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TREATMENT OF 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. Cellulosic natural fibres include flax, 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 compound of the general formula

$$R—CO—N(R'')—CH_2—N(\text{tert})—X \quad (I)$$

as more fully defined below, which is applied from aqueous medium, and we then heat the so-impregnated material to the decomposition temperature of said compound, preferably after previous drying.

In the above general formula R is an aliphatic hydrocarbon radical of 10 or more carbon atoms which may be normal or branched, paraffinoid or ethylenoid; or it may be of a more complicated aliphatic hydrocarbon structure, as in the parent hydrocarbon of the naphthenic acids or their hydrogenation products; while R'' stands for hydrogen or a hydrocarbon radical. It will be noted that R—CO is an acyl radical, that is the radical of the acid of a fat or fatty oil, or the radical of a physically similar acid.

Again, in the formula given above, —N(tert)— stands for a tertiary amine which is either heterocyclic or aliphatic. When —N(tert)— is heterocyclic it is typified by pyridine, but picoline or other pyridine homologue, or quinoline also serve, or an N-alkyl-piperidine or N-benzyl-piperidine or a C-homologue thereof; when —N-(tert)— is aliphatic it is typified by trimethylamine, but trimethylamine, tributylamine, triethanolamine or a dialkylcyclohexylamine will also serve.

Finally in the formula given above X stands for a monovalent acid group.

For a better understanding of the herein following disclosure, but without any intent to limit the generic nature of this invention, the following typical compounds are mentioned as illustrative of the scope of Formula I above:

Stearamido-methyl-pyridinium chloride:

$$C_{17}H_{35}—CONH—CH_2—N(C_5H_5)—Cl$$

Stearo-methylamido-methyl-pyridinium chloride:

$$C_{17}H_{35}—CO—N(CH_3)—CH_2—N(C_5H_5)—Cl$$

Stearamido - methyl - pyridinium - hydrogen - sulfate;

Oleylamido-methyl-pyridinium chloride;

and the corresponding trimethylammonium, triethanolammonium etc. salts.

In carrying the invention into practical effect the compound of Formula I above is dissolved or suspended in aqueous medium, usually water alone to give a dilute aqueous solution or suspension.

In general, the operation of impregnating the cellulosic material 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; then a less satisfactory finish, not so resistant to organic solvents, is obtained.

Thus with woven cotton fabrics, e. g. that known in the trade as limbric, a dilute aqueous solution of the compound e. g. stearamidomethyl-pyridinium chloride, may be employed, and the concentration may be as low as 0.05%. The fab-

ric is padded in this solution, and squeezed. It then contains about its own weight of solution, and thus the amount of compound with which the fabric is impregnated is about the same percentage of the weight of the cloth as the percentage strength of the solution. The padding is conveniently carried out at about 40° C. Higher temperatures are preferably avoided, as the compound used tends to decompose in hot aqueous solution. Thus, a 0.5% aqueous solution of stearamidomethyl-pyridinium chloride becomes useless if it has been kept at 60° C. for more than two hours or at 80° C. for more than one hour.

If desired, however, other adjuvants, such as wetting agents, or buffering agents, may be added to the bath. Suitable wetting agents are the formaldehyde-naphthalene-sulphonic acid condensation products. Alkaline substances or especially substances that have a buffering action, may conveniently be added to assist in keeping the solutions or suspensions neutral or at least not acid to avoid tendering of the cellulosic material.

Suitable such substances are pyridine, borax, disodium hydrogen phosphate or sodium acetate. Hexamethylene-tetramine also is a suitable adjuvant as it decomposes when heated to give ammonia.

The cellulosic material is passed through or dipped in this dilute aqueous bath, the mechanical handling being of course suited to the nature of the material.

After immersion in the aqueous solution the material is preferably but not necessarily dried. If a concentrated solution, even 0.5%, is used, it is not necessary to dry. 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).

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 stearamidomethylpyridinium, 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° C. for e. g. one minute, no water-repellent effect is obtained. On continuing the heating for five minutes, water-repellent properties are indeed conferred on the material, but the so-treated material is sensitive to the action of the solvents.

The baking treatment is essential for the production of permanent water-repellent properties. The impregnated material begins to show water-repellent properties after baking for ten minutes at 65° but the optimum effects are obtained when baking is carried out at 90–120° C. Poor results are obtained at a higher temperature, e. g. 150° 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 stearamidomethylpyridinium chloride one must bake at 105° C. for five minutes, or at 120° C. for one-and-a-half minutes. The baking time should, of course, be kept at minimum to avoid damage to the fabric (tendering).

During the baking treatment there is decomposition of the salt which is made manifest when a pyridinium compound is used, by there being generated an odor of pyridine.

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

Example 1

Cotton sheeting is immersed for ten minutes at 20° C. in an impregnating bath consisting of a solution of five parts of stearamidomethylpyridinium chloride in 1000 parts of water. The impregnated material is then squeezed and dried by heating for ten minutes at 105° C. A fabric having a water-repellent finish and soft handle is obtained. The finish is resistant to dry-cleaning and laundering.

Example 2

A viscose rayon fabric is immersed for ten minutes at 20° C. in a solution of five parts of stearamidomethylpyridinium chloride in 1000 parts of water. The impregnated material is then squeezed and dried by heating at 105° C. for ten minutes. The resulting fabric has a water-repellent finish and a soft handle which is resistant to dry cleaning and laundering.

Example 3

Cotton sheeting is immersed for fifteen minutes at 20° C. in a solution of five parts of stearomethylamidomethylpyridinium chloride in 1000 parts of water. The material is squeezed, dried in a current of warm (30° C.) air and then heated for 20 minutes at 105° C. A fabric is obtained which has a water-repellent finish and a soft handle. The finish is highly resistant to dry cleaning and laundering.

Example 4

Cotton sheeting is padded at room temperature in a solution containing one part of stearamidomethylpyridinium hydrogen sulphate and two parts of pyridine in 197 parts of water The material is squeezed to remove excess solution from the cloth and is then dried in a current of warm air at 30° C. It is then heated for 30 minutes in an oven at 105° C.

The finished material is highly water-repellent and has a pleasing soft handle. This water-repellent softer finish is very resistant to laundering and dry-cleaning.

Example 5

Cotton sheeting which has been dyed to a 2% shade with Chlorazol Fast Red K (Colour Index No. 278) is padded at room temperature in a solution containing 1 part of palmitoamidomethylpyridinium chloride in 199 parts of water. The material is squeezed and dried below 40° C. At this stage the shade of the dyeing is different from that of untreated dyeing, being yellower in tone. The treated material is now heated in an oven for ten minutes at 105° C. This heating

treatment practically restores the original shade, the dyeing being only slightly weaker in tone.

The dyeing now shows an improved fastness to washing (see Schultz, Farbstoff-tabellon, 7th edition, page XXXIII). In addition the material has a soft finish and is water-repellent. The finish is resistant to laundering and dry-cleaning.

Example 6

Cotton sheeting is treated at 35° C. in a continuous padding operation, with a solution containing 1 part of stearomidomethyl pyridinium chloride in 2000 parts of water. The material is squeezed, dried below 40° C. and is then heated for five minutes at 120° C. on a can drier.

The finish on the material is now soft and water-repellent and is resistant to laundering and dry-cleaning.

Example 7

Cotton sheeting is treated at room temperature with a solution containing 1 part of stearamidomethyl pyridinium chloride in 199 parts of water. The material is squeezed, dried at a temperature below 40° C. and is then heated for a period of 1½ minutes at 120° C. on a drying cylinder.

The material has now a very soft finish and it is water-repellent. This finish is resistant to laundering and dry-cleaning processes.

Example 8

1 part of stearamidomethylpyridinium sulphite (which may be prepared in the manner described below) is dissolved in 99 parts of water at room temperature. Cotton sheeting is then padded with this solution, squeezed and dried in warm air (30° C.). The dried fabric is then heated for 20 minutes at 105° C. The resulting fabric has a water-repellent, soft finish, which is resistant to dry cleaning and laundering.

The stearamidomethylpyridinium sulphite used in the above example may be prepared as follows: 30 parts by weight of stearamide, 120 parts by weight of pyridine and 12 parts by weight of paraformaldehyde are stirred together at 90–100° C. Gaseous sulphur dioxide is passed into the heated mixture until a test sample of the mixture dissolves to a clear solution in water. Pyridine and unreacted paraformaldehyde are then evaporated from the reaction mixture by heating at 40–50° C. under reduced pressure, for example, 15 mm. The desired product is thus obtained as a viscous mass which may be further purified, if desired, by washing with acetone.

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 the following may be mentioned—

Stearamidomethylpyridinium m-nitrobenzene-sulphonate
Stearamidomethylpyridinium nitrate
Stearamidomethylpyridinium bromide
Oleylamidomethylpyridinium chloride
Lauramidomethylpyridinium chloride
Lauramidomethylpyridinium sulphate (made from the entire acids of cocoanut oil)

In place of the fatty acids thus referred to, others may be used. Thus, the starting out materials may be the fatty acids of palm oil, cotton seed oil, tallow, or derived acids such as those obtained by the processes of fat hydrogenation.

Some of the said compounds are made by bringing together a hydroxymethylamide of a fatty acid and a tertiary amine salt or an addition compound of a tertiary amine and an inorganic acid anhydride: for example, stearohydroxymethylamide (made from stearamide and paraformaldehyde) is treated with pyradine hydrochloride in pyridine; or stearamide, paraformaldehyde, and anhydrous pyridine hydrochloride, nitrate, m-nitrobenzene-sulfonate or the like are caused to react together in pyridine solution; or stearomethylamide, formaldehyde and hydrogen chloride are caused to interact to give stearomethylamide methyl chloride, which is then combined with pyridine or other tertiary amine.

Instead of pyridine in the last mentioned synthesis, trimethylamine or triethanolamine may be used.

Methods of making some of the compounds the use of which is contemplated in the invention are the subject of British Patents Nos. 471,130 and 475,170, and the corresponding U. S. Patents Nos. 2,131,362 and 2,146,392.

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 0.01% 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 0.01% to 2% or more by weight of the fibre.

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

We claim:

1. The process of treating cellulosic material whereby to impart thereto water-repellent properties which comprises heating the same at a temperature between 70 and 200° C., in the absence of moisture, but in intimate contact with a quaternary organic nitrogen compound formed by the interaction between a tertiary organic nitrogenous base and a higher aliphatic amide of the general formula

$$R{-}CO{-}N(R'')-CH_2-X$$

wherein R is an aliphatic hydrocarbon radical containing at least 10 carbon atoms, R'' is a member of the group consisting of hydrogen and hydrocarbon radicals, while X is the anion of a salt-forming acid.

2. A process for imparting to cellulosic material durable water-repellent properties, which comprises impregnating said material with a quaternary ammonium compound of the general formula

$$R{-}CO{-}N(R'')-CH_2-N\,(tert)-X$$

wherein the group R—CO— represents the acyl radical of a fatty acid having not less than 11 carbon atoms, R'' stands for a member of the group consisting of hydrogen and hydrocarbon radicals, N(tert) stands for the radical of a ter-

tiary nitrogenous base selected from the group consisting of aliphatic and heterocyclic tertiary nitrogenous bases, while X stands for a monovalent acid group, and then heating the impregnated material to a temperature sufficient first to drive off moisture and then to cause decomposition of said quaternary ammonium compound, liberating the free tertiary base.

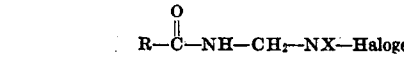
3. Cellulosic textile material impregnated with a surface improving agent according to the process defined in claim 2.

4. A process as claimed in claim 2 wherein the cellulosic material is padded in an aqueous solution, dried at a low temperature, and then baked at a temperature not less than 100° C.

5. A process as in claim 2, the impregnation being effected from aqueous bath and the latter containing further a substance having a buffering action to assist in keeping down the acidity of the medium surrounding the fiber during the heat treatment.

6. A process as in claim 2, the impregnation being effected from aqueous bath and the latter containing sodium acetate.

7. A process for rendering cellulose textile material water-repellent which comprises impregnating the material with a quaternary ammonium compound of the formula

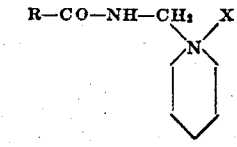


in which R stands for an aliphatic radical containing at least ten carbon atoms and NX for a tertiary amine, and then heating the impregnated material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

8. Cellulosic material impregnated with a surface improving reagent as defined by the process and compounds defined in claim 7.

9. The process of treating cellulosic material whereby to impart thereto improved surface characteristics which comprises impregnating the same with a quaternary compound of the general formula R—CO—NH—CH_2—N(aliph)—X, wherein R is an aliphatic radical having not less than 10 carbon atoms and attached to the CO group above through one of its own carbon atoms; N(aliph) stands for the molecule of a tertiary aliphatic amine, while X is the anion of an ionizable acid; and heating said material in the absence of moisture at a temperature sufficient to decompose the quaternary ammonium compound with the liberation of the free amine.

10. The process of treating cellulosic material whereby to impart thereto improved surface characteristics which comprises impregnating the same with a quaternary compound of the general formula



wherein R is an aliphatic radical having not less than 10 carbon atoms and attached to the CO group above through one of its own carbon atoms, while X is the anion of an ionizable acid, and heating said material in the absence of moisture at a temperature sufficient to decompose said quaternary compound as evidenced by the liberation of free pyridine.

11. A process for rendering cellulose textile material water-repellent which comprises impregnating the material with stearamidomethylene pyridinium chloride, then drying and heating the impregnated material at a temperature sufficient to decompose the compound as evidenced by the liberation of free pyridine.

12. Cellulosic textile material impregnated according to claim 11, said textile material being characterized by having water-repellent properties and a soft feel as compared to the untreated material, which properties are fast to laundering.

13. The process of treating cellulosic textile fabric whereby to impart thereto water-repellent surface characteristics, which comprises treating the same with an aqueous solution of stearamidomethylene pyridinium chloride at a temperature not exceeding 40° C., drying said material at a temperature not exceeding 40° C. and then heating the dried material in the absence of moisture at a temperature between 100 and 120° C.

14. A process as in claim 11 modified to this extent, that the drying step is merged into the subsequent heating step the combined treatment being effected at a temperature of between 90 and 130° C.

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