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WATER REPELLENT TEXTILE AND PROCESS
OF PRODUCING THE SAMEOscar Edelstein, Hamden, Conn., assignor to The
Pond Lily Company, a corporation of Con-
necticutNo Drawing. Application July 15, 1941,
Serial No. 402,561

2 Claims. (Cl. 117—92)

This invention relates to improvements in the manufacture of water repellent textile or fibrous materials. The present application is a continuation-in-part of my application Serial No. 307,416, filed December 4, 1939, now Patent No. 2,323,387, granted July 6, 1943. An object of the present invention is to provide a method for rendering textile or fibrous materials water repellent and for maintaining their water repellence under exceptional conditions such as after repeated and prolonged washings or scourings in boiling solutions of strong soap and water or other detergents; 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 such 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 alkalis.

In an effort to remedy this condition, paraffin which is relatively inert and does not saponify with weak alkalis, 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 inadequately 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 material may be considered as carrying a negative charge, said opposite charges facilitating bonding of the two types of material for the purposes of this invention.

A water repellent agent such as paraffin may be 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. A binder useful for this purpose may be produced by impregnating the fabric with a suitable salt of a metal such as zirconium and forming a hydroxide on the fibers in a desired manner such 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 salt used. The removal of the acid radicals either by heating or by washing after ammonia treatment or as an incident of ammonia treatment alone appears to improve the adsorptive affinity of the hydroxide for the water repellent material. Accordingly the hydroxides remaining on the fabric as the 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 scourings or dry cleanings.

Improved resistance to scouring and dry cleaning treatments is observed with respect to the water repellency of fabrics treated with soluble salts such as formates, acetates, chlorides, sulphates, or other salts of zirconium which may be hydrolyzed to form a deposit consisting of insoluble hydroxides which, when the detrimental and useless substances, as the acid radicals of the salt used, are removed, is highly adsorptive. Such a deposit is adapted more effectively to retain on the fabric an application of a chemically inert wax such as paraffin, which, besides being water repellent, is substantially free from metal soaps or the like and therefore produces on the fibers an enduring optimum water repellent effect. The term "wax" is used herein in its generic sense to include all waxy materials.

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 salt of zirconium, preferably a zirconyl salt of a volatile organic acid such as formic acid; 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; and after ammonia treatment is rinsed in water to remove the detrimental or useless substances such as the acid radicals of the zirconyl salt. It is then squeezed, and dried.

The dried fabric is impregnated with a dispersion in the form of 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.

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 per unit of surface area of a given type of fibrous material or the like, the more durable the water repellency of that particular material. The quantity of repellent material such as paraffin to be deposited is relatively small, good water repellency in certain fabrics being obtained with as little as 3 ounces per 100 pounds of fabric. Larger quantities up to 2 to 3 pounds of paraffin per 100 pounds of fabric produce satisfactory repellency; but, depending on the character of the fibrous material treated, larger quantities of paraffin may noticeably affect the stiffness or feel or appearance of the material.

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.

In one alternative procedure, the fabric or fibrous material is impregnated with the salt solution and water repellent agent simultaneously. In such cases, the zirconyl formate or other impregnating solution used may be mixed with a dispersion in the form of an aqueous emulsion of a water repellent agent such as paraffin and the fabric impregnated with the mixture of zirconyl formate-paraffin emulsion in one operation followed by an alkaline treatment as described above. The use of said paraffin emulsion and zirconyl solution mixture reduces the number of steps in the process. Differently identified aqueous paraffin emulsions available on the market may be used for this purpose, one which gives satisfactory results being known under the trade name Paracol #507-O. S. #219 C, manufactured by the Hercules Powder Company. In another alternative procedure, the fabric is first treated with the paraffin emulsion and thereafter with the zirconyl solution.

In preparing mixtures of zirconyl formate and paraffin emulsion for use as set forth above, it should be noted that even a small amount of sulphate ions present in the formate solution will sometimes cause coagulation, rendering the mixture useless. Consequently it is desirable in such cases that the zirconyl formate be free of sulphate ions.

Although ammonia in water solution is a preferred alkaline treating agent, other alkaline reagents may be used. Such other alkaline reagents include triethanolamine, morpholine, ethylenediamine, or other amines. Some degree of repellency may also be obtained by using as an alkaline treating agent sodium or potassium hydroxide or carbonate solution or even boiling water without addition of an alkaline reagent.

When the salts used for impregnation are those of volatile acids such as formic or acetic, satisfactory results may also be obtained by omitting the alkaline treatment and heating the impreg-

nated fabric to a sufficiently high temperature to drive off the acid and form a hydroxide on the fibers. However, better results are usually obtained by washing with a boiling water solution of ammonia as above described.

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.—38 gallons of 4% water solution of zirconyl formate at a temperature of about 170° F. are mixed with 12 gallons of a 5½% paraffin wax emulsion also at 170° F. A 38 inch wide cotton twill fabric weighing 2¾ yards to the pound is impregnated with this mixture in any suitable apparatus such as a three bowl 50 gallon pad box by running the fabric continuously through the pad at a speed of approximately 40 yards per minute. The fabric is immersed in the mixture for 2 or 3 seconds, then passes through the nip of a pair of squeeze rolls, is immersed for a second period of 2 or 3 seconds and again passes through the nip of a pair of squeeze rolls. The nips or squeezes assist penetration of the liquor into the fabric and remove excess solution from the fabric. After impregnation, the fabric is immediately dried on steam heated drying rolls and then passes to a second three bowl pad box containing about 300 gallons of water to which has been added about 3 gallons of 28% aqua ammonia. The total time of immersion in the ammonia bath is of the order of 10 seconds and the fabric receives two nips or squeezes as in the impregnation step. The ammonia bath is preferably maintained at or near the boiling point. After ammonia treatment, the fabric is passed through a two bowl pad which is continuously supplied with running hot water and then dried on heated drying rolls.

Example 2.—Impregnation of the fabric with a solution of 4% zirconyl acetate, treating the fabric with an ammonia wash consisting of approximately 75 gallons of water and 2 gallons of 28% aqua ammonia, then impregnating the fabric with a paraffin solution consisting of approximately 10 pounds of paraffin dissolved in 30 gallons of carbon tetrachloride.

Example 3.—Initially preparing an emulsion of paraffin with zirconyl acetate, impregnating the fabric with the paraffin acetate emulsion thus prepared in one operation, and then after drying, the fabric is washed in a boiling ammonia solution consisting of approximately 75 gallons of water and 2 gallons of 28% aqua ammonia, which process is carried out in two main steps instead of three steps as set forth in Example 2.

Example 4.—The process of Example 2 can also be worked by substituting an aqueous emulsion of paraffin in place of the volatile solvent solution as a medium for the paraffin.

Example 5.—First immersing the fabric in zirconyl acetate, after which the fabric is freed of surplus solution, thoroughly squeezed, and then in a partially dried or even undried state, it is passed into an aqueous emulsion of paraffin, after which the fabric is then squeezed dry and finally given an ammonia wash of the character set forth in Example 2.

Example 6.—The reverse procedure of Example 5 may be followed in which the fabric is first treated with an aqueous emulsion of paraffin and then impregnated with the acetate, dried, and finally washed with the hot ammonia solution as set forth in Example 2.

Example 7.—38 gallons of a 4% water solution

of zirconyl acetate at a temperature of 170° F. are mixed with 12 gallons of 5½% paraffin wax emulsion also at 170° F. 250 pounds 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.

Example 8.—A cotton fabric is impregnated with a mixture of 38 gallons of a 4% solution of zirconyl acetate and 12 gallons of a 5½% aqueous paraffin wax emulsion made at 170° F. as in Example 7. 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 8a.—A cotton fabric is impregnated with zirconyl acetate, dried at a moderate temperature, and heated for one hour at 240° F. The fabric is then saturated with paraffin dissolved in a volatile solvent, such as carbon tetrachloride; and the excess thereof is removed, after which the fabric is ironed hot to remove the volatile solvent.

Example 9.—The fabric is impregnated with a 4% zirconyl acetate solution, then squeezed until it retains approximately 60% to 70% of its own weight of zirconyl acetate solution and is passed into an aqueous emulsion of paraffin containing approximately 1½% paraffin, after which the fabric is squeezed and dried and washed in boiling ammonia solution and hot water as set forth in Example 1.

In view of the foregoing description, it will be seen that, according to the present invention, fibrous material or fabric impregnated with a water solution of one or more of certain soluble zirconium salts and with a water dispersion of a repellent material, as paraffin, will, when treated with an alkaline solution and rinsed, or when heated for one hour to 240° F., if the salt is that of a volatile acid, have precipitated thereon an adsorptive binder as of hydrated oxide micelles of zirconium said binder is free from acid radicals of the zirconium salt and therefore effectively adsorbs the chemically inert paraffin, holding it tenaciously even when washed in boiling soap solution and/or immersed in commonly used dry cleaning solvents.

For the purpose of interpreting the present disclosure and the claims appended hereto, the term "dispersion", wherever used herein to indicate the condition of the paraffin or the character of the medium in which it is carried when applied to the fabric, is intended to include and generically designate the disclosed solutions, emulsions and/or suspensions of paraffin.

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 the cellulosic fibers 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, acetamide, 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 50 gallons of water, 22 pounds of zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$), 22 pounds formamide. This solution may be applied to and dried into cotton, rayon, or linen, at temperatures which might otherwise be expected to cause tendering of the cellulosic fibers.

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 by the terms of the appended claims.

I claim:

1. In a process of treating a fibrous material with a water repellent agent to render said material water repellent and substantially free from metallic soaps and from the acid radicals of any salt employed in said treatment whereby the water repellent effect produced on said material has improved durability and resistance to the action of strong alkaline detergents and to scouring and dry cleaning, the steps of impregnating said material with a solution of a zirconium salt of a volatile acid, heating said impregnated material at approximately 240° F. to volatilize said volatile acid, thereby leaving on the fibers of said material an insoluble binder comprising zirconium hydroxide, and treating said material with a dispersion of a chemically inert paraffin to produce a water repellent effect thereon.

2. A water repellent fibrous fabric having on the fibers thereof an insoluble binder comprising an insoluble zirconium hydroxide, and a deposit consisting of a chemically inert paraffin adsorptively bound to said fibers whereby the water repellent effect thereof has improved durability and resistance to the action of strong alkaline detergents, and to scouring and dry cleaning.

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 12, for "solutons" read --solutions--; page 3, first column, line 39, Example 9, before the word "dispersion" strike out "water" and insert the same before "repellent" in line 40; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 30th day of January, A. D. 1945.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.