United States Patent

Widder et al.

[15] **3,664,864**

[45] **May 23, 1972**

[54] DURABLY SHAPING KERATINOUS FIBROUS MATERIALS

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[30] **Foreign Application Priority Data**

July 27, 1968 Germany ..... P 17 69 865.6

[52] **U.S. Cl.** **117/119.8**, 8/127.6, 117/11;139.4;65.2, 117/141

[51] **Int. Cl.** **B44d 1/48**, D06n 13/36

[58] **Field of Search** ..... 117/141, 119.8, 140 R, 139.7, 117/135.5, 63, 69; 260/501.12; 8/127.6, 128

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[57] **ABSTRACT**

Durable shaping of keratinous fibrous materials by impregnation with solutions or dispersions of compounds which in the betaine form have the formula $R^1R^4R^5N^{\oplus}—CHR^2—CHR^3—O-SO_2^{\ominus}$ wherein R^1 is an unsubstituted or substituted hydrocarbon radical, R^2 and R^3 each denotes a hydrogen atom or a lower alkyl radical, and R^4 and R^5 each denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical and heating with steam at 100° to 150° C while shaping; fibrous materials thus treated.

12 Claims, No Drawings

DURABLY SHAPING KERATINOUS FIBROUS MATERIALS

It is known that fibrous material containing or consisting of keratin can be durably shaped in the required manner by impregnating it with a mercaptocarboxylic acid and then oxidizing it, or treating it with steam, while shaping. This method has a number of disadvantages which complicate or limit its use. For example, it is difficult to produce consistent results; colored articles readily undergo color changes at the treated places, and intensely red discoloration occurs when iron ions are present; moreover, the treatment has to be carried out by garment manufactures rather than by weavers.

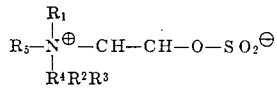
For the last mentioned reason it has been desirable to provide a process which would enable weavers to sensitize fibrous material of the said kind, i.e., impart to it the property, persisting for a prolonged period, of being capable of retaining indefinitely any shape imparted to it by simple measures. One method of achieving this aim which has been suggested is to treat fibrous material of the said kind with sodium or ammonium sulfite, a durable change of shape being obtained by shaping the material while treating it with steam at elevated temperature.

This process, too, does not fully satisfy the processors requirements. The sensitization achieved in the first operation is lost again after some time, so that it is often impossible to keep the material in a sensitized condition for sufficiently long periods on its way from the finisher to the processor.

Salts of monoethanolamine have also been proposed for durable shaping of keratinous fibrous material. However, the effects obtainable are not sufficiently durable to laundering.

We have now found a method for the durable shaping of keratinous fibrous material, e.g., yarn, non-woven fabrics, felts and preferably woven and knitted fabrics, as well as textiles prepared therefrom, particularly garments, of wool or other animal fibers, which method does not have the said disadvantages.

The method of the invention comprises impregnating fibrous material with an aqueous solution or dispersion of a compound which in the betaine form has the general formula

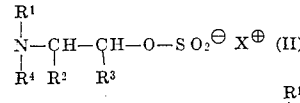


where R^1 is an unsubstituted or substituted hydrocarbon radical, R^2 and R^3 are hydrogen atoms or lower alkyl radicals preferably having from one to five carbon atoms, and R^4 and R^5 are hydrogen atoms or unsubstituted or substituted hydrocarbon radicals preferably having from one to 20 carbon atoms, and heating the impregnated materials with steam at 100° to 150° C while shaping, if desired after drying, intermediate storage and/or making it into garments.

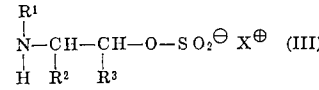
The radicals R^1, R^4 and R^5 in Formula I may be for example alkyl, cycloalkyl, aryl or aralkyl radicals having from one to 20 carbon atoms which may bear substituents such as hydroxyl or alkoxyl groups. Example of suitable radicals are methyl, ethyl, 2-hydroxyethyl, propyl, 2-hydroxypropyl, butyl, 2-ethylhexyl, octyl, dodecanyl, cyclohexyl, phenyl, tolyl, benzyl, methoxyethyl, ethoxyphenyl and 4-ethoxybutyl.

Among the compound to be used according to the invention those are preferred in which the radical R^1 contains up to 15 carbon atoms, R^2 and R^3 are hydrogen or methyl and R^4 and R^4 are hydrogen or aliphatic radicals having up to two carbon atoms.

The substances to be used for the purposes of the invention are shown in Formula I in the betaine form. Provided the radicals R^4 and/or R^5 are not hydrocarbon radicals, the substances may also be present in the form of ordinary salts in which the nitrogen atom has lost its positive charge owing the elimination of a proton, and the negative charge of the resultant anion is compensated by a separate cation X^+.



(II) or



(III)

The nature of the cation X^+ has no appreciable effect on the suitability of the substances to be used according to the invention. It may be for example an alkali metal, ammonium or substituted ammonium ion, in particular one having the formula

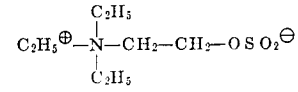
$$R^1—\overset{+}{N}H_3$$

or

$$R^4—\overset{+}{N}H_2—R^4 .$$

Whether the substances to be used according to the invention are present in the impregnating liquor in the betaine form or in the form of a salt II or III depends on the pH of the liquor, also in generally the case with dipolar ions.

Examples of compounds having the above general formulae are



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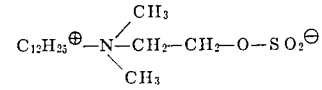

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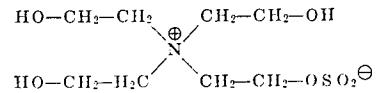

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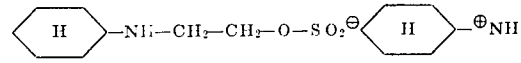
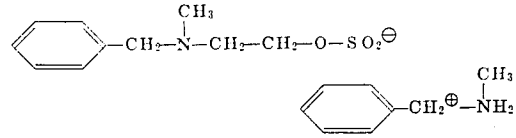


(VII)

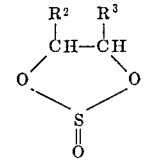
and



(VIII)

The compounds of the general Formula I, II or III may be prepared for example by the method described in U.S. Pat. application Ser. No. 823,160, filed May 8, 1969, by Harry Distler et al. by reaction of amines having the general formula

with 1,2-glycol sulfites of the general formula



where the radicals R^1 to R^5 have the meanings given above.

The compounds of the general Formula I, II or II are used in the form of their aqueous solutions or dispersions, especially their aqueous solutions. They are applied to the fibrous material in the usual manner, for example by knife coating, spraying, dipping or preferably by padding. It has been found advantageous to apply the solutions or dispersions at such a rate that 0.01 to 0.2 mole, preferably 0.02 to 0.1 mole, of a compound of the general Formula I, II or III is applied per kilogram of material to be treated.

It is sometimes expedient to add wetting agents to the impregnating liquors in order to achieve rapid penetration and equal distribution of the ingredients. Non-ionic wetting agents are preferred. Wetting agents are dispensible if the material has already been wetted in an earlier treatment.

The impregnating liquors may contain other ingredients conventionally used for treating keratinous fibers, for example water and oil repellents, such as silicones and compounds having perfluorinated carbon chains. After impregnation the fibrous material can be immediately brought into the desired shape in the presence of steam, if desired after intermediate drying. The special advantages of the new process are however particularly apparent when shaping is carried out later, because after the said intermediate drying operation the impregnated material can be stored for very long periods without the sensitizing effect imparted by the impregnation being lost. Shaping can be carried out at any processing stage in the presence of steam, and the material will retain the shape imparted to it. It is possible to shape mechanically, for example by means of smooth or structured rollers, molds, plating presses or goffering equipment, or manually, for example by ironing. At any rate care must be taken to ensure that hot steam can act on the material while this is being treated. Temperatures between 100° and 150° C are used for shaping.

By the said method the fibrous material can for example be calendered, embossed, goffered, and particularly pleated and creased. The effects obtained are highly durable, i.e., they are not lost in use or any cleaning operations.

Fabrics containing or consisting of keratin fibers, or garments made of such material, can therefore be given an easy-care finish. The process of the invention furthermore results in a substantial improvement in the handle, and the presence in the fibrous material of unreacted compounds of the general Formula I, II or III makes the material easier to shape in garment fabrication.

The new process can be applied with special advantage after a shrink-resist finishing operation, for example a treatment with oxidizing agents such as dichlorocyanuric acid or salts thereof.

The invention is further illustrated by the following examples in which parts are by weight unless otherwise specified.

EXAMPLE 1

Made-up men's trousers of pure wool are sprayed with a 5 percent aqueous solution of the compound of Formula VI at the places where they are to be creased, until the sprayed portions have increased 40 – 50 percent in weight. The trousers are then arranged in the press and treated for 10 to 20 seconds with steam at 100° to 120° C while pressing to give the desired creases. After the steam has been shut off, the trousers are left in the press for another 20 to 30 seconds, suction being applied for 5 seconds to accelerate cooling.

The trousers obtained exhibit extremely durable creases.

EXAMPLE 2

Pure wool cloth (plain weave; 250 g/m²) is padded with a 5 aqueous solution of the substance of Formula VII and squeezed to a wet pickup of 50 percent. The material is then decatized by treating it for 5 minutes with saturated steam at 2 atm. gauge. Suction is applied for 3 to 5 seconds and the cloth dried on a stenter with 3 percent overfeed at 100° C. The cloth thus treated is distinguished by an improved hand, is smoother in appearance, and has improved crease behavior in the wet condition and a durable decatizing effect.

EXAMPLE 3

Cloth of the type described in Example 2 is impregnated and dried as described in that example. It is then stored for 3 months and made into trousers. It is found that the trousers are easier to shape than trousers of the same material which has not been impregnated with the substance of Formula VII. The trousers are steamed in an ironing press in the way described in Example 1. They have sharp and very durable creases and improved crease behavior in the wet condition.

EXAMPLE 4

Made-up men's trousers of pure wool are sprayed with a 5 percent aqueous solution of the compound of Formula IV at the places where they are to be creased, until the sprayed portions have increased 40 – 50 percent in weight. The trousers are then arranged in the press and treated for 10 to 20 seconds with steam at 100° to 120° C while pressing to give the desired creases. After the steam has been shut off, the trousers are left in the press for another 20 to 30 seconds, suction being applied for 5 seconds to accelerate cooling.

The trousers obtained exhibit extremely durable creases.

EXAMPLE 5

Pure wool cloth (plain weave; 250 g/m²) is padded with a 5 percent aqueous solution of the substance of formula V and squeezed to a wet pickup of 50 percent. The material is then decatized by treating it for 5 minutes with saturated steam at 2 atm. gauge. Suction is applied for 3 to 5 seconds and the cloth dried on a stenter with 3 percent overfeed at 100° C. The cloth thus treated is distinguished by an improved hand, is smoother in appearance, and has improved crease behavior in the wet condition and a durable decatizing effect.

EXAMPLE 6

Cloth of the type described in Example 5 is impregnated and dried as described in that example. It is then stored for 3 months and made into trousers. It is found that the trousers are easier to shape and dress than trousers of the same material which has not been impregnated with the substance of Formula V. The trousers are steamed in an ironing press in the way described in Example I. have sharp and very durable creases and improved crease behavior in the wet condition.

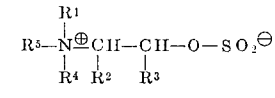
EXAMPLE 7

Made-up men's trousers of pure wool are sprayed with a 5 percent aqueous solution of the compound of Formula VIII at the places where they are to be creased, until the sprayed portions have increased 40 – 50 percent in weight. The trousers are then arranged in the press and treated for 10 to 20 seconds with steam at 100° to 120° C while pressing to give the desired creases. After the stem has been shut off, the trousers are left in the press for another 20 to 30 seconds, suction being applied for 5 seconds to accelerate cooling.

The trousers obtained exhibit extremely durable creases.

We claim:

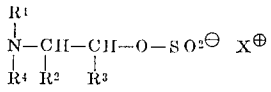
1. A method of durably shaping keratinous fibrous material which comprises impregnating said fibrous material with an aqueous solution or dispersion of a compound which in the betaine form has the general formula



or salt thereof where R^1 is an unsubstituted or substituted hydrocarbon radical, R^2 and R^3 denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical, and heating the impregnated material with steam at 100° to 150° C while shaping.

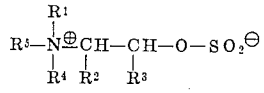
2. A method as claimed in claim 1 wherein the betaine compound used is one where R^1 is an unsubstituted or substituted hydrocarbon radical having up to 15 carbon atoms, and R^2 and R^3 each denotes a hydrogen atom or an alkyl radical having up to two carbon atoms.

3. A method of durably shaping keratinous fibrous material which comprises impregnating said fibrous material with an aqueous solution or dispersion of a compound which in the salt form has the general formula



where R^1 is an unsubstituted or substituted hydrocarbon radical, R^2 and R^3 each denotes a hydrogen atom or a lower alkyl radical, R^4 denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical and $X^{\oplus}$ is a cation, and heating the impregnated material with steam at 100° to 150° C while shaping.

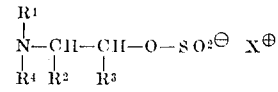
4. Keratinous fibrous material which has been impregnated with an aqueous solution or dispersion of a compound which in the betaine form has the general formula



or salt thereof, where R^1 is an unsubstituted or substituted hydrocarbon radical with one to 15 carbon atoms, R^2 and R^3 are hydrogen atoms or alkyl radicals having from one to 5 carbon atoms, R^4 and R^5 are hydrogen atoms or unsubstituted or substituted hydrocarbon radicals having from one to 20 carbon atoms.

5. Keratinous fibrous material as claimed in claim 4 wherein the betaine compound used is one where R^2 and R^3 each denotes a hydrogen atom or an alkyl radical having up to two carbon atoms.

6. Keratinous fibrous material which has been impregnated with a betaine salt having the formula



where R^1 is an unsubstituted or substituted hydrocarbon radical, R^2 and R^3 each denotes a hydrogen atom or a lower alkyl radical, R^4 denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical, and $X^{\oplus}$ is a cation.

7. Keratinous fibrous material as claimed in claim 6 wherein $X^{\oplus}$ is an alkali metal, ammonium or substituted ammonium cation.

8. A method as claimed in claim 1 wherein said heating while shaping is conducted after drying of the impregnated keratinous fibrous material.

9. A method as claimed in claim 1 wherein said fibrous material is in the form of a garment during said heating while shaping.

10. A method as claimed in claim 3 wherein $X^{\oplus}$ is an alkali metal, ammonium or substituted ammonium cation.

11. A method as claimed in claim 3 wherein R^4 is a hydrogen atom.

12. Keratinous fibrous material as claimed in claim 6 wherein R^4 is a hydrogen atom.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,664,864 Dated May 23, 1972

Inventor(s) Rudi Widder, Harry Distler, and Erwin Haug

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 45, to the right of the formula, insert-- I --; line 64, "compound" should read -- compounds --; line 67, "R^4" should read -- R^5 --.

Column 2, line 19, "in generally" should read -- generally --; line 67, "I, II or II" should read -- I, II, or III --.

Column 4, line 37, "Example 1. have" should read -- Example 1. They have --;lines 67 to 68, claim 1, "denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical" should read -- each denotes a hydrogen atom or a lower alkyl radical, and R^4 and R^5 each denotes a hydrogen atom or an unsubstituted or substituted hydrocarbon radical --.

Signed and sealed this 5th day of December 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents