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TREATMENT OF TEXTILE MATERIALS

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This invention relates to improved textile finishing materials, and methods of treating yarns and fabrics therewith.

It is common practice to treat yarns and fabrics with starch solutions in order to impart a relatively stiffened finish thereto. Starched fabrics however lose their stiffened character and appearance after a single washing, and also tend to dust out. Furthermore, fabrics treated with starch finishes will not retain the stiffened finish after mild washings.

It is the primary object of the present invention to provide a substantially permanent stiffened finish which cannot be appreciably removed by ordinary washing operations and is substantially free of dusting.

Still further objects and advantages of the invention will appear from the following description and appended claims.

In accomplishing the above objects the yarn or fabric is treated, as by dipping or spraying, with an aqueous solution or dispersion of an alkali or amine salt, including sodium, potassium, ammonium and quaternary ammonium salts of copolymerized styrene-maleic anhydride, after which the yarn is treated with a dilute solution of a metal salt. The treated fabric is then dried, whereby an insoluble salt of the copolymer is formed, which remains on the fabric after washing and provides a substantially permanent finish.

Suitable ammonium or amine salts of the copolymer include the salts of ammonia, guanidine, alkylamines, such as methyl, butyl and amyl amine, and quaternary ammonium hydroxides, such as phenyl trimethyl ammonium hydroxide.

The concentration of the styrene-maleic salt solution and the pick-up should be adjusted to deposit on the fabric from 2 to 15% by weight of the styrene-maleic salt, but preferably between about 4 and 7%. The metal salt solution employed is generally dilute, as only small sections of cloth are subjected to this solution at any one time. Moreover, the time of immersion of the cloth in the solution may be varied in accordance with the concentration. In general, solutions of about 1 to 2% strength are used, but stronger solutions may be employed, if desired.

If the metal salt is water-soluble, it may be applied to the fabric before the salt of the anhydride is applied, or after the salt of the anhydride is applied but before drying, or it may be applied after the salt of the anhydride is applied and dried.

In cases in which the metal salt is insoluble in water, these salts are first dispersed in the aqueous bath of the salt of the anhydride before being applied. In such instances from 5 to 30% by weight of the water-soluble metal salt, based on the weight of the salt of the anhydride in the bath, is generally used. Best results are obtained by using from 10 to 30% by weight of the water-insoluble metal salt based on the weight of the salt of the copolymer in the bath. The dispersion should preferably comprise from about 1 to 8% by weight of the salt of the copolymer. The fabrics treated with these combined dispersions as by immersion, dipping, spraying or the like are then dried to form the insoluble metal salt of the anhydride. The dispersion of the water-insoluble metal salt and the salt of the copolymer is supplied, in general, in an amount sufficient to provide from about 1 to 10% by weight of the salt of the copolymer, based on the fabric or yarn, and from 5 to 30% by weight of the water-insoluble metal salt, based on the

weight of the salt of the copolymer applied. Best results are obtained by applying from 1 to 7% by weight of the salt of the copolymer, based on the fabric or yarn, and from 10 to 30% by weight of the water-insoluble metal salt based on the weight of the salt of the copolymer.

Although satisfactory wash resistant finishes are obtained by drying the dispersion of the water-insoluble metal salt and the salt of the copolymer on the fabric or yarn at temperatures of 75 to 150° F. to form the insoluble metal salt of the copolymer, it is preferred to heat the treated fabric or yarn at temperatures between about 180 to 300° F. Such higher drying temperatures provide a fabric or yarn having a finish which is more resistant to washing than the finish on the fabric or yarn which is dried at the lower temperatures.

The metal salts which may be used for the purpose of this invention are salts of aluminum, antimony, arsenic, barium, beryllium, bismuth, cadmium, calcium, cerium, cesium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, platinum, silver, strontium, tin, zinc and zirconium. A large variety of water-insoluble metal salts are useful in the compositions and methods of this invention. One particularly suitable class of water-insoluble salts are the water-insoluble salts of metals of Group II A of the periodic table, that is, water-insoluble salts of beryllium such as beryllium carbonate, water-insoluble salts of magnesium such as magnesium pyrophosphate, tribasic magnesium phosphate and the like and water-insoluble salts of calcium and barium such as calcium or barium carbonate, oxalate, triphosphate, sulfate and the like. The water-insoluble salts, and particularly the water-insoluble carbonates, of Group II A metals are preferred.

It is also possible to use water-insoluble salts of metals of Group II B of the periodic table, that is, water-insoluble salts of zinc, cadmium and mercury. As examples of such salts may be mentioned the oxalates and tribasic phosphates of these metals including the mercuric and mercurous compounds, zinc and cadmium carbonate, mercurous carbonate, basic mercuric carbonate and the like.

Water-insoluble salts of metals of Group I B of the periodic table, that is, water-insoluble salts of copper, silver and gold are generally suitable. As examples of such salts may be mentioned basic cupric carbonate, tribasic cupric phosphate, cupric oxalate, cuprous carbonate, silver pyrophosphate, silver carbonate and the like. The use of water-insoluble salts of copper is particularly advantageous since such salts react with the salt of the copolymer on drying on the material to form an insoluble finish on the material consisting of the copper salt of the copolymer which is not only resistant to laundering but is also resistance to fungus and bacteria.

It is also possible in accordance with this invention to use water-insoluble salts of metals of Group III A of the periodic table, for example, the water-insoluble salts of aluminum. As examples of suitable water-insoluble aluminum salts may be mentioned aluminum oxalate, aluminum phosphate, basic aluminum acetate and the like.

In general, the water-insoluble salts of metals of Group IV A and IV B of the periodic table are useful. Thus, it is possible to use such water-insoluble heavy metal salts as basic zirconium oxalate, titanium sulfate [$Ti_2(SO_4)_3$], stannic phosphate and the like.

It is also possible to use water-insoluble salts of the metals of Group VIII of the periodic table, that is, water-insoluble salts of iron, cobalt and nickel. As examples of such water-insoluble salts may be mentioned basic ferric acetate, ferric pyrophosphate, ferric phosphate, cobaltous carbonate, cobaltous phosphate, nickel carbonate, basic nickel carbonate, nickel phosphate, nickel oxalate and the like.

The copolymer of styrene and maleic anhydride used in accordance with this invention is a well established product which may be prepared in several ways. One of the well-known methods is mass polymerization, which involves heating styrene and maleic anhydride at temperatures between about 100 and 300° F. for several

hours or more. Preferably, the materials are heated cautiously, as in a water bath. Another method which may be used is known as the solvent process which involves reacting the styrene and maleic anhydride at slightly elevated temperatures in the presence of a solvent which is capable of dissolving both the starting materials and the finished polymer, such as acetone. If desired, the copolymerization may be carried out in the presence of a catalyst, such as benzoyl peroxide. Still another method which can be used is the solvent-non-solvent method which involves carrying out the reaction as above, but in a solvent which is capable of dissolving only the starting material and not the final copolymer.

The copolymer of styrene and maleic anhydride produced by the above or by any other well-known method of manufacture is soluble in acetone, but insoluble in alcohol or benzene, and forms water-soluble salts of ammonia or alkali metals. Instead of styrene, substituted styrenes, such as methyl or butyl styrene, chlorostyrene or the like, may be used to prepare copolymers which are soluble in dilute aqueous solutions of alkali or ammonia. Instead of maleic anhydride, partially esterified maleic anhydride, such as the half ester of isopropyl maleate, may be used. It is also possible to prepare and use in accordance with this invention copolymers of styrene and maleic anhydride which have been copolymerized with relatively small amounts of other unsaturated compounds, such as vinyl acetate, vinyl chloride, vinyl ethyl ether, indene, vinyl methyl ketone, acrylic esters and the like.

A further understanding of the invention will be obtained from the following examples, the parts being given by weight.

Example I

A solution of an ammonium salt of a styrene-maleic anhydride resin was prepared by mixing together 600 parts of styrene-maleic anhydride, prepared by copolymerizing equimolecular quantities of styrene and maleic anhydride at about 200° F. in a water bath, 400 parts of 26% NH_4OH and 9000 parts of water. The resulting mixture was then heated to 200 to 212° F. with stirring, and maintained at this temperature until a uniform, somewhat viscous transparent solution resulted. This required about one hour.

Spun rayon fabric and heavy cotton sheeting were dipped in the bath prepared as described above, after which it was passed through a padder adusted for 100% pick-up. The bath was maintained at about 120° F. during the treatment to insure uniform penetration. The treated sheeting was then dried, after which the dried sheeting was immersed in a 2% zirconium oxychloride solution for 10 minutes at 120° F. Following this the treated fabric was thoroughly rinsed and dried. The finished fabric was resistant to washing and showed good water-repellency.

Example II

Samples of spun rayon fabric and cotton fabric treated with ammonium salt solutions prepared as described in Example I were treated with 1% solutions of aluminum formate, copper acetate and antimony chloride respectively for 10 minutes at 120° F. The fabrics were then thoroughly rinsed and dried. The treated fabrics had a full firm hand and were resistant to washing.

Example III

One thousand parts of a 7% aqueous solution of the ammonium salt of the copolymer of styrene and maleic anhydride were mixed with 20 parts of powdered $CaCO_3$ and ball milled for 24 hours. Samples of spun rayon and cotton sheeting were immersed in the dispersion thus prepared and then padded, the pad being adjusted to deposit on the fabric 7% solids. The treated fabrics were then dried at 200° F. for 5 minutes and cured for 5 minutes at 280° F. The resulting fabrics were resistant to washing and had a stiff finish.

Example IV

One thousand parts of a 7% aqueous solution of the ammonium salt of the copolymer of styrene and maleic anhydride and 20 parts of powdered zinc carbonate were stirred vigorously to form a dispersion of the zinc carbonate in the copolymer salt solution. A spun viscose rayon fabric was immersed in the resulting dispersion immediately after the dispersion had been prepared and the fabric was then squeezed between pad rolls using a pressure of 160 pounds per linear inch on the rolls. The fabric was then framed and dried at 200° F. for 30 minutes. The resulting fabric had a stiff finish which was resistant to laundering.

Example V

One thousand parts of a 7% aqueous solution of the ammonium salt of the copolymer of styrene and maleic anhydride and 20 parts of powdered ferric phosphate were stirred vigorously to form a dispersion of the ferric phosphate in the copolymer salt solution. A spun viscose rayon fabric was immersed in the resulting dispersion immediately after the dispersion had been prepared and the fabric was then squeezed between pad rolls using a pressure of 160 pounds per linear inch on the rolls. The fabric was then framed and dried at 200° F. for 30 minutes. The dried fabric had a crisp, stiff finish which was not materially altered by washing with a 1% soap solution for 5 minutes.

Example VI

One thousand parts of a 7% aqueous solution of the ammonium salt of the copolymer of styrene and maleic anhydride and 20 parts of powdered aluminum phosphate were stirred vigorously to form a dispersion of the aluminum phosphate in the copolymer salt solution. A spun viscose rayon fabric was immersed in the resulting dispersion immedaitely after the dispersion had been prepared and the fabric was then squeezed between pad rolls using a pressure of 160 pounds per linear inch on the rolls. The fabric was then framed and dried at 200° F. for 30 minutes. The resulting fabric had a stiff finish which was resistant to washing.

Although the examples refer to the treatment of cotton and viscose fabrics, the process is also applicable to acetate rayon, nylon, glass, linen, flax, hemp, jute, ramie, wool, silk, cuprammonium rayon and synthetic protein fabrics, and fabrics containing mixtures and blends of any of the above materials.

By treating fabrics with the finishing agents described herein, a substantially permanent, stiffened finish is obtained, due to the fact that only relatively small amounts of the dried and reacted resin are lost on washing, i. e. of the order of 2 to 10%. The finished fabric is also smooth and substantially free of dusting in contrast to the well-known starch treated fabrics. When the resin is applied to the warp yarn and insolubilized thereon, there is the further advantage that the weaving operation is improved owing to the higher tensile strength of the yarn, its increased resistance to abrasion, and its generally stiffened character. The fabric prepared from treated yarn has the desired finish characteristics without further treatment, but if desired it may be subjected to additional finishing operations. The styrene-maleic salt may also be applied to the yarn without insolubilization, after which the yarn is woven, and the metal salt solution is applied.

It is customary to apply the sizing or finishing materials described herein to yarns or fabrics. However, it is possible to obtain similar results by treating fibers, either initially or at any stage of their processing prior to spinning, after which the fibers may be spun and woven to obtain fabrics of the desired finish characteristics. Yarns prepared from such treated fibers may also be readily woven. It is also possible to treat in accordance with this invention fibers which are to be used as such, as for example in cotton batting, or in the preparation of non-woven fabrics.

It is believed that the insolubility, resistance to washing and water-repellency of fabrics treated according to this invention are due to the metathesis of the metal ion for the ammonium or alkali ion in the salt of the styrene-maleic anhydride copolymer. This exchange may take place before, during or after the drying operation.

It should be understood that the aqueous solutions referred to in the appended claims are intended to include aqueous dispersions, as it is possible that the ammonium or amine salts in the solution are actually present in the form of a colloidal dispersion.

This application is a continuation-in-part of my copending application Serial No. 770,943, filed August 27,

1947, now U. S. Patent No. 2,586,477 issued February 19, 1952.

What is claimed is:

1. The method of finishing a textile material which comprises treating the material with an aqueous dispersion of (1) a salt of a copolymer of a substance selected from the group consisting of styrene, methyl styrene, butyl styrene and chlor styrene with a substance selected from the group consisting of maleic anhydride and the half ester of isopropyl maleate, said salt being selected from the group consisting of alkali and amine salts, and (2) from about 5 to 30% by weight, based on the salt of the copolymer, of calcium carbonate, said dispersion being supplied in an amount sufficient to provide from about 1 to 10% by weight of the salt of the copolymer, based on the material, and from about 5 to 30% by weight of said calcium carbonate based on the salt of the copolymer, and then drying the material at a temperature of 180 to 300° F. to form the insoluble calcium salt of said copolymer.

2. The method of finishing a textile material which comprises treating the material with an aqueous dispersion of an ammonium salt of a copolymer of styrene and maleic anhydride and from about 5 to 30% by weight, based on said ammonium salt, of calcium carbonate, said dispersion being supplied in an amount sufficient to provide from about 1 to 10% by weight of said ammonium salt, based on the material, and from about 5 to 30% by weight of said calcium carbonate, based on the ammonium salt thus applied, and then drying the material at a temperautre of 180 to 300° F. to form the insoluble calcium salt of said copolymer.

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