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CELLULOSIC MATERIAL

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This invention relates to a treatment of cellulosic materials whereby they are given a permanent "finish" and other improved properties.

We use the term cellulosic materials to include cotton and other cellulosic natural fibres and regenerated cellulose substances in the form of fibre or film. Cellulose natural fibres include flex, jute, hemp, and sisal, wood pulp and other seed coat or bast or other vegetable structural fibrous matter. These and cotton are used in the manufacture of yarn and knitted and woven fabrics, and for making paper and cardboard.

The invention is applicable to the treatment of fibres in any stage of their manufacture. It is, however, particularly directed to the manufacture of woven materials with improved properties. When woven material or spun yarn is in question, the invention is not limited to the treatment of fabrics or yarns composed wholly of the cellulosic material, but includes also a treatment of composite fabrics or yarns, for instance, of union fabrics.

The improved properties conferred on the cellulose materials after they have been treated according to the invention may be collectively described as permanent water-repellent properties. In particular, woven fabrics may be so treated as to become water-repellent or showerproof, and this finish is permanent, that is, it is unaffected or not seriously affected by exposure to the weather, or by laundering, dry-cleaning, or other cleansing operations. Moreover, the handle of the treated materials (i. e. yarns and fabrics) is soft. By appropriate modification, when necessary, of the mode of treatment according to this invention, fabrics and yarns of varied soft handle may be obtained. This softening effect is likewise, of course, permanent.

The process of this invention is applicable to cellulosic materials whether or not they have been dyed. When, however, the materials have been dyed with certain dyestuffs substantive towards cellulose, namely, those of the "direct cotton colour" group, then another effect of the treatment is that the dyestuffs become more permanently attached to the material, i. e. dyestuffs of this group become fixed.

According to the invention we impregnate the said cellulosic materials with a quaternary ammonium salt of the general formula

$$R—O—CH_2—NR'R''R'''Hal$$

which is applied from aqueous solution and we then heat the so-impregnated material to the decomposition temperature of the said salt, preferably after previous drying.

In the general formula

$$R—O—CH_2—NR'R''R'''Hal$$

R stands for an aliphatic hydrocarbon radical of 12 or more carbon atoms which may be normal or branched paraffinoid, or ethylenoid, or may be more complicated as in naphthenyl alcohol, $NR'R''R'''$ stands for a tertiary amine which is either heterocyclic or aliphatic and the

$$R'R''R'''$$

not necessarily representing monovalent radicals but two may go together, or all three may go together as in pyridine, and Hal stands for halogen, preferably chlorine or bromine.

When $NR'R''R'''$ is heterocyclic it is typified by pyridine, but picoline or other pyridine homologue, or quinoline also serve, or an N-alkylpiperidine or N-benzyl-piperidine or C-homologue thereof; when $NR'R''R'''$ is aliphatic it is typified by trimethylamine, but triethylamine, tributylamine, triethanolamine or a dialkylcyclohexylamine will also serve.

The above compounds are synthesized by methods which are more fully discussed hereinbelow; but for the purpose of classification they may be looked upon as ethers derived from long-chain alcohols on the one hand and from the hydroxy methylene halide of a nitrogenous tertiary base on the other hand, according to the following scheme:

$$R—OH+HO—CH_2—NR'R''R'''Hal \rightarrow R—O—CH_2NR'R''R'''Hal+H_2O$$

In carrying the invention into practical effect the salt $R—O—CH_2—NR'R''R'''Hal$ is dissolved in aqueous medium, usually water alone to give a dilute aqueous solution. If desired, however, other adjuvants, such as wetting agents, or buffering agents, may be added to the bath. The cellulosic material is passed through or dipped in this dilute aqueous bath, the mechanical handling here being suited to the nature of the material. It is then dried and heated as described. The production of the desired effects is dependent to some extent on the conditions of drying and heating. Drying is preferably carried out at a relatively low temperature (hereinafter referred to as the drying temperature). The heating is at a higher temperature (conveniently called the baking temperature).

During heating there is decomposition of the salt, which is made manifest by there being ger-

erated an odour of pyridine when the salt is a pyridinium salt.

The operation of impregnation may be carried out preferably at a temperature below 40° C. especially when dilute aqueous solutions (e. g. 0.1%) are used; with more concentrated solutions (e. g. 1%) a hotter, even boiling solution may be applied. However, when kept at temperatures above 40° C. the solution may become acid and a less satisfactory finish, not so resistant to organic solvents, is obtained.

The drying temperature is preferably low. It is kept low in order that there may be no premature decomposition of the salt. But temperature of drying is a less important factor than speed and other conditions of drying. Thus, for instance, a cotton fabric impregnated with an aqueous solution of octadecycloxymethylpyridinium chloride and dried in more or less stagnant air, as in an oven without artificial circulation, should preferably be not submitted to a drying temperature of more than 30° C. inasmuch as the higher the temperature at this stage the more the intensity of the ultimate water repellent effect tends to diminish. When, on the other hand, the impregnated material is dried in a brisk current of hot air so that the water is removed rapidly (in about 3 minutes) then the drying temperature may rise to 80° C. without disadvantage.

Again, if the wet material impregnated in a 1% aqueous solution is dried on a steam-heated cylinder at 120° for e. g. 1 minute, no water-repellent effect is obtained. On continuing the heating for 5 minutes, water-repellent properties are indeed conferred on the material, but the so-treated material is sensitive to the action of solvents.

The baking treatment is essential for the production of permanent water-repellent properties. The impregnated and dried material begins to show water-repellent properties after baking for 10 minutes at 70° but the optimum effects are obtained when baking is carried out at 90–95° C. The time of baking necessary to produce the desired finishes varies with the baking temperature and depends also on the nature of the impregnation reagent. The time of baking can be shortened at higher temperatures. For example using octadecyloxymethylpyridinium chloride one must bake at 90–95° C. for at least 10 minutes, whereas at 115–120° C. 3 minutes will serve. The baking time should of course, be kept at a minimum to avoid damage to the fabric (tendering).

The following examples illustrate but do not limit the invention. The parts are by weight.

Example 1

2 parts of the ether of octadecyl alcohol and N-hydroxymethyl pyridinium chloride, conveniently also known as octadecyloxymethylpyridinium chloride, are dissolved with stirring in 98 parts of water at room temperature. Cotton fabric is then padded with this solution, squeezed and dried in warm air (30° C.). The dried material is then baked for half an hour at 90° C., cooled and washed in benzene. A water-repellent fabric of pronounced soft handle is obtained. The finish is resistant both to dry-cleaning and laundering.

Example 2

2 parts of the quaternary pyridinium halide of the preceding example are dissolved at room temperature in 245 parts of water and a cotton-wool union material padded with this solution. The material is squeezed and dried at 30° C., and then heated at 100° C. for 1 hour. A water-repellent fabric showing a very pronounced soft handle is obtained.

In the above example other cellulosic material, e. g. viscose artificial silk fibres and fabrics can be used.

Example 3

Cotton woven fabric, e. g. calico (1 part) dyed with a 3.6% shade of Chlorazol Blue BS (Colour Index No. 406) is treated for 20 minutes at 20° C. in 20 parts of a solution containing 1 part of octadecyloxymethylpyridinium chloride per 1000 parts of water. The dyeing is then squeezed and rinsed lightly and dried at a temperature of 40° C. At this stage the dyeing is different in shade from the original, being greener in tone. The dyed material is then baked for 30 minutes at 105° C., the shade unexpectedly returning to that of the original untreated dyeing. This treatment results in an appreciable improvement in the washing fastness of the dye on the dyed material and at the same time imparts to it a very soft handle and makes it waterproof.

Example 4

Cotton woven material, e. g. calico (1 part) dyed with a 2.0% shade of Chlorazol Fast Red FS (Colour Index No. 419) is treated as in Example 3. In this case after treatment with the quaternary salt and drying, the dyeing is much yellower in tone, but after baking, the original shade is restored. The washing fastness of the dyeing is much improved and a soft finish and water-repellent properties are imparted to the fabric.

Example 5

Unsized paper is passed through a 1% solution of octadecyloxymethylpyridinium chloride in water, passed between rollers to remove excess liquor and dried. It is then heated at 120° C. for 20 minutes. A water-repellent effect is produced on the paper.

If desired the final heating may be carried out on a rotary drying cylinder at 100° C. to 120° C.

Example 6

A regenerated viscose film is passed through a bath containing a 1% aqueous solution of octadecyloxymethylpyridinium chloride, drained and dried at 30°. It is then heated at 100° for 30 minutes. The surface of a film so treated is not readily wetted by water.

Example 7

A sisal rope is impregnated by immersing it until it is saturated in a bath at 40° C. containing 10 parts of octadecyloxymethylpyridinium chloride per 1000 parts of water.

It is then dried below 40° C. and then heated for 10 minutes at 110° C. The rope has increased flexibility and excellent water-repellent properties.

Example 8

Cotton sheeting is passed at room temperature in a continuous padding operation through an aqueous solution made from 1 part of cetoxymethylpyridinium chloride dissolved in 99 parts of water. The impregnated fabric is squeezed until it contains about its own weight of liquor and dried in a current of warm air at 40° C. The dried sheeting is then exposed to a temperature of 160° C. for a period of approximately 2 min-

utes. The treated pieces may be washed in benzene; a water repellent fabric of pronounced soft handle is obtained. The finish is resistant to laundering and dry cleaning.

Equally satisfactory results are obtained when the heating is carred out continuously on cans or by placing pieces in an oven.

Example 9

Viscose taffeta material dyed to a 2% shade with Chlorazol Fast Red KS (Colour Index No. 278) is given two ends on a jig in a solution containing 1 part by weight of oleyloxymethylpyridinium chloride in 199 parts by weight of water. At this stage the dyeing is different in shade from the original, being yellower in tone. The drying material is now exposed to a temperature of 120° C. for 4 minutes on drying cylinders. As a result of this baking treatment the original shade is partly restored, the shade being now only very slightly yellower in hue than that of the original. The finished fabric is rinsed thoroughly in benzene and dried. This treatment imparts an improved wash fastness of the dye on the material. It imparts also a soft, desirable finish and makes the fabric water-repellent. This soft, water-repellent finish is very resistant to laundering and dry cleaning.

In a manner similar to the above examples other compounds following the generic formula above indicated may be used for the purposes of this invention. Among the numerous compounds actually tried by us the following may be mentioned:

The ether of sperm oil alcohols (a mixture of mainly C_{10} to C_{20} alcohols, saturated and unsaturated) and hydroxymethylpyridinium chloride; the corresponding ether of naphthenyl alcohol, cetyloxymethylpyridinium chloride or bromide, and the dodecyl- and tetradecyl-oxymethyl pyridinium chlorides; octadecyl-, cetyl-, and dodecyl - oxymethyl - triethyl - ammonium chlorides; octadecyloxymethyl-quinolinium chloride and the corresponding salt made from the chloromethyl ether and triethanolamine.

Many of the above compounds in the above table are known in the art and have been prepared according to the literature by various methods, for instance, by the action of hydrogen chloride gas on a mixture of formaldehyde of 40 per cent strength and the corresponding long-chain alcohols, followed by the addition of pyridine (see British Patent No. 390,553). Also, in British Patent No. 394,196 the combination of octadecyl-chloromethyl-ether and triethylamine is described, as well as the production of a mixed ether from sperm oil alcohols and hydroxymethyl pyridinium or quinolinium chlorides.

Those compounds in the above table which have not been described in the art may likewise be synthesised by similar methods.

It will be understood that the above examples are merely illustrative, and that the details of procedure may be varied within wide limits, without departing from the spirit of this invention. For instance, the temperature of the baking treatment may vary from 70° C. to 200° C., the duration of the treatment being conveniently adjusted so as to avoid undue injury to the fibre. In practice the time of the baking-treatment may vary from a few seconds to one hour.

Likewise the drying treatment may vary as to time and temperature as already indicated above.

The concentration of the treating agent in the aqueous solution may vary from 0.1% to 2% or even higher if desired. The quantity of the agent applied with respect to the weight of fibre treated may be so chosen by controlling the amount of solution left upon the fibre after the bulk of the liquid has been squeezed out and may be from 0.1% to 2% by weight of the fibre.

Many other variations and modifications will be apparent to those skilled in this art.

In the claims below the phrases "higher alkyloxy" and "higher aliphatic" shall be understood as referring to alkyloxy and aliphatic radicals, respectively, having 12 or more carbon atoms, said phrases being otherwise inclusive of open chain, branched chain, paraffinoid and ethylenoid radicals as well as of cycloaliphatic radicals as in naphthenyl alcohol.

We claim:

1. A process for treating cellulosic material whereby to impart thereto an improved permanent finish, which comprises impregnating the same with a compound of the general formula R—O—CH_2—NR'R''R'''—Hal, wherein R stands for an aliphatic radical containing not less than 12 carbon atoms, and wherein R', R'' and R''' represent three aliphatic radicles, while Hal stands for halogen, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose said quaternary compound, as evidenced by liberation of the free base.

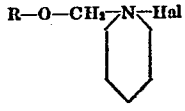
2. A process for treating cellulosic material whereby to impart thereto an improved permanent fininsh, which comprises impregnating the same with a compound of the general formula R—O—CH_2—NX—Halogen, wherein R stands for an aliphatic radical containing not less than 12-carbon atoms, while NX designates an organic heterocyclic nitrogeneous base, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose said quaternary compound, as evidenced by liberation of the free base.

3. A process for treating cellulosic material whereby to impart thereto an improved permanent finish, which comprises impregnating the same with a higher alkyloxy methylene pyridinium halide, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose said quaternary compound, as evidenced by liberation of the free base.

4. A process for treating cellulosic material whereby to impart thereto a water-repellent finish, which comprises impregnating the same with an aqueous solution of a compound of the general formula R—O—CH_2—NX—Halogen, wherein R stands for an aliphatic radical containing not less than 12 carbon atoms, while NX designates a nitrogenous tertiary base, drying the material under conditions avoiding excessive decomposition of said quaternary compound, and then heating the dried impregnated material at a temperature sufficient to decompose said quaternary compound, as evidenced by liberation of the free base.

5. A process for treating cellulosic material whereby to impart thereto a water-repellent finish, which comprises impregnating the same with an aqueous solution of a higher alkyloxy methylene pyridinium halide, drying the material under conditions avoiding excessive decomposition of said quaternary compound, and then heating the dried impregnated material at a temperature sufficient to cause chemical change in said quaternary compound, as evidenced by the liberation of pyridine.

6. A process for treating cellulosic fibrous material whereby to impart thereto a water-repellent finish, which comprises impregnating said fibrous material at a temperature below 40° C. with an aqueous solution of a long chain alkoxy methylene pyridinium halide of the general formula



wherein R is an aliphatic radicle having from 16 to 20 carbon atoms, and Hal stands for chlorine or bromine, drying the material at a temperature not exceeding 40° C. and then baking the dried impregnated material at a temperature between 70 and 150° C. for a period of time between 2 minutes and ½ hour.

7. A process for treating cellulosic fabric whereby to impart thereto a water-repellent finish, which comprises impregnating said fabric with an aqueous solution of octa-decoxy methylene pyridinium chloride, drying the impregnated fabric at a temperature not exceeding 40° C., and then heating the dried material in the absence of moisture at a temperature between 105 and 120° C. whereby to decompose the pyridinium compound and split off the pyridine.

8. Cellulosic fibrous material having water-repellent properties and being produced by the process defined in claim 3.

9. Cellulosic fabric impregnated according to the process defined in claim 6, said fabric being characterised by having water-repellent properties and a soft handle as compared to untreated fabric.

10. In the process of treating textile material with a quaternary nitrogeneous compound having a methylene group attached to the quaternary nitrogen atom and a higher aliphatic hydrocarbon radical attached to said methylene group by the aid of an oxygen atom, the step which comprises heating fabric impregnated with said compound at a temperature of at least 105° C. in the absence of moisture.

11. In the process of treating cellulosic fibrous material with a higher alkyloxymethylene-pyridinium halide in aqueous solution, whereby to improve its surface characteristics, the steps which comprise first removing moisture from the impregnated fibrous material at a temperature sufficient to decompose said pyridinium compound, and then heating the dried material in the absence of moisture to a temperature sufficient to decompose said pyridinium compound as evidenced by the liberation of pyridine.

12. A process for rendering cellulose textile material water-repellent which comprises impregnating the material with an alkoxy methylene quaternary ammonium compound having the formula R—O—CH_2—NX—Halogen in which R stands for an aliphatic radical containing at least twelve carbon atoms and NX for a tertiary amine, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

13. A process for rendering cellulose textile material water-repellent which comprises impregnating the material with octadecyloxymethylene pyridinium chloride, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose the compound with the liberation of the free amine.

14. Cellulosic textile material having water-repellent properties and being the product of a process as defined in claim 13.

15. Cellulosic textile material shaving water-repellent properties and being the product of a process as defined in claim 12.

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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 4, first column, line 23, claim 7, for "octa-decoxy" read --octadecoxy--; same page, second column, line 11, claim 11, for the word "sufficient" read --insufficient--; 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 8th day of July, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)