COMPOSITION COMPRISING AN ORGANOPOLY-SILOXANE AND COLLOIDAL SILICA, AND TEXTILE TREATED THEREWITH

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This invention relates to textile finishes and relates more particularly to finishes which when applied to textile materials impart highly desirable properties thereto. It is an object of this invention to provide a new and useful textile finish containing a silicone.

Another object of this invention is the preparation of textile materials possessing highly satisfactory characteristics due to the presence thereon of the finish of the instant invention.

Other objects of this invention will be apparent from the following detailed description and claims. In this description and claims all proportions are by weight unless otherwise indicated.

In accordance with one aspect of this invention a silicone having hydrogen atoms directly attached to silicone atoms is blended with a colloidal dispersion of silica. Advantageously, both the silica and the silicone are dispersed in water, preferably together with a curing catalyst for the silicone.

When applied to textile materials having a basis of cellulose esters of low hydroxyl content and then heated to cause curing of the silicone, the compositions of this invention produce a highly durable, water-repellent finish, which imparts to said textile materials increased abrasion-resistance and tear strength and improved recovery from creasing. The use of these compositions decreases the tendency for the individual fibers or yarns to become fused or cut when fabrics having a basis of cellulose ester of low hydroxyl content are sewn at the high speeds employed in modern factory sewing machines. At the same time it reduces the slippage and separation of the fibers and the tendency to form weaker seams which occur when the silicone is used without the silica on such fabrics.

The compositions of this invention also impart a desirable dry, crisp, scroopy hand to the fabric of cellulose ester of low hydroxyl content.

The use of the compositions of this invention also imparts to textile materials of cellulose esters of low hydroxyl content an improved resistance to degradation when exposed to strong sunlight under glass.

In the processing of fabrics of cellulose esters of low hydroxyl content there is generally employed a step of heat-treating the fabric to improve its safe ironing point temperature, its glazing resistance, its resistance to shrinkage on pressing with moist steam, the fastness of dyes on said fabric, and the resistance of dyes on said fabric to gas-fading and ozone-fading. In this heat-treating step the fabric may be heated to a temperature of about 190° or 200° or, preferably, about 210° to 250° C., as in an air oven or under radiant heat or in contact with hot rolls. Lower heat-treating temperatures may be employed when the fabric is treated in other media, e.g. saturated steam, all as set forth in the copending application of Salvin et al., Serial No. 472,758, filed December 1, 1954. The compositions of this invention may be applied to the textile material before the dry heat-treating operation and the curing of the compositions may be effected concurrently with heat-treating or even before the heat-treating. In such cases the presence of the compositions of this invention prevents the stiffening of the fabric which sometimes occurs on heat-treating.

The compositions of this invention have shown their greatest usefulness in the treatment of textile material having a basis of a cellulose ester of low hydroxyl content, for example, having less than 0.29 hydroxyl group per anhydroglucose unit in the cellulose molecule thereof.

Particularly good results have been obtained with cellulose acetate of at least 61% acetyl value, calculated as combined acetic acid. Other organic acid esters of cellulose of low hydroxyl content include highly esterified cellulose propionate, cellulose butyrate, cellulose acetate-propionate, cellulose acetate-formate and cellulose acetate-butyrate. If desired, the textile material having a basis of a cellulose ester of low hydroxyl content may be subjected, prior to the application of the composition of this invention, to a treatment for the saponification of the fiber surfaces of said textile material. This saponification treatment may, for example, be carried out by applying to the textile material an aqueous sodium hydroxide solution of at least 20%, e.g. 25%, concentration at a temperature of about 20 to 40° C., and after several minutes, e.g. 10 minutes, rinsing the fabric with water and dilute acetic acid. Such a treatment produces a textile material in which the fibers have a thin substantially completely saponified cellulose skin, while the fiber interiors remain intact. Thus, when the saponification treatment is applied to a fabric composed of fibers of cellulose acetate of acetyl value of at least 61%, the overall acetyl value will only be reduced by about 1 or 2% or less, even though the fiber surfaces are substantially completely saponified.

The compositions of this invention may also be applied to other textile materials, such as cellulose esters of higher hydroxyl content, e.g. cellulose acetate of 53 to 55% acetyl content, viscose rayon, nylon, e.g. nylon 6 or nylon 66, polyethylene terephthalate, acrylonitrile homopolymers and copolymers, vinyl chloride polymers and copolymers, and wool, or blends of any of these fibers with any one or more of the other fibers. Outstanding results have been obtained by the use in the compositions of this invention of the siloxanes which are composed of siloxane polymers in which there are a plurality of

CH₃
-O-Si-O-

units, combined, if desired with

CH₃
-O-Si-O-

units. However, the methyl radicals of these units may be replaced, entirely, or in part, by other alkyl groups, e.g. ethyl, propyl, butyl, or aryl groups, e.g. phenyl or tolyl, or aralkyl groups, e.g. benzyl, or by other organic substituents attached to silicon by carbon-silicon bonds. The siloxanes may also contain

CH₃
CH₃
end groups and small amounts of

CH₃

-cross-linking groups, although, as it well known in the art, the number of such cross-linking groups should not be such as to cause the product to be thermoset before its application to the textile material. Here also the methyl groups may be replaced, entirely or in part, by other or-
organic radicals as indicated above. The molecular weights and chemical structures of the silicones are preferably such as to cause said silicones to be fluid at room temperature. Examples of suitable commercially available silicones are those sold under the names "Decotex 102," "Decotex 104," "Decotex 108," "Hydropruf," "Hydropruf SP," "Repel-o-tex P-30" and "Cravenite W." Combinations of two or more of these silicones may be used, if desired.

The colloidal dispersion of silica used to form the compositions of this invention may be a silica sol, such as described in U.S. Patents Nos. 2,285,449, 2,285,477, 2,244,325 or 2,375,738. For example, it may contain essentially spherical colloidal silica particles varying in diameter from 40 to 80 millimicrons or even smaller and may be substantially free from silica gel. Examples of suitable commercially available colloidal dispersions of silica are those sold under the names "Syton W-200" and "Ludox," and dispersions of the product, known as "Dow Corning Silica," produced by the burning of silicon tetrachloride.

The blending of the silicone and the silica may be carried out by mixing an aqueous emulsion of the silicone, containing an emulsifying agent with an aqueous dispersion of the colloidal silica. The particle size of the emulsified liquid silicone is desirably below 5 microns, but results being obtained when this particle size is 2 microns or less. The relative proportions of silica and silicone and the concentrations of these ingredients in the aqueous mixture may be varied over a wide range. For example, there may be employed 0.5 to 2 parts, preferably 0.5 to 1 part of silica per part of silicone while the total concentration of silicone and silica in the aqueous mixture may be 0.5 to 4%, preferably 1 to 2%. Combining the ranges, this corresponds to a range of 0.17 to 2.66% by weight of the dispersion for each of the silicone and the silica.

It is generally necessary to include in the mixture a curing catalyst for the silicone. Such catalysts are commonly metal salts, such as organic acid salts of zine, tin, lead, aluminum, or zirconium, or mixtures thereof, the organic acid portion of the salt being for example, the octate radical or the naphthenate radical, or mixtures thereof. Suitable proportions of catalyst are, for example, 15 to 30%, based on the silicone.

When the textile material employed in the practice of this invention comprises a cellulose fiber, e.g., viscose rayon or cotton, or blend of a cellulose fiber and a cellulosic fiber, or blend of a low hydroxyl content, or of higher hydroxyl content, it is often advantageous to mix the compositions of this invention with an aqueous dispersion or solution of a amidesaldehyde resin, such as a urea-formaldehyde or melamineformaldehyde resin or resin-forming composition, of the type usually employed in treating textile materials containing cellulose fibers.

The compositions of this invention may be applied to the textile material in any suitable manner which will insure uniform distribution of the silicone and silica on the material. Padding, as by the use of a three-roll padding, is very effective for this purpose. It is desirable that the textile material be in as clean a state as possible and that all foreign materials, such as yarn lubricants, size components, scouring agents and wetting agents, be removed from the surface of the textile material before the composition is applied. It is also desirable that the textile material be buffered to a pH of about 6 to 8 and then dried before it is treated with a composition of this invention. This improves the absorption and penetration of the composition in the padding operation.

The amount of the composition applied to the textile material is such that there is deposited on said material about 0.5 to 1%, preferably 0.5 to 0.2%, of the composition on the textile material, temperatures of about 160° C. or above are very suitable. For example, the curing treatment may involve heating for 4 to 8 minutes at 160 to 170° C. As previously pointed out, curing may take place simultaneously with a heat treating of the fabric, e.g. for 10 to 20 seconds at 210 to 230° C. After curing the textile material may be subjected to any desired treatment, i.e., rinsing or scouring, desizing, dyeing, button breaking or hot- or cold-calendering. The following examples are given to illustrate the invention further.

Example I

A suitlng fabric made of staple fibers of cellulose acetate of 61.5% acetyl value is singed, boiled off and then dyed in a finish to a medium gray shade with a mixture of high-temperature slow-dyeing acetate dyes, comprising 1,8-dihydroxy-4-(para-beta-hydroxyethyl)anilino-5-nitro antroquinone, 4-nitro-2-methylsulfonephenylazo-4'-(N-beta-hydroxyethyl-N-difluoroethyl)aminobenzene and 2-nitro-4-sulfanilamido diphenylamine. The dyed fabric is dried in air and padded with an aqueous dispersion of silicone and silica, said dispersion containing 5 grams per liter of "Decotex 104" (methyl hydrogen polysiloxane), 15 grams per liter of "Decotex 108" (methyl hydrogen polysiloxane), 10 grams per liter of "Syton W-200" (aqueous dispersion of about 25% silica, substantially free from electrolytes and of sub-microscopic particle size) and 5 grams per liter of "Catalyst XEY-16" (an aqueous dispersion of 20% zinc octoate). The fabric picks up 80% of its weight of this dispersion. After drying the fabric is heat-treated at 204° C. for 15 seconds, in a radiant heater, and then calendered. When the treated fabric is exposed under glass to Florida sunlight for 400 hours it retains 95% of its tensile strength. The treated fabric has a spray rating of 100 when tested according to A.A.T.C.C. test No. 22-41. It has good hand and improved tear strength and abrasion resistance, and does not tend to slip or form weak seams.

Example II

A taffeta fabric composed of continuous filaments of cellulose acetate of 54.5% acetyl value is scoured in a jig, frame dried and padded with an aqueous dispersion containing 10 grams per liter of "Decotex 104," 15 grams per liter of "Decotex 108," 20 grams per liter of "Syton W-200" and 8 grams per liter of Catalyst XEY-16. The fabric, which picks up 80% of its weight of this dispersion, is frame-dried, then calendered for five minutes at 160° C., and thereafter calendered. The fabric is water-repellent, has a desirable scrobble and rustle and does not tend to slip or form weak seams.

It is to be understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of our invention.

Having described our invention, what we desire to secure by Letters Patent is:

1. A composition for the treatment of textile materials to improve the physical properties thereof, said composition comprising a mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and a colloidal dispersion of particles consisting essentially of silica.

2. A composition for the treatment of textile materials to improve the physical properties thereof, said composition comprising an aqueous dispersion containing emulsified therein an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds aryl, aralkyl and alkyl groups, and colloidal dispersed silica.

to improve the physical properties thereof, said composition comprising an organopolysiloxane having hydrogen atoms and methyl radicals directly attached to silicon atoms, colloidal dispersed particles consisting of silica, and a curing catalyst for said organopolysiloxane.

4. A composition for the treatment of textile material to improve the physical properties thereof, said composition comprising an organopolysiloxane having hydrogen atoms and methyl radicals directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of ary1, aralkyl and alkyl groups, colloidal dispersed particles consisting essentially of silica, and a curing catalyst for said silicone, said catalyst comprising a metal salt of an organic carboxylic acid.

5. Process for improving the physical properties of a textile material, which comprises applying the composition of claim 1 to the textile material, and curing said organopolysiloxane on said material.

6. Process for improving the physical properties of a textile material, which comprises applying the composition of claim 2 to the textile material, and curing said organopolysiloxane on said material.

7. Process which comprises applying the composition of claim 1 to a textile material having a basis of a cellulose ester containing not over 0.29 alcoholic hydroxyl groups per anhydroglucose unit of the cellulose molecule thereof, and curing the organopolysiloxane of said composition on said material.

8. Process which comprises applying the composition of claim 1 to a textile material having a basis of a cellulose acetate of at least 61% acetyl content, calculated as combined acetic acid, and curing the organopolysiloxane of said composition on said material.

9. Process for the treatment of textile material having a basis of a cellulose ester containing not over 0.29 alcoholic hydroxyl groups per anhydroglucose unit of the cellulose molecule thereof which comprises applying thereto a mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and a colloidal dispersion of silica, and heat-treating said textile material to raise the safe ironing temperature of said textile material while curing said organopolysiloxane.

10. Process for the treatment of textile material having a basis of cellulose acetate of at least 61% acetyl content, calculated as combined acetic acid, which comprises applying thereto an aqueous dispersion of a mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and an aqueous colloidal dispersion of silica, drying said mixture on said textile material, and heat-treating said textile material to raise the safe ironing temperature of said textile material while curing said organopolysiloxane.

11. Cellulose acetate textile material carrying thereon a cured mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and colloidal particles consisting of silica.

12. Textile material having a basis of cellulose acetate of at least 61% acetyl content, calculated as combined acetic acid, carrying thereon a cured mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and colloidal particles consisting of silica.

13. Textile material having a basis of a cellulose ester containing not over 0.29 alcoholic hydroxyl groups per anhydroglucose unit of the cellulose molecule thereof and carrying thereon a cured mixture of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups and colloidal particles consisting of silica, the amount of silica being 0.5 to 2% of the weight of said textile material and the amount of silicone being one half to twice the amount of organopolysiloxane.

14. Process for the production of textile treating composition which comprises blending a colloidal aqueous dispersion of silica with an aqueous emulsion of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having attached to silicon atoms by carbon-silicon bonds organic substituents selected from the group consisting of aryl, aralkyl and alkyl groups, and mixtures thereof, and (c) colloidally dispersed in the composition, dense, discrete amorphous silica particles varying in size and shape so as to impart water repellency thereto, the composition comprising (a) an aqueous emulsion having a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having a repeating structure of the formula

\[
\text{R} = \text{Si-O-} \text{R}
\]

where R is selected from the group consisting of hydrogen, phenyl, benzy1, and alkyl groups having up to 14 carbon atoms, (b) a catalyst for promoting polymerization of the organopolysiloxane, said catalyst being a metal salt of an acid selected from the group consisting of octoic acid, napthenic acid and mixtures thereof, and (c) colloidalily dispersed in the composition, dense, discrete amorphous silica particles varying in size and shape so as to impart water repellency thereto, the composition comprising (a) an aqueous emulsion having a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having a repeating structure of the formula

\[
\text{R} = \text{Si-O-} \text{R}
\]

where R is selected from the group consisting of hydrogen, aryl, aralkyl and alkyl groups, (b) a catalyst for promoting polymerization of the organopolysiloxane, said catalyst being a metal salt of an acid selected from the group consisting of octoic acid, napthenic acid and mixtures thereof, and (c) colloidalily dispersed in the composition, dense, discrete amorphous silica particles vary-
ing from 40 to 80 millimicrons in diameter, the composition containing from about 0.17 to 2.66 percent by weight of the polysiloxane solids, about 0.17 to 2.66 percent by weight of the amorphous silica, and about 0.025 to 0.7 percent by weight of the polymerization catalyst.

18. A composition for applying to hydrophilic surfaces to impart water repellency thereto, the composition comprising (a) an aqueous emulsion having a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having repeating structure of the formula

\[ \text{R} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{R} \]

where \( \text{R} \) is selected from the group consisting of hydrogen, aryl, aralkyl and alkyl groups, (b) a catalyst for promoting polymerization of the organopolysiloxane, said catalyst being a metal salt of an organic carboxylic acid, and (c) collooidally dispersed in the composition, dense, discrete amorphous silica particles varying from 40 to 80 millimicrons in diameter, the composition containing from about 0.17 to 2.66 percent by weight of the polysiloxane solids, about 0.17 to 2.66 percent by weight of the amorphous silica, and about 0.025 to 0.7 percent by weight of the polymerization catalyst.

19. A composition for applying to hydrophilic surfaces to impart water repellency thereto, the composition comprising (a) an aqueous emulsion having a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having repeating structure of the formula

\[ \text{R} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{R} \]

where \( \text{R} \) is selected from the group consisting of hydrogen, aryl, aralkyl and alkyl groups, and (b) collooidally dispersed in the composition, dense, discrete amorphous silica particles varying from 40 to 80 millimicrons in diameter, the composition containing from about 0.17 to 2.66 percent by weight of the polysiloxane solids, and about 0.17 to 2.66 by weight of the amorphous silica.

20. A composition for applying to hydrophilic surfaces to impart water repellency thereto, the composition comprising (a) an aqueous emulsion having a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having repeating structure of the formula

\[ \text{R} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{R} \]

where \( \text{R} \) is selected from the group consisting of hydrogen, aryl, aralkyl and alkyl groups, and (b) collooidally dispersed in the composition, dense, discrete amorphous silica particles.

21. A composition for treating textiles comprising (a) an aqueous emulsion containing a dispersed phase consisting of an organopolysiloxane having hydrogen atoms directly attached to silicon atoms and having a repeating structure of the formula

\[ \text{R} - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{R} \]

where \( \text{R} \) is selected from the group consisting of hydrogen, phenyl, benzyl and alkyl groups of up to 14 carbon atoms and not more than one \( \text{R} \) in the repeating structure may be hydrogen, (b) as a catalyst for promoting polymerization of the organopolysiloxane, a metal salt of an acid selected from the group consisting of octoic acid, naphthenic acid, and mixtures thereof, and (c) collooidally dispersed in the composition dense, discrete, colloidal amorphous silica particles.

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