TEXTILE BACKING AGENT COMPRISING AN AQUEOUS DISPERSON OF A CARBOXYL-CONTAINING POLYMER AND THE REACTION PRODUCT OF EPICHLOROHYDRIN WITH AN ALKYLENE POLYAMINE

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The invention relates to coatings, sizes, and impregnants for textile materials and more particularly to compositions dispersed in aqueous media which are applied to, or on, fabrics or carpets, and similar materials to improve the wash resistance thereof.

The application of synthetic latexes to textile fabrics is well known. It is also known to prepare tufted rugs and carpets by mechanically punching (forcing) yarns and/or fibers through loosely-woven fabrics such as burlap and subsequently securing the yarns and fibers by applying a formulated natural or synthetic latex to the back of such articles followed by drying. The resistance of such fabricated articles to deterioration during laundering and washing-in-place is dependent to a large extent upon the water resistance of the adhesive backing supplied by the dried latex formulation. To provide the necessary water resistance, earlier prior art developed vulcanized adhesives using compounding formulations based on the known art of vulcanization of rubber. Such systems, however, are complex and relatively expensive. Furthermore, because of formulation exactness and detail, the vulcanization-type formulation is generally prepared by custom compounders and sold to the textile mills rather than being prepared at the carpet mill itself. The vulcanized systems have been replaced in many applications by non-vulcanized latexes commonly referred to as "self-curing" with which a degree of water resistance is obtained from carboxyl-containing latexes through cross-linking by the application of heat. The water resistance provided by the latter system is minimal for many applications and insufficient for other uses. It would be very desirable to have a composition which can be used readily at the textile mills (i.e., does not require extensive formulation on-the-job) which is sufficiently stable that it can be stored for long periods; e.g., three months; and which contributes water resistance equal to or better than that provided by vulcanized latexes, while retaining the simplicity of handling and economy provided by the "self-cure" carboxylated latexes.

An object of the present invention is to provide new compositions which are useful as coatings, sizes, and impregnants for textile fabrics. A further object is to provide a backsize for rugs and carpets. A still further object is to supply new coatings, sizes, and impregnants for textile fabrics which provide improved resistance to deterioration of the article from laundering or washing-in-place. Yet another object is to provide aqueous textile backsize compositions which are coagulably stable for extended periods.

These and other objects are obtained in an aqueous dispersion comprising a water-soluble amine-epichlorohydrin adduct, as hereinafter described, blended with a carboxyl-containing film-forming latex. Such blends are stable as aqueous dispersions for periods greater than about three months. The application of such compositions (including fillers and thickeners) to a tufted rug, for example, followed by drying and subsequent curing by heating provides a backing which is resistant to deterioration resulting from repetitive laundering or washing-in-place. The latex and the amine-epichlorohydrin adduct must be selected so that the blend thereof is stable as an aqueous dispersion during normal working periods. This dispersion stability is required during blending and application to the substrate. In general, dispersion stability for a minimum of two hours is necessary and for at least eight hours is preferable for operability. However, of greater advantage are products with longer term colloidal stability, such as three months or more, in order to facilitate storage prior to application to the textile fabric. Blends of the epichlorohydrin-amine adduct and the carboxyl-containing latexes according to the following description fulfill these and other requirements.

The amine component of the water-soluble amine-epichlorohydrin adduct is an alkylene polyamine of the formula

\[ \text{RNH}(-\text{CH}_2\text{)}_n\text{NH}_2 \]

wherein \( n \) is an integer from 2 to 3 and \( n \) is a cardinal number from 0 to 4.

Specific representative alkylene polyamines are ethylenediamine (i.e., an amine when \( n = 0 \) in the above formula), diethylenetriamine, triethylenetetramine, tetraethylenepentamime, pentethylenhexamine and dipropylenetriamine.

The components of the amine-epichlorohydrin adduct are used in such proportions that for each mole of primary amino groups, i.e., \(-\text{NH}_2\), of about 0.5 to about 1.0 moles of epichlorohydrin and for each mole of secondary amino groups, i.e.,

\[ \text{RNH}(-\text{CH}_2\text{)}_n\text{NH}_2 \]

there are from about 0.3 mole to about 0.8 mole of epichlorohydrin. While epichlorohydrin is the preferred epichlorohydrin, epibromohydrin may be used, if desired, with similar results. Thus, the halogen in the epibromohydrin has an atomic number of 17 or 35. The amine-epichlorohydrin adduct ordinarily is prepared by dissolving the epichlorohydrin in water then mixing the alkylene polyamine with the resulting solution using mild agitation. Control of the temperature of the solution from about 0° C to about 40° C and a low percent solids in the aqueous medium are conducive to formation of an adduct of a molecular weight range and viscosity which is advantageous in the practice of the invention. However, increased temperatures such as up to 85° C. or higher, may be used, as indicated by a subsequent example. A mineral acid such as hydrochloric acid may be added to stop, or "kill," the reaction to prevent the formation of an adduct having too high a viscosity.

The amine-epichlorohydrin adduct conveniently is prepared and used as an aqueous solution containing about 10 percent by weight of the adduct, calculated as the free base, although this is not a critical limitation, since compositions containing higher or lower proportions of adduct may be used so long as the inherent viscosity of the adduct is less than about 0.13 as measured at 25° C in a solution of 1 gram of the adduct per 100 ml of water containing 5 percent of hydrogen chloride. If water containing 5 percent of sodium chloride is used as the solvent, then the inherent viscosity should be less than about 0.13. Throughout this specification, by the term "calculated as the free base" is meant that any salt-forming ingredients associated with the adduct are not included in the weight of the adduct in the calculations.

The terms "amine-epichlorohydrin adduct," "epibromohydrin-amine adduct" and "adduct" wherever used in this specification refer to compositions of the foregoing description.
The latex which is used with the amine-epihalohydrin adduct as heretofore defined is characterized as being film-forming below about 100° C. and contains as an essential ingredient from about 0.5 percent to about 10 percent, preferably from about 1 percent to about 4 percent, by weight of monomers having a pendant carbonyl group, based on the weight of the polymer in the latex. Larger proportions of carbonyl-containing monomers, such as up to about 30 percent by weight, may be prepared and used but such materials require higher amounts of the amine-epihalohydrin adduct to achieve the requisite water resistance and undesirable stiffness may result. Thus, ordinarily such compositions are not preferred.

To prepare the latexes applicable to the practice of the invention at least two polymerizable, ethylidene unsaturated monomers, of the class of styrene and monomers copolymerizable with styrene, are copolymerized in an emulsion system to form a latex copolymer which is film-forming below 100° C. or which can be made film-forming at that temperature by the addition of solvents or plasticizers. At least one of the monomers polymerized to form a latex for use in the instant invention consists of those polymerizable, ethylidene unsaturated monomers which have pendant carbonyl groups, while the other contains only monomers which after polymerization can be converted to carbonyl groups. Such carbonyl-containing monomers are represented by the α,β-ethylenically unsaturated monocarboxylic acids, the α,β-ethylenically unsaturated dicarboxylic acids, and mixtures and salts thereof. Specific examples of such ethylidene unsaturated monomers having pendant carbonyl groups are acrylic acid, methacrylic acid, itaconic acid, fumaric acid, maleic acid, ethyl acid maleate, butyl acid maleate, salts of such acids, and the like. Mixtures of α monocarboxylic acid and a dicarboxylic acid, each having ethylenic unsaturation, often are used. Sometimes as many as three or more different α,β-ethylenically unsaturated carboxylic acids are combined in the recipe.

Among the ethylidene unsaturated monomers of the class of styrene and monomers copolymerizable with styrene are the monomers having carbonyl groups described above, the alkyl-aryl compounds (the styrene compounds), the derivatives of ethylidene unsaturated acids such as acrylic esters, acrylic nitriles, maleic esters, fumaric esters, and unsaturated alcohol esters, the unsaturated ketones, the conjugated diolenes, and other compounds containing one or more ethylenic linkages capable of participation in polymerization.

Specific examples of such ethylidene unsaturated compounds are styrene, α-methylstyrene, α-ethylstyrrene, ar-ethylstyrrene, α-ar-dimethylstyrrene, ar-ar-dimethylstyrrene, ar-butylstyrrene, vinylmethylnaphthalene, methylstyrrene, cyanostyrene, acetylacetylene, monochlorostyrene, dichlorostyrene and other halostyrenes, methyl methacrylate, ethyl acrylate, butyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, lauryl methacrylate, phenyl acrylate, acrylonitrile, methacrylonitrile, ethyl α-chloroacrylate, diethyl maleate, polyglycol maleate, vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene bromide, vinyl methyl ketone, methyl isopropenyl ketone, vinyl ethyl ether, 1,3-butadiene, isoprene and the like.

The optimum amount of the monomers, having carbonyl groups, which are copolymerized in the latex will vary somewhat according to the properties desired for the polymer to be used. The lower amount, in general, will be used where the pendant reactive carbonyl groups of the latex polymer are in relatively greater concentration on the surface of the particles rather than homogeneously scattered throughout the particles and where a minimum amount of cross-linking is desired.

The latexes are copolymerized in aqueous emulsion containing surface active agents, catalysts, modifiers, etc., and under conditions of time, temperature, pressure, agitation, etc., in accordance with well known principles of emulsion polymerization. However, because of the effects provided by the carbonyl-containing monomers, the kinds of constituents employed in the aqueous phase of the emulsion polymerization are selected to be compatible with such monomers. For example, only anionic or non-ionic emulsifiers ordinarily are used. Moreover, since the carbonylic substituents (particularly in the form) confer surface active properties to the monomer and to the resulting copolymer in the latex, the amount of conventional surface active agent can often be markedly reduced or even eliminated in the emulsion polymerization step. The latexes may be prepared by copolymerization of monomers selected as hereinafore described or there may be substituted for each latexes water dispersions of prepared polymers which have been modified, e.g., by grafting or by other means, to have pendant carbonyl groups or polymers which are hydrolyzable to give water dispersions of polymers having such carbonyl groups.

To the latex there is added the amine-epihalohydrin adduct in an amount to provide from about 0.1 part to about 5 parts, preferably from about 0.5 part to about 2 parts, of the adduct (calculated as the free base) per 100 parts of polymer solids in the latex. As suggested above, the ratio is based on the amount and proportion of carbonyl groups in the latex polymer. For example, when the latex polymer contains 1 part of copolymerized carbonyl-containing monomer per 100 parts total weight of polymer, then the amount of adduct usually used ranges from about 0.10 part to about 2 parts whereas the range is from about 0.10 part to about 5 parts of the adduct when the polymer contains 10 parts of acid, calculated as above.

The blend of a latex comprising a carbonyl-containing polymer and an amine-epihalohydrin adduct as heretofore described is required for the practice of this invention. However, the vulcanizing ingredients which ordinarily are required for the prior art materials which contain latexes are unnecessary. Calcium carbonate is the most commonly used filler but other mineral pigments such as titanium dioxide, mica, clay, lead carbonate, ochre, manganese silicate, lead chromate and other inorganic salts, e.g., sulfates and arsenates, may be used if desired as a portion of the filler. Such fillers may be used in amounts varying from about 75 parts, or lower, to about 600 parts per 100 parts of polymer solids in the latex of the composition. The blends comprising the carbonyl-containing latex and the epihalohydrin-amine adduct are applied to numerous textile fabrics with advantageous results. Such blends are applied by numerous types of apparatus, e.g., roll coaters, knife coaters and spray coaters. The composite material is then passed through an oven for removal of volatile materials, especially moisture, usually at a temperature of from about 200° F. to about 350° F., preferably from about 260° F. to about 325° F. Concurrently with the removal of the volatile materials in the oven, the heating which facilitates such removal also speeds the interaction of the carbonyl groups of the polymer, provided by the latex, with the reactive groups of the epihalohydrin-amine adduct so that the composition becomes cured or cross-linked. The compositions thus provide coatings, impregnants and backings for rubbers, rubbers and carpets, tufted rugs and carpets, flocked carpets, upholstery fabrics and non-woven fabrics. The fibers comprising such textile fabrics may be either natural or synthetic or mixtures thereof.

The advantageous water resistance of the products of this invention are illustrated by the wash resistance test.
WASH RESISTANCE TEST

The wash resistance test is carried out in a domestic oscillating-agitator automatic washer using water at 160° F. and 30 g. of a commercial built-detergent of the type customarily used in a home laundry. The carpet or rug sample is washed in the usual wash cycle for 15 minutes then subjected to the normal rinse and spin-dry cycle of the machine. The samples of the material are then examined for the visible effect resulting from such treatment and are rated in the following manner:

<table>
<thead>
<tr>
<th>Observable Effect</th>
<th>Numerical Rating</th>
<th>Verbal Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>No visible effect</td>
<td>1</td>
<td>Excellent</td>
</tr>
<tr>
<td>Very slight edge fraying</td>
<td>4</td>
<td>Good</td>
</tr>
<tr>
<td>Holds in body of material but tears on edges</td>
<td>7</td>
<td>Fair</td>
</tr>
<tr>
<td>No protection</td>
<td>10</td>
<td>Poor</td>
</tr>
</tbody>
</table>

To illustrate more fully the practice of this invention to those skilled in the art, the following examples are given, without any limitations being intended thereby. In the examples all parts and percentages are by weight unless otherwise specified.

Example 1

Into a 20-gallon reactor was placed 120 pounds of water then there was added thereto 2,542 grams (56 pounds) of ethylene diamine and the reactor was closed. The temperature of the resulting aqueous solution spontaneously rose from 23° C. to 28° C. while the pressure was maintained at slightly less than atmospheric. Over a period of about 10 minutes, 23 pounds of epichlorohydrin was then added while the temperature was controlled at 45° C. by cooling water circulating in the reactor jacket. Stirring in the reactor was continuous from the start of addition of materials until 30 minutes after the last of the epichlorohydrin was added. The resulting product, having 15.2 percent—calculated as the free base—of an adduct, was filtered through glass wool. The ethylenediamine-epichlorohydrin adduct thus obtained had an inherent viscosity of 0.075 in hydrochloric acid when measured at 25° C. in the concentrations described above. A 7.6-gram portion of the solution of ethylenediamine-epichlorohydrin adduct (1.0 gram, calculated as the free base) was mixed using mild agitation with 200 parts of a latex, at 50 percent solids concentration, comprising a copolymer of 42 percent of styrene, 56 percent of 1,3-butadiene, 1.75 percent of acryllic acid and 0.25 percent of fumaric acid, based on the copolymer weight. Then 300 parts of calcium carbonate, sufficient sodium polyacrylate thickener to adjust the viscosity to about 4000 centipoises (10 parts of a 10-percent solution, or 1 part of solids), and sufficient water to adjust the solids concentration of the mixture to 70 percent were blended therein. The resulting formulation in the proportion of 20 ounces dry weight per square yard was applied to a loop-pile tufted wool carpet prepared from 30 ounces of wool yarn tufted into 10-ounce burlap (per square yard) and cured for 12 minutes at 300° F. in a forced-air oven.

The back-sized tufted carpet thus obtained was checked for wash resistance according to the procedure hereinbefore described and a rating of excellent (1) was obtained.

Example 2

An ethylenediamine-epichlorohydrin adduct was prepared as described in Example 1 except that no cooling water was used and the jacket was maintained at the temperature of the reactants so that the temperature was allowed to rise as determined by the exothermic nature of the reaction. The highest temperature reached was about 85° C. The inherent viscosity was 0.095 in aqueous sodium chloride and 0.075 in hydrochloric acid when measured at 25° C. in the concentrations described above. A blend of the ethylenediamine-epichlorohydrin adduct with another portion of the same latex as in Example 1 was prepared using the same proportions. Back-sized carpet samples prepared therefrom and tested for wash resistance as in Example 1 also achieved a rating of excellent (1).

Example 3

Ethylenediamine-epichlorohydrin adducts were prepared by the procedure of Example 1 except differing amounts of epichlorohydrin were used per mole of ethylenediamine. Blends were prepared with other portions of the latex of Example 1 in the proportion of one part of the adduct per 100 parts of solids in the latex. Back-sized carpet samples were prepared and tested in the same manner as described in Example 1. The results are shown in Table I.

**Table I**

<table>
<thead>
<tr>
<th>Moles of epichlorohydrin per moles of ethylenediamine:</th>
<th>Wash resistance rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Poor (10)</td>
</tr>
<tr>
<td>2</td>
<td>Fair (7)</td>
</tr>
<tr>
<td>3</td>
<td>Excellent (1)</td>
</tr>
<tr>
<td>4</td>
<td>Fair (7).^1^</td>
</tr>
</tbody>
</table>

^1 Also tends to cause instability in the aqueous dispersion.

Example 4

Other amine-epichlorohydrin adducts were prepared in the manner of Example 1 but using different amines. Epichlorohydrin was used in the proportion of 1 mole of epichlorohydrin per gram-atomic weight of nitrogen in the amine. Such adducts were prepared from ethylenediamine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. Each of these adducts was blended with a latex comprising a copolymer of 39.4 percent of styrene, 58.2 percent of butadiene, 12 percent of fumaric acid and 1.2 percent of acrylic acid in the portion of 1 part of the adduct to 100 parts of copolymer, solids basis, to form aqueous dispersions which were stable for at least 90 days at temperatures between about 32° F. and about 100° F. When back-sized tufted carpet samples were prepared from the resulting aqueous dispersions as in Example 1 and then tested for wash resistance, they showed effective cure for wash stability, i.e., they had a rating of from 1 to 4.

The attempted preparation of an adduct with each of diethylenetriamine, ethylenediamine and dipropylentetramine, but substituting glycidol for epichlorohydrin, was carried out in the same manner as in preparing the adducts of Example 4, using the same proportions, i.e., one mole of glycidol per gram-atomic weight of nitrogen in the amine. The resulting compositions, not examples of this invention, were blended in the same proportions with the same latex as described for Example 4; back-sized carpet samples, prepared therefrom in the manner previously described, attained a rating of from 7 to 10 in the wash resistance test. In other tests using the same amines but differing ratios of glycidol, as the proportion of glycidol was progressively increased the wash resistance of carpet samples prepared therefrom progressively decreased.

Example 5

Blends of the ethylenediamine-epichlorohydrin adduct of Example 4 and the latex of Example 1 were prepared in the manner of Example 1 but using different proportions of adduct and latex. Back-sized carpet samples were prepared and tested also in the same manner as in Example 1. The results are shown in Table II.
When epichlorohydrin is substituted on an equimolar basis for the epichlorohydrin in the adducts of the above examples, similar advantageous results are obtained. Likewise, similarly advantageous results are obtained when there are substituted for the latexes in the above examples of this invention other carboxyl-containing latexes such as latexes comprising copolymers of

(a) styrene, 1,3-butadiene and acrylic acid

(b) ethyl acrylate, n-butyl acrylate and acrylic acid

(c) styrene, 1,3-butadiene, acrylic acid and methacrylic acid

d) ethyl acrylate, methyl methacrylate and acrylic acid

e) styrene, n-butyl acrylate, acrylonitrile and acrylic acid

(f) other latexes which are film-forming below about 100° C. and which comprise polymers containing carboxyl groups wherein the carboxyl-containing component of the copolymer is present in an amount from about 0.5 to about 10 percent by weight calculated as acrylic acid, based on the total copolymer weight.

In further comparisons with the products of this invention the epichlorohydrin-amine adducts of Example 1, when blended with conventional commercial latexes (such as Dow Latex 51XK) containing copolymers of styrene and 1,3-butadiene but having no carboxyl-containing monomers copolymerized therein, cause such instability of the latex that a homogeneous blend cannot be prepared. By adding considerable extra surfactant, a minimum amount of stability barely sufficient to allow mixing of the latex and adduct and immediate application to a tufted-carpet is obtained. However, such coatings show no appreciable improvement over similar coatings prepared from the same latex but having no epichlorohydrin-amine adduct blended therewith.

What is claimed is:

1. An aqueous dispersion comprising a stable blend of

A. a latex comprising a copolymer of at least 2 polymethylenes of ethylenically unsaturated monomers selected from the group consisting of vinyl aromatic hydrocarbons, acrylic esters, acrylic nitriles, maleic and fumaric esters, unsaturated alcohol esters, unsaturated ketones, and conjugated dienes, and from about 0.5 percent to about 10 percent by weight of at least one additional monomer containing a carboxyl group and

B. from about 0.1 part to about 5 parts, for each 100 parts of copolymer in the latex, of a water-soluble adduct of an epichlorohydrin and an alkylene polycrylamine of the formula

\[ \text{H}_2\text{N}-(\text{CH}_2\text{CH}_2\text{NH})_n-\text{(CH}_2\text{CH}_2\text{)}_2-\text{NH}_2 \]

wherein \( x \) is an integer from 2 to 3 and \( n \) is a cardinal number from 0 to 4, said adduct having for each mole of primary amino groups in the alkylene polycrylamine from about 0.75 mole to about 1.8 moles of epichlorohydrin and for each mole of secondary amino groups in the alkylene polycrylamine from about 0.3 mole to about 0.8 mole of epichlorohydrin, and said adduct having an inherent viscosity of less than about 0.1 as determined at 25° C. in a solution of 1 gram of said adduct per 100 milliliters of water containing 5 percent by weight of hydrogen chloride.

2. The aqueous dispersion of claim 1 in which the ethylenically unsaturated monomers comprise from about 1 percent to about 4 percent by weight of monomer containing a carboxyl group.

3. The aqueous dispersion of claim 1 in which the monomers containing a carboxyl group comprise acrylic acid.

4. The aqueous dispersion of claim 1 in which the monomers containing a carboxyl group comprise fumaric acid.

5. The aqueous dispersion of claim 1 in which the ethylenically unsaturated monomers comprise styrene.

6. The aqueous dispersion of claim 1 in which the ethylenically unsaturated monomers comprise 1,3-butadiene.

7. The aqueous dispersion of claim 1 in which the ethylenically unsaturated monomers comprise a mixture of styrene and 1,3-butadiene.

8. The aqueous dispersion of claim 1 in which the monomers containing a carboxyl group comprise a mixture of a monocarboxylic acid and a dicarboxylic acid, each of said acids having \( \alpha, \beta \)-ethylenic unsaturation.

9. The aqueous dispersion of claim 1 in which the epichlorohydrin is epichlorohydrin.

10. A process of treating a textile comprising the steps of:

A. coating a textile fabric with an aqueous composition comprising a stable blend of

(1) a latex of a carboxyl-containing polymer and

(2) from about 0.1 part to about 5 parts, for each 100 parts of carboxyl-containing polymer in the latex of a water-soluble adduct of an epichlorohydrin and an alkylene polycrylamine having the formula

\[ \text{H}_2\text{N}-(\text{CH}_2\text{CH}_2\text{NH})_n-\text{(CH}_2\text{CH}_2\text{)}_2-\text{NH}_2 \]

wherein \( x \) is an integer from 2 to 3 and \( n \) is a cardinal number from 0 to 4, said adduct having for each mole of primary amino groups in the alkylene polycrylamine from about 0.75 mole to about 1.8 moles of epichlorohydrin and for each mole of secondary amino groups in the alkylene polycrylamine from about 0.3 mole to about 0.8 mole of epichlorohydrin, and said latex comprising a copolymer of at least two polymethylenes of ethylenically unsaturated monomers selected from the group consisting of vinyl aromatic hydrocarbons, acrylic esters, acrylic nitriles, maleic and fumaric esters, unsaturated alcohol esters, unsaturated ketones, and conjugated dienes, and from about 0.5 to about 10 percent by weight of at least one additional monomer containing a carboxyl group.

11. The process of claim 10 in which the ethylenically unsaturated monomers comprise from about 1 percent to about 4 percent by weight of monomers containing a carboxyl group.

12. The process of claim 10 in which the monomers containing a carboxyl group comprise acrylic acid.

13. The process of claim 10 in which the monomers containing a carboxyl group comprise fumaric acid.

14. The process of claim 10 in which the monomers containing a carboxyl group comprise a mixture of a monocarboxylic acid and a dicarboxylic acid, each of said acids having \( \alpha, \beta \)-ethylenic unsaturation.

15. The process of claim 10 in which the ethylenically unsaturated monomers comprise styrene.

16. The process of claim 10 in which the ethylenically unsaturated monomers comprise styrene and 1,3-butadiene.

17. The process of claim 10 in which the ethylenically unsaturated monomers comprise a mixture of styrene and 1,3-butadiene.

18. The process of claim 10 in which the epichlorohydrin is epichlorohydrin.

19. A wash-resistant treated textile comprising a textile fabric having an adherent coating comprising an interaction product of a carboxyl-containing polymer and from about 0.1 part to about 5 parts, for each 100 parts of
carboxyl-containing polymer, of a water-soluble adduct
of an epihalohydrin and an alkylene polyamine of the
formula

\[ H_2N-[(CH_2)_xNH]_n-(CH_2)_x-NH_2 \]

wherein \( x \) is an integer from 2 to 3 and \( n \) is a cardinal
number from 0 to 4, said carboxyl-containing polymer
being a copolymer of at least 2 polymerizable ethylene-
ically unsaturated monomers selected from the groups
consisting of vinyl aromatic hydrocarbons, acrylic esters,
acrylic nitriles, maleic and fumaric esters, unsaturated al-
cohol esters, unsaturated ketones, and conjugated diole-
fines, and from about 0.5 percent to about 10 percent by
weight of at least one additional monomer containing a
carboxyl group, said adduct having for each mole of pri-
mary amino groups in the alkylene polyamine from about
0.75 mole to about 1.8 moles of epihalohydrin and for
each mole of secondary amino groups in the alkylene
polyamine from about 0.3 mole to about 0.8 mole of epih-
halohydrin, and said adduct having an inherent viscosity
of less than about 0.1 as determined at 25°C in a solu-
tion of 1 gram of said adduct per 100 milliliters of water
containing 5 percent by weight of hydrogen chloride.

20. The wash-resistant treated textile of claim 19 in
which the textile fabric is tufted.

21. The wash-resistant treated textile of claim 19 in
which the textile fabric is a carpet.

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