acrylic polymer which is formed from said acrylic monomers in the presence of said water-dispersible polyurethane and acrylic support resin is present at from about 25 to 85% by weight.

8. The composition of any of claims 1-7 characterized in that said support resin comprises the bulk polymerization reaction product of styrene, alpha-methylstyrene, butylacrylate, methylethacrylate, and (meth)acrylic acid.

9. The composition of any of claims 1-8 characterized in that the acrylic monomers making up said acrylic polymer comprises a mixture of (meth)acrylic acid esters, preferably including a hydroxy(meth)acrylic acid ester.

10. Method of forming an aqueous polymer dispersion characterized by the steps of (1) providing a mixture of water-dispersible polyurethane and acrylic support resin, and (2) polymerizing in the presence of said mixture of step (1) at least one acrylic monomer to form a water-dispersible polymer composition of said polyurethane, said support resin, and said formed acrylic polymer.

11. The method of claim 10 characterized in that said acrylic support resin has a Tg between about -40 and 135°C and an acid value between about 50 to 260, and the monomers polymerized in the presence of the water-dispersible polyurethane and acrylic support resin are selected whereby when copolymerized in the absence of the support resin and water-dispersible polyurethane will provide a polymer having a Tg value of between -40 to 135°C.
12. The method of claims 10 or 11 characterized in that said water-dispersible polyurethane is a reaction product of an aliphatic diisocyanate, or an aromatic diisocyanate, and a low molecular weight linear polyol.

13. The method of claim 12 characterized in that said water-dispersible polyurethane is anionic.

14. The method of claims 11, 12 or 13 characterized in that the monomers forming the acrylic polymer including unsaturated aromatic monomers, preferably styrene or alphamethylstyrene.

15. The method of claims 11, 12, 13 or 14 characterized in that said water-dispersible polyurethane is present at from about 10 to 65% by weight, said acrylic support resin is present at from about 5 to 25% by weight, and said acrylic polymer which is formed from said acrylic monomers in the presence of said water-dispersible polyurethane and acrylic support resin is present at from about 25 to 75% by weight.

16. The method of any of claims 11, 12, 13 or 14 characterized in that said water-dispersible polyurethane is present at from about 5 to 65% by weight, said acrylic support resin is present at from about 5 to 35% by weight, and said acrylic polymer which is formed from said acrylic monomers in the presence of said water-dispersible polyurethane and acrylic support resin is present at from about 25 to 85% by weight.

17. The method of any of claims 11-16 characterized in that said support resin comprises the bulk polymerization reaction product of styrene, alpha-methylstyrene, butylacrylate, methylethacrylate, and (meth)acrylic acid.

18. The method of any of claims 11-17 characterized in that the acrylic monomers making up said acrylic polymer comprises a mixture of (meth)acrylic acid esters and styrene-type monomers.

19. An aqueous floor polish characterized by

(a) from 40-85 weight percent of an aqueous
dispersion of the water-dispersible polymer composition of claims 1-9;
(b) from 0-10 weight percent wax;
(c) from 0-10 weight percent Carbitol;
(d) from 0-6 weight percent surfactant;
(e) from 0-2.5 weight percent plasticizer;
(f) from 0-2.5 weight percent levelling agent;
and
(g) the balance of the composition water.
**INTERNATIONAL SEARCH REPORT**

**International Application No.** PCT/US89/01299

### I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

<table>
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<th>IPC4:</th>
<th>C08K 5/00; C08L 75/04; C08F 2/16</th>
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<tr>
<td>U.S. CL:</td>
<td>524/366, 458, 460, 487, 507, 556; 525/125, 126</td>
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### II. FIELDS SEARCHED

<table>
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Documentation searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched

### III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tr>
<td>E, Y</td>
<td>US, A, 4,820,762 (TSAUR) 11 APRIL 1989 (SEE COL. 4, LINES 21-57).</td>
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<td>X</td>
<td>US, A, 4,318,833 (GUAGLIARDO) 09 MARCH 1982 (SEE COL. 2, LINES 28-32; COL. 5, LINES 20-40).</td>
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<td>US, A, 4,317,895 (GUAGLIARDO) 02 MARCH 1982</td>
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* Special categories of cited documents:
  * "A" document defining the general state of the art which is not considered to be of particular relevance
  * "E" earlier document but published on or after the international filing date
  * "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)
  * "O" document referring to an oral disclosure, use, exhibition or other means
  * "P" document published prior to the international filing date but later than the priority date claimed
  * "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
  * "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
  * "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.

* "A" document member of the same patent family

### IV. CERTIFICATION

Date of the Actual Completion of the International Search: 27 JUNE 1989

Date of Mailing of this International Search Report: 18 AUG 1989

International Searching Authority: ISA/US

Signature of Authorized Officer: A. L. CARRILLO

Form PCT/ISA/210 (second sheet) (Rev.11-87)
V. X: OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(1) (a) for the following reasons:

1. □ Claim numbers ______, because they relate to subject matter 12 not required to be searched by this Authority, namely:

2. □ Claim numbers ______, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out 13, specifically:

3. □ Claim numbers 6-9 and 14-18, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. XI: OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

I. Claims 1-9 drawn to a composition; Class 525, subclass 125.

II. Claims 10-18 drawn to a method of making a composition; Class 525, subclass 126.

III. Claim 19 drawn to an aqueous floor polish; Class 525, subclass 81+.

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. □ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

□ The additional search fees were accompanied by applicant's protest.

□ No protest accompanied the payment of additional search fees.