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PROCESS OF PRODUCING WATER
REPELLENT TEXTILE MATERIALOscar Edelstein, New Haven, Conn., assignor to
The Pond Lily Company, a corporation of Con-
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This invention relates to improvements in the manufacture of water repellent textile or fibrous materials. An object of said invention is to provide a method for rendering textile or fibrous materials water repellent and for maintaining their water repellency under exceptional conditions, such as after repeated and prolonged washings and/or scourings in boiling solutions of soap and water, and/or after dry cleaning with usual solvents, such as gasoline, naphtha, carbon tetrachloride, acetone, alcohol, ether and the like.

Heretofore, the art of rendering textile or fibrous materials water repellent has commonly relied upon agents involving the chemical combination of certain metals and fatty acids to produce insoluble metallic soaps as stearates of metals such as aluminum.

These compounds while imparting more or less water repellent properties when applied to fibrous materials, as textiles, nevertheless are comparatively easily destroyed and removed in scouring operations employing soap and mild alkalies.

In an effort to remedy this condition, paraffin, which is relatively inert and does not saponify with weak alkalies has also been used in conjunction with aluminum acetate. When this mixture (usually in the form of an emulsion) is applied to fabric and dried, it provides a heterogeneous film which is little or not at all resistant to laundering.

The method of the present invention includes forming on the fibers of the material to be treated an adherent binder having a strong affinity for a water repellent agent such as paraffin. In accordance with my present understanding, the improved water repellency obtained thereby may be explained in part by the fact that the affinity of the binder for the water repellent agent appears to be adsorptive. Such binders may, on this hypothesis, be considered as carrying a positive electrical charge; and the water repellent materials may be considered as carrying a negative charge, said opposite charges facilitating bonding of said two types of materials for the purposes of this invention.

A water repellent agent such as paraffin is effectively secured to the fibers of a fabric with suitably adsorptive binders in the form of adsorptive metal hydroxides formed in situ on the fabric or fibrous material. Hydroxides useful for this purpose are produced by impregnating the fabric with suitable metal salts, including those of zirconium, aluminum, magnesium, ce-

rium, thorium, barium, chromium, nickel, lead or titanium, and forming the hydroxides on the fibers, as by heating or by treating with ammonium hydroxide solution and washing with water to remove detrimental or useless substances such as the acid radicals of the salts used. The removal of the acid radicals either by heating or by washing after ammonia treatment appears to improve the adsorptive affinity of the hydroxide for the water repellent material. Accordingly, the hydroxides remaining on the fabric as a result of my improved method are in an environment or condition to effectively adsorb and retain the paraffin, so that the treated fabric retains its water repellency after and in spite of repeated scouring and dry cleaning.

Improved resistance to scouring and dry cleaning treatments is observed in respect to the water repellency of fabrics treated with soluble metal salts such as acetates, formates, chlorides, sulphates or other salt of metals above mentioned and which form insoluble hydroxides which are adsorptive and adapted to yield a water repellent effect in conjunction with paraffin, fatty acids, or natural or synthetic gums, resins, waxes or other water repellent matter.

The hydroxides of the various metals mentioned differ in their individual properties; some, for example, are more soluble in alkaline solution than others, and some possess greater adsorption power than others. But all applications thereof to fibrous materials in the manner described above display improved durability.

A typical embodiment of the method of the present invention includes the following steps:

A textile, fibrous material, or fabric is impregnated with a water solution of a water soluble metal salt of the above-mentioned group yielding insoluble and adsorptive hydroxides.

The metal salts preferred for presently known purposes are zirconyl acetate or a combination of aluminum and magnesium acetates.

Surplus metal salt solution is removed and the fabric dried at a moderate temperature. The dried fabric is immersed in a solution of boiling water containing ammonia, rinsed in water and the water removed, as by wringing and drying.

The dried fabric is impregnated with a solution of paraffin dissolved in carbon tetrachloride, toluol or other volatile and inert solvent which is removed, as by squeezing and drying the fabric.

The effect of paraffin thus deposited on the binder and so on the fibers is to produce a water repellent film or surface thereon.

The deposited metal hydroxide binder alone produces little or no water repellent effect. Its function in the present invention being mainly as a binder to fasten the paraffin, stearic acid, wax or other more water repellent agent to the fiber.

The quantities and proportions of the binding and repelling agents to be used are significant chiefly to the extent that in general the more hydroxide or binder deposited, the more durable will be the water repellency of that particular material. The quantity of paraffin to be deposited is quite small; good water repellency in certain fabrics being obtained with as little as 3 oz. per 100 lbs. of fabric. Larger quantities up to 2 to 3 lbs. of paraffin per 100 lbs. of fabric work satisfactorily in so far as the intrinsic water repellent properties are concerned. The larger quantity of paraffin, however, may noticeably affect the stiffness, feel, or appearance of said materials.

The quantities of the metal salts and paraffin or other waxes to be used will therefore ordinarily be governed by the commercial considerations of cost, durability required, and the appearance and feel of the particular fabrics treated and their contemplated fields of use.

The following examples of preferred modes of carrying out the invention are given by way of illustration and the invention is in no way restricted thereto.

Example 1.—700 yards of 38 inch wide cotton gabardine weighing approximately 6 oz. to the linear yard are impregnated with a water solution of twenty per cent (20%) aluminum acetate and ten per cent (10%) magnesium acetate, then squeezed and dried. The dried fabric is then saturated with a boiling aqueous ammonia solution comprising approximately seventy-five (75) gallons of water containing two (2) gallons of twenty-eight per cent (28%) aqua ammonia, to precipitate the hydroxides of aluminum and magnesium on the fibers. After this ammonia treatment, the fabric is washed in hot water, dried, and impregnated with a paraffin solution of approximately ten (10) pounds of paraffin dissolved in thirty (30) gallons of carbon tetrachloride. The fabric is again dried and the product thus produced has an unusually durable water repellence.

The desired effect of the magnesium hydroxide in the procedure above set forth is to prevent the aluminum hydroxide from being readily dissolved by alkali in soaps or other detergent materials since aluminum hydroxide is amphoteric and hence tends to dissolve in alkaline solutions. The magnesium hydroxide may form an adsorption complex with the acid side of the aluminum hydroxide, which is not readily dissolved by alkali. Hydroxides of other metals, as calcium, also serve a similar purpose when used with aluminum hydroxide.

Example 2.—The procedure of Example 1 is followed except that a water solution of 4% zirconyl acetate is used in place of the magnesium and aluminum acetate solution.

Example 3.—38 gallons of a 4% water solution of zirconyl acetate at a temperature of 170° F. are mixed with 12 gallons of a 5.5% paraffin wax emulsion also at 170° F. 250 lbs. of cotton fabric are impregnated with said paraffin-acetate mixture, and then, after drying, are washed in a boiling ammonia solution of approximately 75 gallons of water and 2 gallons of 28% aqua ammonia and washed free of soluble salts and dried.

In preparing emulsions of zirconyl acetate and paraffin for use in the above method of Example 3, it should be noted that even a small amount of sulphate SO_4 ions present in the acetate solution will sometimes cause coagulation, rendering the mixture useless. Consequently, it is desirable in such cases that the zirconyl acetate be free of sulphate ions.

In a modification of this invention as illustrated in Example 3, urea is added to the zirconyl acetate solution prior to mixing with the above described paraffin emulsion in the following proportion: 4 lbs. urea are added to 10 gallons of zirconyl acetate solution. This procedure is indicated where the zirconyl acetate contains a trace of sulphates, which would cause coagulation of the paraffin emulsion and render the mixture unsuitable for use. With urea present in proper quantities, however, no coagulation of the emulsion occurs. It remains stable and can be heated to 212° F. without separating the paraffin or otherwise deteriorating for its intended purpose.

Example 4.—A cotton fabric is impregnated with a mixture of 38 gallons of a 4% water solution of zirconyl acetate and 12 gallons of a 5.5% aqueous paraffin wax emulsion made at 170° F. Surplus mixture is removed in any suitable manner as by passing the fabric through a wringer and the fabric is then heated for one hour at 240° F.

Example 5.—In the process of Example 1, 30 gallons of an aqueous emulsion containing 1.5% paraffin are substituted in place of the carbon tetrachloride-paraffin solution.

Example 6.—The fabric is impregnated with a 4% zirconyl acetate solution and then squeezed until it contains approximately 60% to 70% of its own weight of zirconyl acetate solution and is passed into an aqueous emulsion of paraffin containing approximately 1.5% paraffin, after which the fabric is squeezed and dried and washed in a boiling ammonia solution and hot water as set forth in Examples 1 and 2.

Example 7.—The fabric is first treated with the 1.5% aqueous paraffin emulsion of Example 6 and then impregnated with the zirconyl acetate, dried, and washed with the boiling ammonia solution and hot water as set forth in Examples 1 and 2.

Differently identified aqueous paraffin emulsion preparations available on the market may be used in carrying out the above described procedures, one which gives satisfactory results being known under the trade name Paracol #507—O. S. #219 C, manufactured and sold by Hercules Powder Company.

While ammonia in water solution is the preferred precipitating agent employed in the above examples to form the hydroxide on the fibre, other alkaline agents may be used, such as triethanolamine, morpholine, ethylene-diamine or other amines.

In view of the foregoing description, it will be seen that by employing the present invention, fibrous material or fabric impregnated with a water solution of one or more of certain soluble metal salts and a water repellent material, when treated with an alkaline solution and rinsed, will have precipitated thereon an adsorptive binder as of hydrated oxide miscelles of said metals which adsorb a water repellent material and hold it tenaciously, even when washed in boiling soap solution and/or immersed in commonly used dry cleaning solvents.

If the metal salts are those of the volatile acids, such as acetic or formic, good results can be obtained by driving off the acid by heating at a sufficiently high temperature; but better results are obtained by washing with the boiling water solution of ammonia as above described.

If the metal salts employed in the solutions are those of mineral acids, such as sulphuric or hydrochloric acid, the addition thereto of a buffer or protective agent is desirable to inhibit or prevent excessive tendering of cellulosic fibres, such as cotton, linen, or rayon. Examples of such agents are ammonium acetate or ammonium formate, or a compound selected from the class of acid amides, such as carbamide, acetamid or formamide.

The following is an illustrative example of a typical binder solution containing a metal salt of a mineral acid together with a buffer or inhibiting agent:

Dissolve in fifty (50) gallons of water

	Pounds
Zirconyl chloride $ZrOCl_2 \cdot 8H_2O$	22
Formamide.....	22

This solution may be applied to and dried into cotton, rayon, or linen at a relatively high temperature without causing tendering of the cellulosic fibre.

Having thus described various embodiments of my invention both as to process and as to product, and having given specific illustrative examples thereof, I desire it to be understood that specific terms and illustrations so employed are used in a descriptive sense only, and not for purposes of limitation, the scope of the invention being defined and limited only by the terms of the appended claims.

I claim:

1. A process of treating a fibrous material with a water repellent agent to produce a water repellent material substantially free from metallic soaps whereby the water repellent effect produced on said material has improved durability and resistance to the action of strong alkaline detergents, comprising the steps of impregnating the fibers of said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, zirconium, cerium, thorium, chromium, nickel, lead, barium, and titanium, drying said material after impregnation, treating the dried material with an alkaline solution to form a metal hydroxide on the fibers thereof, and depositing a coating consisting of wax on the fibers of said material to render said material water repellent.

2. A process of treating a fibrous material with a water repellent agent to produce a water repellent material substantially free from metallic soaps whereby the water repellent effect produced on said material has improved durability and resistance to the action of strong alkaline detergents, comprising the steps of impregnating the fibers of said material with an aqueous solution of a salt of a metal selected from the group consisting of aluminum, zirconium, cerium, thorium, chromium, nickel, lead, barium, and titanium, drying said material after impregnation, treating the dried material with ammonium hydroxide to form a metal hydroxide on said fibers, and depositing paraffin on the fibers of said material to produce a water repellent effect thereon.

OSCAR EDELSTEIN.