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WATER REPELLENT FABRICS AND COMPOSITION AND PROCESS FOR MAKING SAME

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1

The present invention relates to new materials which produce water-repellent textiles when deposited thereon and to the process for the preparation of such textiles. More particularly, this invention relates to compositions which, when deposited on textiles and heated thereon at an elevated temperature form a permanent water-repellent finish of soft feel.

It has been found that linear polymeric polycarboxylic acids (such as a copolymer of styrene and maleic anhydride) and a relatively non-volatile aliphatic primary amine such as stearylamine may be converted into coatings which show a remarkable resistance to water, aqueous soap solution, and dry-cleaning naphthas. Also, these reaction products are compatible with waxes, which further increases the water repellency of coated textiles and in addition imparts a soft feel to the treated textile.

In addition, it has been found that water-soluble salts of the heretofore mentioned polycarboxylic acids (for example, such salts as from ammonia, picoline, pyridine, vinyl pyridine and the like), act as dispersing agents in the formulation of stable dispersions or emulsions of long-chain amines and natural or synthetic waxes.

It is therefore apparent that the primary object of the present invention is to provide a water-dispersible composition containing an alkaline salt of an acidic polymer such as a styrene-maleic copolymer, a long-chain aliphatic amine such as stearylamine, and an added wax (natural or synthetic) which, when applied to cloth, the impregnated cloth dried, and heated at elevated temperatures, imparts a suitable water-repellency to the cloth.

Surprisingly, it has been found that the materials of the present invention impart to textiles a water-repellent finish having extraordinary durability. This effect is not predictable from the nature of the components of the composition and it is therefore thought that additional complex reactions occur during heating to give this surprising durability to the finish.

According to a preferred process of the present invention, a solution of a long-chain amine such as stearlyamine and a wax such as candelilla wax in a solvent such as xylol is heated to about 60°–100° C. A neutral salt of styrene-maleic (either anhydrous or in the form of an aqueous solution) is then added while agitating and cooling to room temperature. A uniform, soft paste containing, preferably, 40% to 60% active material is thus secured, which readily emulsifies in hot water (70°–90° C.) to form a homogenous dispersion of emulsion which is stable. Dispersions containing from 1% to 10% active material, when applied to cloth, dried, and baked, impart excellent water-repellency and soft feel even after subjecting the treated cloth to repeated washings and dry cleanings. While it has been found that baking temperatures of 160° C. are preferred, baking conditions covering a temperature range of 100°–200° C. over a period of 1 to 60 minutes are suitable. The cloth is preferably a cellulosic fabric.

2

The present invention is concerned with the use of a linear polymeric polycarboxylic acid as a primary constitutent of the herein-described water-repellent materials, since on baking it combines with the long-chain amine and the fabric to form water-resistant products and, furthermore, in the form of the ammonium salt it serves as a dispersing medium for the long-chain amines and waxes, thus giving water-dispersible products which are readily and cheaply applied to the cloth. The linear polymeric polycarboxylic acids used herein consists of a linear carbon atom chain having carboxyl groups along the length thereof. They are characterized by the formation of water-soluble salts which act as emulsifying agents in aqueous solution for waxes and long-chain primary amines. Illustrations of such acids suitable for use herein are polyacrylic acid, polymethacrylic acid, copolymers of alpha-beta ethylenically unsaturated monocarboxylic or dicarboxylic acids with polymerizable compounds containing a single unsubstituted methylene group joined directly to a carbon atom through a double bond, and the like. More particularly, the present invention is concerned with the copolymers of styrene and maleic anhydride as the linear polymeric polycarboxylic acid. Methods described in the literature teach the practice of heating styrene and maleic anhydride in the presence of small percentages of benzoyl peroxide to form a copolymer soluble in dioxan, acetone and the like. Proportions of 1 mole of maleic anhydride to 2 moles of styrene are preferably employed although as high as 4 moles of styrene to 1 mole of maleic anhydride and as little as 1 mole of styrene to 1 mole of maleic anhydride have been found to be applicable. While copolymers of styrene and maleic anhydride are emphasized, it is apparent that fumaric acid, itaconic anhydride, citraconic anhydride, chloromaleic anhydride, acrylonitrile, acrylic acid and its esters, methacrylic acid and its esters, and the like may be also employed. Hydrolyzed polymers of acrylonitrile, acrylic acid esters, meth-

acrylic acid esters, and the like have been employed in place of the styrene-maleic copolymers.

As has been previously stated, water-soluble salt of the copolymer is employed in the process of the present invention. While a readily volatile base such as ammonia has been specifically mentioned and is to be preferred since it is most readily removed under the baking conditions employed, it is also apparent that the neutral salts of less volatile bases such as ethylene diamine, picoline, pyridine, vinyl pyridine, diethylamine, dimethylamine and the like may be also employed.

As the long-chain aliphatic amine component of the products of the present invention, stearylamine has been found to be admirably suitable. However, laurylamine, myristylamine, palmitylamine, arachidylamine, tallow amine, and the like may be employed. It is also apparent that reaction products of long-chain aliphatic saturated monocarboxylic acids and mono or polyalkylene polyamines, such as the reaction product of equal moles of ethylene diamine and stearic acid which contains a long-chain hydrocarbon radical and a primary amine group may also be employed as the long-chain amine. It will be apparent that numerous modifications are possible and should be considered within the scope of the present invention. The long-chain hydrocarbon radical preferably contains from 10 to 22 carbon atoms.

The amount of long-chain amine varies from less than 1 to not more than 2 moles (say, from .3 to 1.9 moles) per mole of dicarboxylic acid in a copolymer such as styrene-maleic or, in general, from .15 to about .95 mole per carboxyl group of the linear polymeric polycarboxylic acid. Apparently during heating of the fabric (which carries a dry deposit from the treating emulsion), the volatile base of the polycarboxylate salt is eliminated and a reaction occurs in which both the primary amine and the cellulose of the fabric react with the polymeric polycarboxylic acid, the primary amine by amide or imide formation and the cellulose by superficial esterification. The wax, which is uniformly distributed in the applied composition, acts as a plasticizer for the finish and imparts a soft feel to the cloth.

Numerous natural waxes such as candelilla wax, carnauba wax, beeswax, paraffin microcrystalline wax, and the like may be employed. Also such synthetic waxes as glyceryl tristearate, or glyceryl stearate modified with polycarboxylic acids may be employed. Amino alcohols, such as trihydroxy-methyl aminomethane, may also be used to form the above-mentioned synthetic waxes. The proportion of wax employed in the preparation of the products of the present invention is not limiting, but it is preferred to employ at least 1 part and as much as 4 parts of wax for 1 part of styrene-maleic and long-chain aliphatic amine combined, since in addition to good water repellency, a soft feel is also imparted to the treated textiles.

It has been heretofore mentioned that from 1% to 10% of the reaction products of the present invention are sufficient to impart a durable water-repellent finish to textiles. In the preparation of aqueous dispersions, it has been found that the use of approximately 1% aqueous 28% ammonia and up to 1% (based upon the dispersion) of an ammonium salt of an inorganic acid assists in the formation of stable dispersions. Among the ammonium salts of inorganic acids most applicable are ammonium dihydrogen phosphate, di-ammonium hydrogen phosphate, triammonium phosphate, ammonium hydrogen sulphate, diammonium sulphate and the like.

Therefore, the compositions of the present invention for producing water-repellent finishes on textiles, by impregnating the textiles therewith, removing water by drying and finally heating an elevated temperature of from 100° to 200° C., consist of emulsions which contain, as the dispersing phase, an aqueous solution of a salt of a volatile base and a linear polymeric polycarboxylic acid (such as the ammonium salt of a styrene-maleic copolymer) and, as the disperse phase, a mixture of a wax and a relatively non-volatile long-chain aliphatic primary amine.

The following examples are given by way of illustration only and should not be considered to be limiting. All proportions are in parts by weight.

Example 1

30 parts of a styrene-maleic copolymer (formed from 2 moles of styrene and 1 mole of maleic anhydride), 50 parts of 28% aqueous ammonia solution, and 180 parts of water are warmed together to form a clear solution.

150 parts of candelilla wax and 50 parts of stearylamine are melted together at 90° C. The aqueous solution of the ammonium salt of the styrene-maleic copolymer is added with rapid agitation. A smooth dispersible paste is secured which contains 50% active ingredients.

10 parts of the above paste is agitated in 190 parts of water at 80° C. to form a stable emulsion. A piece of O. D. poplin is impregnated, dried, and baked for 10 minutes at 145°–150° C. The treated textile possesses a spray rating of 100, after dry cleaning 70, and after washing 80.

Example 2

30.6 parts of stearylamine, 51.8 parts of candelilla wax, and 103 parts of microcrystalline white paraffin wax (M. P. 190° F.–195° F.) are warmed with 154.8 parts of xylene. At 60° C.–70° C. 46.8 parts of dried ammonium salt of a styrene-maleic copolymer (formed from 2 moles of styrene to 1 mole of maleic anhydride) are added with agitation to form a smooth, homogeneous paste having 60% active ingredients.

24 parts of the above paste are added to a solution at 90° C. of 1.2 parts of ammonium dihydrogen phosphate, 4 parts of 28% aqueous ammonia, and 370.8 parts of water to form a stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked for 15 minutes at 160° C. The treated textile possessed an initial spray rating of 100, after dry cleaning 90, and after washing 80.

Example 3

2.5 parts of stearylamine and 6 parts of xylene are warmed together to form a clear solution. 3.5 parts of the dried ammonia salt of a styrene-maleic anhydride copolymer (formed from 2 moles of styrene to 1 mole of maleic anhydride) are added with agitation to form a smooth, homogeneous paste having 50% solids. While rapidly agitating, a solution having 2 parts of ammonium dihydrogen phosphate in 112 parts of hot water (80° C.) is added to form a homogeneous, stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked for 15 minutes at 160° C. The treated textile possessed an initial spray rating of 90, and 60 after dry cleaning.

Also, the treated textile possessed a harsh hand. No wax is used in this example.

Example 4

2.1 parts of stearylamine, 3.4 parts of candelilla wax, 6.7 parts of microcrystalline yellow paraffin wax (M. P. 190° F.–195° F.), and 9.4 parts of xylol are warmed to 60° C. to form a clear solution. While cooling, 2.95 parts of the pyridine salt of styrene-maleic anhydride copolymer (formed from 2 moles of styrene and 1 mole of maleic anhydride) are added with agitation to form a homogeneous paste.

15 parts of the above paste, 0.54 part of ammonium dihydrogen phosphate and 185 parts of water at 90° C. are agitated to form a stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked at 160° C. for 15 minutes. The treated textile possesses an initial spray rating of 90 and after dry cleaning 70.

Example 5

2.1 parts of stearylamine, 3.4 parts of candelilla wax, and 6.7 parts of microcrystalline yellow paraffin wax (M. P. 190° F.–195° F.) are warmed to 60° C. in 9.4 parts of xylene to form a clear solution. While cooling, 2.95 parts of the α-picoline salt of styrene-maleic anhydride copolymer (formed from 2 moles of styrene and 1 mole of maleic anhydride) are added with stirring to form a homogeneous paste.

15 parts of the above paste, 0.54 part of ammonium dihydrogen phosphate and 185 parts of water at 90° C. are agitated together to form a homogeneous dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked at 160° C. for 15 minutes. The treated textile possesses an initial spray rating of 80, and after dry cleaning 70.

Example 6

3.06 parts of stearylamine, 5.18 parts of candelilla wax, and 10.3 parts of microcrystalline white paraffin wax (M. P. 190°–195° F.) are warmed with 15.48 parts of xylene. At 60°–70° C. 4.68 parts of dried ammonium salt of a methyl methacrylate-maleic anhydride copolymer (formed from 1.5 moles of methyl methacrylate and 1 mole of maleic anhydride) are added with agitation to form a smooth, homogeneous paste having 60% active material.

24 parts of the above paste are added to a solution at 90° C. of 1.2 parts of ammonium dihydrogen phosphate, 4 parts of 28% aqueous ammonia, and 370.8 parts of water to form a stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked for 15 minutes at 160° C. The treated textile possesses an initial spray rating of 100, after dry cleaning 70, and after washing 80.

Example 7

2.68 parts of an amine (prepared by heating 20.6 parts of diethylene triamine (1 mole) and 56.4 parts of stearic acid (1 mole) together to 220° C.–250° C. for 6 hours while removing 3.6 parts of water) of formula

$$NH_2CH_2CH_2NHCH_2CH_2NHCOC_{17}H_{35}$$

4.17 parts of candelilla wax, 8.35 parts of microcrystalline white paraffin wax (M. P. 190°–195° F.), and 12.52 parts of xylene are warmed to 60° C. to form a clear solution. 3.58 parts of the ammonium salt of a styrene-maleic anhydride copolymer (from 2 moles of styrene and 1 mole of maleic anhydride) are added while agitating

and cooling to form a homogeneous, water-dispersible paste having 60% active ingredients.

18 parts of the above paste is dispersed in an aqueous solution at 90° C. having 1.2 parts of ammonium dihydrogen phosphate, 6 parts of concentrated ammonia and 274.8 parts of water. A piece of O. D. poplin is impregnated, dried, and baked at 150° C. for 10 minutes. The treated textile possesses an initial spray rating of 90 and after dry cleaning 70.

Example 8

The preparation of Example 7 is repeated using 3.85 parts of the amine. The textile treated in the same manner has an initial spray rating of 80 and after dry cleaning 70.

Example 9

2.5 parts of stearylamine and 6.0 parts of carnauba wax are warmed with 8 parts of xylene to form a clear solution. 3.5 parts of the dried ammonium salt of styrene-maleic anhydride copolymer (formed from 1 mole of styrene to 1 mole of maleic anhydride) are added with agitation to form a smooth, homogeneous paste having 60% active ingredients. While rapidly agitating, a solution having 2 parts of ammonium dihydrogen phosphate in 378 parts of hot water (80° C.) is added to form a homogeneous, stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked for 15 minutes at 160° C. The treated textile possesses an initial spray rating of 90 and 60 after dry cleaning.

Example 10

2.1 parts of tallow amine, 3.4 parts of candelilla wax, 6.7 parts of micro-crystalline white paraffin wax (M. P. 170°–175° C.), and 9.4 parts of xylol are warmed together to 60° C. to form a clear solution. While cooling, 2.95 parts of the ammonia salt of styrene-maleic copolymer (2 moles of styrene and 1 mole of maleic anhydride) are added with agitation to form a homogeneous paste.

15 parts of the above paste are agitated in a solution of 0.6 part of ammonium dihydrogen phosphate, 2.4 parts of 28% aqueous ammonia solution, and 185 parts of water at 90° C. to form a stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked at 160° C. for 15 minutes. The treated textile possesses an initial spray rating of 90 and after dry cleaning 60.

Example 11

2.1 parts of stearylamine, 10.1 parts of candelilla wax, and 9.4 parts of xylol are warmed together to 60° C. to form a clear solution. 5 parts of the ammonium salt of polyacrylic acid (prepared by the hydrolysis of an emulsion of polyethyl acrylate which is acidified, dissolved in aqueous ammonia, and the aqueous solution evaporated to dryness to secure the ammonium salt) are added with agitation to form a homogeneous paste. 15 parts of the above paste are agitated in a solution of 24 parts of 28% aqueous ammonia solution and 185 parts of water at 90° C. to form a stable dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked at 160° C. for 15 minutes. The treated textile possesses an initial spray rating of 80 and after dry cleaning 60.

Example 12

4 parts of a copolymer of styrene and maleic anhydride (containing 2 moles of styrene and

1 mole of maleic anhydride), 6 parts of 28% aqueous ammonia, and 20 parts of water are warmed together to form a clear syrupy solution.

6 parts of stearylamine, and 15 parts of a wax consisting of a modified alkyd resin (having an acid number of 19.3 and prepared from 32 parts of pentaerythritol, 169.2 parts of stearic acid, and 14.8 parts of phthalic anhydride) are warmed together to form a clear wax melt. The above aqueous solution of the ammonium salt of styrene maleic anhydride copolymer is added with rapid agitation to form a homogeneous paste. 193 parts of water at 80° C. are now added and agitation continued to form a homogeneous dispersion. A piece of O. D. poplin cloth is impregnated, dried, and baked at 150° C. for 15 minutes. The treated textile possesses an initial spray rating of 90 and after dry cleaning 60.

Example 13

18 parts of a synthetic wax (prepared by the distillation of 26.8 parts of a 50% solution of a methylolmelamine resin in methanol, 84.9 parts of stearamide and 100 parts of xylol together until the resulting wax solution contained 55.1% wax solids) are mixed together with 2 parts of stearylamine, 6 parts of xylol, and 4 parts of the ammonium salt of a styrene-maleic anhydride copolymer (having 2 moles of styrene to 1 mole of maleic anhydride) to form a homogeneous paste. 290 parts of water at 90° C. are now added and agitation continued until a homogeneous dispersion results. A piece of O. D. poplin cloth is impregnated, dried, and baked at 150°–160° C. for 15 minutes. The treated textile has an initial spray rating of 90 and after dry cleaning 80.

Example 14

4.5 parts of a styrene-maleic copolymer (containing 3 moles of styrene and one mole of maleic anhydride), 5.0 parts of 28% aqueous ammonia solution, and 20 parts of water are warmed together to form a solution.

15 parts of candelilla wax and 5 parts of stearylamine are melted together to 90° C. The aqueous solution of the ammonium salt of the styrene maleic copolymer is added with rapid agitation. A smooth, dispersible paste is secured having 50% active ingredients.

10 parts of the above paste is agitated in 190 parts of water at 80° C. to form a stable dispersion. A piece of O. D. poplin is impregnated, dried, and baked for 10 minutes at 145°–150° C. The treated textile has a slightly harsher feel than that from Example 1. It has an initial spray rating of 90 and after dry cleaning 70.

Example 15

5.0 parts of a styrene-maleic copolymer (formed from 1 mole of styrene and 1 mole of maleic anhydride), 5 parts of 28% aqueous ammonia solution, and 15 parts of water are warmed together to form a clear solution.

15 parts of candelilla wax and 5 parts of stearylamine are melted together to 90° C. The aqueous solution of the ammonium salt of the styrene maleic copolymer is added with rapid agitation. A smooth paste is obtained having 55% active ingredients.

10 parts of the above paste is agitated in 190 parts of water at 80° C. to form a stable dispersion. A piece of O. D. poplin is impregnated, dried, and baked for 10 minutes at 150° C. The treated textile possesses a soft hand. It has an initial spray rating of 90 and after dry cleaning 60.

Example 16

8.4 parts of stearylamine, 12.2 parts of candelilla wax, 18.2 parts of microcrystalline white wax (M. P. 190°–195° F.), and 16.7 parts of xylene are warmed to 60° C. to form a clear solution.

11.3 parts of the ammonium salt of a styrene-maleic anhydride copolymer (containing 2 moles of styrene and 1 mole of maleic anhydride) are mixed together to form a thin slurry.

The above wax-xylene solution is then added while stirring and cooling to form a homogeneous, water-dispersible paste having 60% active ingredients.

40 parts of the above paste are dispersed in an aqueous solution at 90° C. of 2 parts of ammonium dihydrogen phosphate, 4 parts of 28% aqueous ammonia solution and 354 parts of water. A piece of O. D. poplin cloth is impregnated, dried, and baked at 160° C. for 3 minutes. The treated textile possesses an initial spray rating of 100 and a hydrostatic resistance of 52 cm.

Thus it may be seen that the water repellent products of the present invention in addition to giving high spray ratings, also possess the unique property of imparting a very high hydrostatic resistance to the treated textiles.

We claim:

1. A composition particularly adapted for rendering fabrics water-repellent when said fabrics are impregnated therewith and heated, comprising an emulsion containing, as the dispersing phase, an aqueous solution of a salt of a volatile base and a linear polymeric polycarboxylic acid and, as the disperse phase, a wax and an aliphatic hydrocarbon primary amine containing from 10 to 22 carbon atoms, the amount of amine being from 0.15 to 0.95 mole per carboxyl group and the amount of wax being from 1 to 4 parts per 1 part of the polymeric acid and the amine combined.

2. A composition particularly adapted for rendering fabrics water-repellent when said fabrics are impregnated therewith and heated, comprising an emulsion containing, as the dispersing phase, an aqueous solution of a salt of a volatile base and a linear polymeric polycarboxylic acid consisting of a copolymer of an alpha-beta ethylenic dicarboxylic acid and a polymerizable compound containing a single unsubstituted methylene group joined directly to a carbon atom through a double bond, and, as the disperse phase, a wax and an aliphatic hydrocarbon primary amine containing from 10 to 22 carbon atoms, the amount of amine being from 0.15 to 0.95 mole per carboxyl group and the amount of wax being from 1 to 4 parts per 1 part of the polymeric acid and the amine combined.

3. A composition particularly adapted for rendering fabrics water-repellent when said fabrics are impregnated therewith and heated, comprising an emulsion containing, as the dispersing phase, an aqueous solution of a salt of a volatile base and a copolymer of maleic anhydride and styrene, and, as the disperse phase, a wax and an aliphatic hydrocarbon primary amine containing from 10 to 22 carbon atoms, the amount of amine being from 0.15 to 0.95 mole per carboxyl group and the amount of wax being from 1 to 4 parts per 1 part of the maleic anhydride-styrene copolymer and amine combined.

4. A composition particularly adapted for rendering fabrics water-repellent when said fabrics

are impregnated therewith and heated, comprising an emulsion containing, as the dispersing phase an aqueous solution of the ammonium salt of a copolymer of maleic anhydride and styrene, and, as the disperse phase, a wax and an aliphatic hydrocarbon primary amine containing from 10 to 22 carbon atoms, the amount of amine being from 0.15 to 0.95 mole per carboxyl group and the amount of wax being from 1 to 4 parts per 1 part of the maleic anhydride-styrene copolymer and amine combined.

5. A composition particularly adapted for rendering fabrics water-repellent when said fabrics are impregnated therewith and heated, comprising an emulsion containing, as the dispersing phase an aqueous solution of the ammonium salt of a copolymer of maleic anhydride and styrene and, as the disperse phase, candelilla wax and stearyl amine, the amount of amine being from 0.15 to 0.95 mole per carboxyl group and the amount of wax being from 1 to 4 parts per 1 part of the maleic anhydride-styrene copolymer and amine combined.

6. A fabric rendered water-repellent by impregnating the fabric with the composition of claim 1, removing water from the impregnated fabric, and heating same at an elevated temperature of from 100° to 200° C.

7. A fabric rendered water-repellent by impregnating the fabric with the composition of claim 2, removing water from the impregnated

fabric, and heating same at an elevated temperature of from 100° to 200° C.

8. A fabric rendered water-repellent by impregnating the fabric with the composition of claim 3, removing water from the impregnated fabric, and heating same at an elevated temperature of from 100° to 200° C.

9. A fabric rendered water-repellent by impregnating the fabric with the composition of claim 4, removing water from the impregnated fabric, and heating same at an elevated temperature of from 100° to 200° C.

10. A fabric rendered water-repellent by impregnating the fabric with the composition of claim 5, removing water from the impregnated fabric, and heating same at an elevated temperature of from 100° to 200° C.

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