WATER-REPELLENT TREATMENT FOR HYDROPHOBIC TEXTILE MATERIALS


13 Claims. (Cl. 117—138.8)

This invention relates to the treatment of certain hydrophobic textile fabrics to impart a water repellent finish which is durable to laundering as well as to dry cleaning.

It has been proposed to waterproof textiles with waxes, metal salts and various other water repellent agents. Many of the wax emulsions or dispersions suggested have lacked sufficient stability in shelf storage or when diluted in a pad bath or both. Moreover, the resulting textile finishes of the prior art were seldom of a durable or permanent nature, especially to laundering. While it has been proposed to correct these defects by the addition of various synthetic resins, this, of course, complicates the treatment and increases the cost of the finish.

The object of the invention is to provide a water repellent treatment for fabrics containing certain synthetic fibers which is durable to both laundering and dry cleaning.

Other objects and advantages of the invention will be apparent to those skilled in the art especially upon consideration of the detailed disclosure hereinafter.

It has been found that the treatment of fabrics containing hydrophobic thermoplastic synthetic fibers with certain aqueous dispersions of waxes and metal salts produces wash-durable water-repellent finishes. This effect is quite unexpected since the same effect is not produced on hydrophilic fabrics such as cotton and rayon goods. The present process is especially applicable to fabrics containing fibers composed of polyethylene glycol terphthalate esters, the homo- and co-polymers of acrylonitrile and linear polyamides such as nylon.

The present invention accordingly comprises the treatment of textile fabrics containing hydrophobic, thermoplastic, synthetic textile fibers with a stable aqueous dispersion of a hydrocarbon wax, an amine soap and lower aliphatic monocarboxylic acid salts of aluminum and a metal of the group consisting of zirconium and titanium followed by the drying of the treated fabric to produce a wash-durable water repellent finish thereon. A narrower aspect of the invention is concerned with the inclusion of an ester wax in the dispersion.

Fabrics suitable for treatment in the novel process include those containing at least about 30% by weight of hydrophobic synthetic textile fibers. In general, it may be said to be applicable to those containing fibers having a moisture regain by the hydrophobic fibers of less than 5% by weight upon reaching equilibrium in an atmosphere having a relative humidity of 65% at 70° F. Among this group are the linear polyamides, copolymers of vinylidene chloride and vinyl chloride and the polymeric acrylonitrile fibers, polysteres and especially polyethylene glycol terphthalate. The terms polymeric acrylonitrile is used here to include not only the homopolymers of acrylonitrile but also copolymers of this material with one or more compatible ethylenic monomers such as methyl acrylate, vinyl acetate, vinyl chloride, the vinyl pyridines as exemplified by 2-methyl 5-vinyl pyridine, etc., wherein the monomer contains at least about 25% acrylonitrile by weight, including the products of both wet spinning and dry spinning operations. The novel treatment is, of course, applicable to fabrics woven, knitted or felted from these hydrophobic fibers in blends with natural and hydrophilic fibers as well as those processed from stock made entirely of hydrophobic fibers; however, the durability of the finish to washing is somewhat reduced in the case of such blends.

In order to prepare a treating bath of the type employed in the novel process a hydrocarbon or mineral wax such as paraffin, slack wax, ozokerite, etc., is generally used to form a concentrated emulsion in water using an amine soap as the dispersing agent. This concentrated emulsion, which may contain from about 20 to about 60% solids, is stable for prolonged periods at atmospheric temperatures above its freezing point. A small amount of an ester wax, for example, between about 1.0 and about 3.5 parts of carnauba, montan, candelilla, ceresin and like waxes per 100 parts by weight of hydrocarbon wax, is a desirable additive since it reduces the particle size of the dispersed particles of hydrocarbon wax in a concentrated emulsion of a treating bath. However, excessive quantities of an ester wax appear to reduce the stability of the treating bath. Carnauba wax is especially preferred for the purpose by reason of its hardness. The hydrocarbon and ester waxes should have melting points of at least about 110° F. and preferably about 120° F.

For dispersing the wax or waxes an amine soap of a fatty acid containing at least about 8 carbon atoms and preferably at least 12 up to 22 or more carbon atoms is used. Stearic acid soaps are preferred but those derived from lauric, palmitic, myristic, oleic, behenic and like acids may be used if desired either in whole or in part. Animal, marine and vegetable oils are suitable sources for the fatty components of these soaps. Any water-soluble aliphatic amine may be employed in forming the soap, but the lower alkylamines are preferred as exemplified by the primary, secondary, and tertiary amines of ethanoll, propanol, isopropanol and the several butaols. Triethanolamine is outstanding for the purpose. Other suitable amines include the various primary, secondary and tertiary methyl, ethyl, propyl, isopropyl and butyl amines. The amine soaps may be either prepared in advance or in situ by the addition of the amine and an appropriate fatty acid. To form the concentrated wax emulsion the amine soap or its constituents are added to water which is heated well above the melting of the wax or wax mixture and then the wax is added in the molten state with stirring until a homogeneous emulsion is obtained. It has been found that the wax particles in such emulsions are predominantly smaller than one micron with most of the larger particles ranging between one and three microns in size. From 5 to 25 parts of the soap should be present for each 100 parts by weight of hydrocarbon wax and in most instances optimum results are obtained with a quantity of amine soap ranging from 10 to 20% of the wax. There is reason to believe that the presence of an excessive quantity of an emulsifying agent will reduce the spray rating of the impregnated fabric.

In addition to the wax emulsion described, the agent used for impregnating or coating the cloth also contains at least two metal salts. An aluminum salt is an essential ingredient and a salt of either zirconium or titantium is also required. For each 100 parts by weight of the mineral wax between about 10 and about 80 parts of the aluminum salt may be used and the optimum quantity is
between 15 and 45 parts while the quantity of zirconium or titanium salt should be between about 5 and about 40 parts with the best results being obtained with from 10 to 20 parts. Zirconium salts are preferred for the purpose as they produce higher spray retentions on textile fabrics than wax dispersions containing salts of titanium. The salts of formic, acetic and propionic acids have been found to be capable of producing the desired results. These lower aliphatic monocarboxylic acid salts are available commercially in the form of concentrated aqueous solutions containing an excess of the organic acid in order to avoid the presence of the oxides or hydroxides of aluminum, zirconium and titanium. For example, one suitable 26% aqueous zirconium acetate solution has a pH of about 3.7 and contains 13% ZrO₂ and 12.5% by weight of acetic acid. This material has also been termed zirconyl acetate and diacetato-zirconyl acid, and the solid approximates the formula H₂ZrO₄(CH₃COO)₂. It is of course contemplated that the metal salt solution may also be prepared by mixing in water one or more of the aliphatic acids mentioned or soluble salts thereof together with one or more soluble salts of aluminum or zirconium or titanium with other acids. For example, a solution equivalent to the zirconium acetate solution described above may be formed in water by mixing relative proportions of 126 grams of zirconium oxycarbonyl (ZrOCl₂) of 40% ZrO₂ content with 100 grams of sodium acetate and the proper quantity of water. Accordingly, the term “salts” is used herein in reference to aqueous dispersions or solutions to include those prepared in either manner.

In making up the dispersion for treating the textile fabric water is heated in a suitable vessel to a temperature above the melting point of the hydrocarbon wax, as for instance 170–180°F. Then the required amount of the concentrated anionic wax is added with stirring until the wax is thoroughly dispersed. Overheating should be avoided as this may result in breaking the wax emulsion. Next a concentrated solution of metal salts is added rapidly while stirring at a moderate speed and maintaining the temperature above 130°F. The agitation is stopped as soon as mixing is complete and the resulting bath is stable at room temperature as well as at elevated temperatures. Although the spray or pad bath may be prepared with a hydrocarbon wax content ranging from about 0.5 up to about 10% by weight along with the other ingredients in the proportions indicated above, concentrations of between 1.5 and about 3% are recommended for optimum results. Upon addition of the mixed salt solution a surprising effect has been observed in that the dispersion is changed from a negatively charged emulsion to one which is cationic or positively charged without a coagulation which usually occurs in such cases. After the dilute dispersion has been formulated the pH should be adjusted to be between 3 and 6 and preferably between 4 and 5 by the addition, if required, of a compatible acid. Acetic, formic and propionic acids are among the suitable acids.

The liquid treating agent may be applied to the synthetic textile fabric by any suitable conventional equipment such as sprays or preferably a pad bath with the customary squeeze rolls. In any event, the wet pick-up should be regulated in known manner to deposit between about 1 and about 10% of solids based on the dry weight of untreated fabric; a dry add-on of from 2 to 4% being recommended for best results. The dilute emulsion may be applied at room temperature but temperatures of the order of 140°F. are advised for maximum penetration of the agent through the cloth. For better understanding of the nature and objects of this invention reference should be had to the accompanying examples in which all proportions are expressed in terms of weight unless otherwise specified.

**Pad bath 1**

Into 90 parts of water at 175°F. is added with stirring, 5 parts of a wax emulsion of pH 8.5 and having the following composition:

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffin (128–130°F. melting point)</td>
<td>160</td>
<td>9</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Carnauba wax (No. 1 yellow)</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>50</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Water</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

A mixture of 40% stearic acid, 48% palmitic acid and 8% oleic acid.

The gentle agitation is continued until a homogeneous mixture is obtained; then 5 parts of salt solution having a pH of 3.95 is added rapidly with continuing gentle stirring. The metal salt solution contains 5.0% zirconium acetate, 5.0% aluminum formate and 5.0% aluminum acetate with the balance being made up of water with small stabilizing amounts of the organic acids. Stirring is discontinued as soon as thorough mixing is obtained and the temperature of this mixture is observed to be 145°F. The paraffin content of the treating bath is 2.2%, the total solids amount to 3.37% and the pH is 4.5. Cotton and a series of hydrophobic, thermoplastic, synthetic textile fabrics are paddled through Pad Bath I at 120°F. with the squeeze rolls adjusted to provide an 80% wet pick-up. After air-drying the various pieces of cloth are cut into swatches for determining the water repellency by spray tests according to the American Association of Textile Chemists and Colorists test method 22–52 (1952 A. A. T. C. C. Yearbook p. 136). Samples of the treated fabric are subjected to six repeated laundering operations in about a 0.5% soap solution according to A. A. T. C. C. test method 40–52. Other samples of the treated fabrics are subjected to 20 minute dry cleaning cycles in Vanrol No. 2 mineral spirits in a tumble jar rotating at 55 R. P. M. followed by steam pressing to remove all traces of the solvent. Spray tests are run on cotton for comparative purposes as well as on the laundered and dry cleaned specimens and the results are set forth in the table below.

**A. A. T. C. C. Spray Ratings**

<table>
<thead>
<tr>
<th>Ex. no.</th>
<th>Material</th>
<th>Initial</th>
<th>After 1 Wash</th>
<th>After 6 Washes</th>
<th>After 1 Dry Cleaning</th>
<th>After 3 Dry Cleanings</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cotton (control)</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Nylon</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>Polyethylene</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>Cuprolymer of 90% nylon, 10% vinyl pyridine, 2% vinyl acetate, 2%</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>100% Polyacrylonitrile</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>Copolymer of 90% vinyl chloride, 10% acrylonitrile</td>
<td>100</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

**Pad bath II**

This dispersion is prepared in the same manner as Pad Bath I except that montan wax is substituted for carnauba wax in the same quantity in the concentrated wax dispersion and the concentrated metal salt solution contains 5.0% titanium formate in lieu of the zirconium acetate. In addition, the final treating bath is composed of 85 parts of water, 5 parts of concentrated wax emulsion and 10 parts of the metal salt solution to give the relative proportions of metal salts. After padding the same variety of woven fabrics through this dispersion followed by drying in the air spray ratings similar to those obtained with Pad Bath I are noted on both cotton and the synthetic fabrics before and after dry cleaning and in the manner prescribed to increase the fabric's water repellency.

From the above examples it is apparent that the treatment imparts a substantial permanent water repellent finish to fabrics containing synthetic fibers whereas a treated cotton cloth loses substantially all of its water.
repellency in washing and must be treated again after each laundering operation.

We claim:
1. A process which comprises applying a stable aqueous dispersion of 100 parts by weight of a hydrocarbon wax, between about 5 and about 25 parts of an amine soap, between about 10 and about 80 parts of an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms, and between about 5 and about 40 parts of a salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms with a metal of the group consisting of zirconium and titanium to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers and drying the treated fabric to produce a wash-durable water repellent finish thereon.

2. A process which comprises applying at a pH between about 3 and about 6 a stable positively charged oil-in-water dispersion comprising 100 parts by weight of a hydrocarbon wax, between about 1 and about 3.5 parts of an ester wax, between about 5 and about 25 parts of a lower alkanolamine soap, between about 10 and about 80 parts of an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms and between about 5 and about 40 parts of a salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms with a metal of the group consisting of zirconium and titanium to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers and drying the treated fabric to produce a wash-durable water repellent finish thereon.

3. A process which comprises applying at a pH between about 3 and about 6 a stable positively charged oil-in-water dispersion comprising 100 parts by weight of a hydrocarbon wax and between about 1 and about 3.5 parts of an ester wax in the discontinuous phase dispersed in a continuous aqueous phase containing between about 5 and about 25 parts of an ester soap, between about 10 and about 80 parts of an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms and between about 5 and about 40 parts of a salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers and drying the treated fabric to produce a wash-durable water repellent finish thereon.

4. A process according to claim 3 in which the fabric contains polymeric acrylonitrile fibers.

5. A process according to claim 3 in which the fabric contains fibers of copolymerized acrylonitrile and methyl acrylate.

6. A process according to claim 3 in which the fabric contains fibers of copolymerized acrylonitrile and vinyl chloride.

7. A process according to claim 3 in which the fabric contains fibers of copolymerized vinylidene chloride and vinyl chloride.

8. A process according to claim 3 in which the fabric contains nylon fibers.

9. A process according to claim 3 in which the said fabric contains polyethylene glycol terephthalate fibers.

10. A process which comprises applying at a pH between 3 and 6 a stable positively charged oil-in-water dispersion comprising 100 parts by weight of a hydrocarbon wax and between about 1 and about 3.5 parts of a Carnauba wax in the discontinuous phase dispersed in an aqueous solution of between about 5 and about 25 parts of triethanolamine stearate, between about 10 and about 80 parts of an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms and between about 5 and about 40 parts of a salt of a zirconium salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers in sufficient quantity to deposit between about 2 and about 5 percent thereof based on the weight of the dry fabric and drying the treated fabric to produce a wash-durable water repellent finish thereon.

11. A process according to claim 10 in which the particles of wax in said dispersion are predominantly smaller than 1 micron in size.

12. A process which comprises applying a stable aqueous dispersion of a hydrocarbon wax, an amine soap in lesser quantity than the wax but sufficient to disperse the wax without substantially reducing the water-repellent characteristics of the final treated article, an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms in lesser quantity than the wax, and a salt in lesser quantity than the wax of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms with a metal of the group consisting of zirconium and titanium to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers and drying the treated fabric to produce a wash-durable water repellent finish thereon.

13. A process which comprises applying at a pH between about 3 and about 6 a stable positively charged oil-in-water dispersion comprising a hydrocarbon wax, an ester wax in an amount less than the hydrocarbon wax but insufficient to substantially reduce the stability of the dispersion, a lower alkanolamine soap in an amount less than the hydrocarbon wax but sufficient to disperse the wax without substantially lowering the water repellent characteristics of the final treated fabric, an aluminum salt of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms in an amount less than the hydrocarbon wax and a salt in an amount less than the hydrocarbon wax of an aliphatic monocarboxylic acid containing from 1 to 3 carbon atoms with a metal of the group consisting of zirconium and titanium to a textile fabric containing hydrophobic thermoplastic synthetic textile fibers and drying the treated fabric to produce a wash-durable water repellent finish thereon.

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