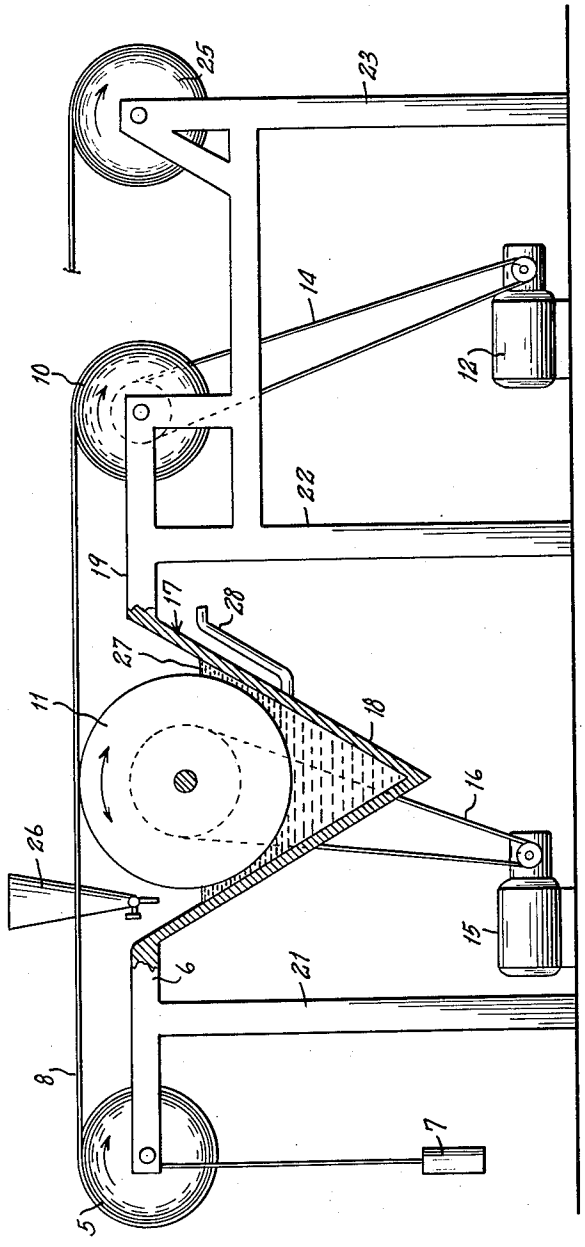
Oct. 30, 1962 G. C. TESORO ETAL 3,061,399

TREATING COTTON TO IMPROVE WET AND DRY CREASE RECOVERY IN ONE OPERATION

Filed Feb. 9, 1959



INVENTORS
GIULIANA C. TESORO
PAUL I. LINDEN

BY

Kenyon & Kenyon

ATTORNEYS

United States Patent Office

3,061,399

Patented Oct. 30, 1962

3,061,399

TREATING COTTON TO IMPROVE WET AND DRY CREASE RECOVERY IN ONE OPERATION

Giuliana C. Tesoro, Dobbs Ferry, N.Y., and Paul I. Linden, North Arlington, N.J., assignors to J. P. Stevens & Co., Inc., New York, N.Y., a corporation of Delaware

Filed Feb. 9, 1959, Ser. No. 791,950
11 Claims. (Cl. 8—120)

This invention relates to an improved method of treating cotton material to obtain a product of substantially improved wet and dry crease recovery.

There are numerous known methods by which the dry crease recovery of cotton material may be improved. These methods improve the dry crease recovery of cotton materials but do not sufficiently modify or improve the wet crease recovery properties of said materials.

On the other hand, there are some procedures which are known to improve the wet crease recovery of cotton fabrics substantially, while leaving the dry crease recovery properties essentially unchanged. When the cotton material is reacted with a cross-linking agent such as a dihalohydrin in presence of an aqueous solution of a strong base, the wet crease recovery of the cotton is greatly improved, without significant change in the dry crease recovery of the treated material.

It is apparent that from the standpoint of behaviour in use and in the course of normal laundering procedures, a cotton fabric which possesses both improved dry crease recovery and improved wet crease recovery is highly desirable. A cotton fabric which possesses such a combination of properties can compete in the market with fabrics manufactured from synthetic fibers, which are known to resist creasing in use (in the dry state), during laundering (in the wet state), and during drying (either at room temperature or in a heated tumble drier) and which are advertised as requring no ironing.

Heretofore, it was thought possible to improve the wet and the dry crease recovery of cotton fabrics only by a sequence of two operations, one of which was designed to improve wet crease recovery and the other to improve dry crease recovery. We have now found that the wet and the dry crease recovery of cotton fabrics may be improved in a single operation, by employing a process which is described herein.

Thus, an object of this invention is to provide a method by which the dry and the wet crease recovery of cotton material are improved substantially in one operation.

Another object of this invention is to provide a process by which the dry and the wet crease recovery of cotton textiles are improved substantially in an economical and efficient manner.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

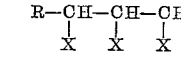
The present invention contemplates improving the dry and the wet crease recovery of cotton materials by treating the same with an aqueous solution containing a strong base and a low molecular weight alkanol including polyhydric alkanols, and with a cross-linking agent selected from the group consisting of dihalohydrins and epoxyhalides.

It was previously found that treatment of cotton material with an aqueous solution of a strong base and with a cross-linking agent selected from the group consisting of dihalohydrins and epoxyhalides, resulted in greatly improved wet crease recovery of the cotton material, but the dry crease recovery was not significantly improved. We have now found, unexpectedly, that when a substantial portion of the water in the alkaline solution used in this treatment is replaced by a corresponding amount of alcohol, the dry crease recovery of the treated cotton material is greatly improved, and excellent wet crease recovery is obtained as well.

While the improvement obtained in dry crease recovery when the amount of water present during the treatment is decreased (for example, by replacing a portion of the water with alcohol) is plausible and readily explained on the basis of theoretical principles, it is indeed surprising to find that under suitable conditions, this improvement in the dry crease recovery is not accompanied by a corresponding decrease in the wet crease recovery of the treated cotton material.

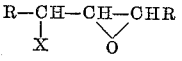
The cross-linking agent of the present invention may be represented by the following structural formulae:

(I)



wherein R is selected from the group consisting of hydrogen and alkyl radicals containing 1 to 5 carbon atoms and X may be chlorine, bromine and hydroxyl and the molecule must contain one hydroxyl and two halogen substituents, and

(II)



wherein R is selected from the group consisting of hydrogen and alkyl radicals containing 1 to 5 carbon atoms and X is either chlorine or bromine. Specific examples of such cross-linking agents are 1,3-dichloropropanol-2; 1,2-dichloropropanol-3; epichlorohydrin (1-chloro-2,3-epoxypropane); 1,3-dibromopropanol-2; 1-chloro-2,3-epoxy-3 methylpropane; 1,3-dichloro-2-hydroxy-3 methylpropane and the like.

The cross-linking reaction is carried out in the presence of a strong base. The basic strength of this material should be such that an aqueous solution containing one equivalent per liter of the base exhibits a pH of 10 or higher. Specific examples of such bases are the hydroxides, carbonates, alcoholates of the alkali metals, quaternary ammonium hydroxides, and the like. The base is a necessary reactant because it combines with the hydroxyl groups of the cellulose molecule in the cotton forming a reactive site for the cross-linking reaction. For example, if the base is sodium hydroxide, the sodium atom will replace the hydrogen atom of the hydroxyl groups in the cellulose molecule prior to participating in the cross-linking reaction. Since the cross-linking reaction is carried out in the presence of water, the strong base employed should be water soluble so as to insure uniform distribution of such base throughout the cotton material. The amount of base employed in the treatment is generally about 4 to 20% based on the weight of the cotton material treated. The crease recoveries do increase when increasing amounts of the base are employed, providing the amount of cross-linking agent is simultaneously increased to an equivalent extent. Control of the amount of base is, thus, a necessary but not a sufficient condition for obtaining the desired crease recovery. For a given amount of base within the specified range, the desired crease recovery can be obtained only if the required amounts of other reactant materials are present, maintaining the ratio of base to cross-linking agent within the range of 0.8 to 1.3, on a chemical equivalent basis. The strong base is generally applied to the cotton material as an aqueous solution. The water plays an important role in the process of this invention. As stated, it allows uniform distribution of the base throughout the cotton material. In addition, by swelling the cotton fibers it allows the base to penetrate within the fiber and react with the cellulose forming the required intermediate for the cross-linking reaction. The amount of water present during the reaction must be sufficient

to provide these effects to a significant degree. On the other hand, the amount of water must not be so great as to cause flow of cross-linking agent present in liquid form, away from the fibers. It is apparent that such flow would tend to remove the reactant materials from the cotton and thus adversely affect the course of the reaction and the improvement in crease recovery resulting from it. Generally, the amount of water present during the reaction should be between 15 and 100% based on the weight of the cotton material. Preferably, the amount of water employed should be between 20 and 60% based on the weight of cotton material treated.

The monohydric alkanol may contain about 1 to 3 carbon atoms in the molecule, and include such compounds as methanol, ethanol and/or propanol. The polyhydric alkanols are water soluble and include the glycols and glycerol. The glycols include, for example, the alkylene glycols in which the molecule may contain from about 2 to 4 carbon atoms. Specific examples of such alcohols are methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol, or the like. The amount of alcohol employed, based on the weight of cotton material, is about 10% to 70%. In a preferred operation, about 20 to 55% of the alcohol is employed in the treatment.

While the greatest improvements in wet and dry crease recovery depend on the ratio of base to cross-linking agent, it should be understood that even outside the preferred range of ratio 0.8 to ratio 1.3, more significant improvements in dry crease recovery can be obtained in presence of alcohol or glycol than in absence of such additive.

The cotton material may be in the form of yarn or fabric although, in general, it is expected that the present invention will find greater usefulness in the treatment of fabrics.

The treatment is conducted under conditions promoting the desired reactions. In terms of total time, it may take about 0.5 to 20 hours to achieve significant cross-linking as evidenced by measurement of wet crease recovery. The time of treatment may vary from the range thus specified; however, less satisfactory results are likely to be obtained if the reaction time is less than 0.5 hour and the benefit to be gained by extending the reaction time above 20 hours is not significant.

The time required for the reaction depends, to some extent, on the temperature prevailing on the cotton material while the cross-linking reaction takes place. The reaction takes place at a satisfactory rate at ambient temperature but, in general, the temperature may range from ambient level to about 60° C. if the process of the invention is operated at atmospheric pressure. At higher temperature, there is a tendency for the water and/or alcohol and some of the reactant materials to evaporate thus causing impairment of the reaction. This may be tolerated for the sake of accelerating the reaction and reducing the process time, or a system may be devised to maintain the quantity of water and/or alcohol and cross-linking agent as specified hereinabove even at elevated temperature. If desired, the reaction may be carried out at super-atmospheric pressure and, thus, a higher temperature may be used. However, at higher temperature, there is a tendency for the base to cause degradation of the cotton material and this should be avoided. The degradation effect of the base depends on specific conditions prevailing, and the permissible limits of temperature will vary accordingly.

In the operation of the process, the aqueous solution of the strong base and alcohol is applied to the cotton material by padding. The quantity of solution absorbed by the cotton may be controlled by wringing the material through the use of rollers or by other commonly known extraction procedures. After applying the aqueous solution, the cross-linking agent is applied by brush applicator or by means of a roller. After completing the application of the cross-linking agent, the material

is wrapped or encased in a moisture-proof or air-proof wrapper or container for the 0.5–20 hour period mentioned above. At the end of the specified reaction time, the cotton is washed in order to remove residual unreacted cross-linking agent and base, and soluble by-products such as, for example, sodium chloride. While the entire reaction mechanism is not completely understood, it is believed that the following reactions are among those which occur to a significant degree during the process of the invention:

(1)

$$\text{Cell*-OH} + \text{NaOH} \xrightarrow{H_2O} \text{Cell-ONa}$$

*Cellulose molecule.

(2)

$$\text{ClCH}_2\text{CH(OH)—CH}_2\text{Cl} + \text{NaOH} \xrightarrow{H_2O} \text{ClCH}_2\text{CH(O)CH}_2 + \text{NaCl}$$

(3)

$$\text{Cell-OH} + \text{Cl-CH}_2\text{-CH(O)CH}_2 \longrightarrow \text{Cell-O-CH}_2\text{-CH(OH)-CH}_2\text{Cl}$$

(4)

$$\text{Cell-ONa} + \text{Cell-O—CH}_2\text{—CH(OH)—CH}_2\text{Cl} \longrightarrow \text{Cell-O CH}_2\text{—CH(OH)—CH}_2\text{—O-Cell} + \text{NaCl}$$

(5)

$$2\text{Cell-ONa} + \text{Cl—CH}_2\text{CH(OH)—CH}_2\text{Cl} \longrightarrow \text{Cell-O—CH}_2\text{CH(OH)—CH}_2\text{—O-Cell} + 2\text{NaCl}$$

It is apparent from the above equations that a suitable cross-linking agent is epichlorohydrin or a substituted epichlorohydrin or a material which in the presence of a strong base, will form epichlorohydrin or a substituted epichlorohydrin as shown, for example, in Equation 2.

Various experiments were performed on cotton fabrics in the apparatus shown in the accompanying drawing which forms part of this specification.

Prior to the treatment of the cotton material in the apparatus shown in the drawing, the fabric sample, varying in length from 9 to 20 feet, and about 12 inches wide, was wound on a roll and placed on a laboratory padder. In the padding operation, the fabric received one dip and and one nip before being rewound on a second roll which served as the feed roll in the apparatus shown in the drawing. In the drawing, the feed roll on which the cotton fabric, treated with aqueous base, has been wound is shown as roll **5**, supported on the horizontal frame **6**. A drag **7** was placed on the feed roll **5** in order to maintain even tension on the cotton fabric **8** as it unwound from the feed roll **5**. The cotton fabric **8** was maintained in a horizontal position in its transfer from the feed roll **5** to the take-off roll **10**. The applicator roll **11** also referred to as kiss roll, was located between the feed roll **5** and the take-off roll **10**. The upper part of the applicator roll **11** touched the cotton fabric **8**. The take-off roll **10** was driven by a motor **12** and an endless belt **14**, whereas the applicator roll **11** was driven by a similar motor **15** and a similar endless belt **16**. The supporting frame **17** consisted of a horizontal support **6** previously mentioned, which was integral with a V-shaped feed pan **18**, centrally located with respect to support **6** and another horizontal support **19**. The take-off roll **10** was mounted at the end of support **19**. The frame **17** contained three vertical legs **21**, **22** and **23** which kept the horizontal supports **6** and **19** at an elevated position. Finally, the cotton fabric was rewound from the take-off roll **10** on to a core of tubing shown as **25**. The tubing and sample after treatment, were removed from the roll **25** and wrapped in polyethylene sheeting or other moisture-proof material.

In the operation of the apparatus shown in the drawing, the first portion of the sample (designated as the front lead) was pulled across the applicator roll **11** and attached to the take-off roll **10**. The take-off roll **10** was rotated at a faster speed than the applicator roll **11**. The cross-linking agent was fed from a funnel **26** to the feed pan **18** so as to maintain a constant level **27** by means of the overflow conduit **28**. As the applicator roll **11** revolved, cross-linking agent was transferred from the feed pan **18** to the fabric **8** by means of said roll **11**. As the transfer of cross-linking agent from the feed pan **18** to the fabric **8** took place, the cross-linking agent was being replenished as previously indicated by means of the constant level device consisting of the funnel **26** and the overflow conduit **28**.

The applicator roll **11** and the take-off roll **10** were stopped before the last 2 feet of fabric came in contact with the cross-linking agent and this last part (designated as the rear lead) was cut off.

After rewinding, and standing for a specified time, the treated samples were washed in an automatic home type clothes washer, operated on an 8 minute washing cycle, using water at 140° F. and ½ ounce of glacial acetic acid per gallon of water during the wash cycle.

The amounts of base and cross-linking agent deposited on the fabric during treatment were determined by analysis of the fabric prior to washing. The analysis was carried out by cutting a 1–2 gram swatch from the center portion of the treated fabric, extracting with distilled water at the boil until the base and halide had been completely removed from the sample, and titrating aliquots of the combined extracts to determine residual base, ionic halide, and total halide. From the values obtained in these titrations and from the weight of the extracted fabric sample after drying, the amount of base and cross-linking agent present on the fabric during treatment were calculated. Employing the procedure described above, various tests were made and these are reported in Table I below.

The experiments summarized in the table were carried out on cotton sheeting fabric commonly designated as 180 type sheeting.

Table I

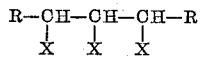
Example No.	Percent NaOH in Padding Solution	Percent Ethyl Alcohol in Padding Solution	Percent NaOH OWF[1]	Percent Cross-linker[2] OWF[1]	Ratio[3]	Crease Recovery[4]	
						Wet	Dry
1	12.5	30	7.5	10.5	1.4	185	151
2	12.5	30	7.5	12.8	1.2	230	162
3	12.5	30	7.5	18.7	0.8	251	190
4	15	30	9.5	17.4	1.1	256	195
5	15	30	9.5	26.4	0.7	151	160
6	12.5	0	9.0	21	0.8	259	160
Untreated control fabric						129	138

[1] OWF = on the weight of fabric.
[2] Cross-linker = 80% dichloropropanol, 20% inert ingredients.
[3] Ratio = equivalents NaOH on fabric/equivalents dichloropropanol on fabric.
[4] The values given for wet crease recovery were obtained by a modification of the technique known as the "Monsanto method" determining crease angle. The method is described, for example, in the 1958 Technical Manual of the American Association of Textile Chemists and Colorists, vol. XXXIV, pages 157–158, Tentative Test method 66–1956. For the purposes of wet crease recovery tests, the fabric sample was dipped in water prior to the measurement of crease angle in order to obtain wet crease recovery values, rather than the dry crease recovery values for which the method was originally designed. The values given in the table represent the sum of crease angles determined in the warp and filling directions. Such values are commonly referred to as "crease angle, total".

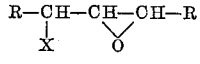
By comparing Examples 3 and 6 (in Table I), which were carried out with the same ratio of base to cross-linking agent (0.8), the significant improvement in dry crease recovery obtained by using 30% ethanol in the padding solution is clearly illustrated. It is also apparent from Examples 2, 3 and 5 that excellent wet and dry crease recoveries are obtained in presence of alcohol, when the ratio of base to cross-linking agent is 0.8 to 1.2.

We claim:

1. A process for imparting improved wet and dry crease recovery characteristics to a cotton textile comprising the steps of treating a cotton textile with a strong base in the presence of water and at least one alcohol selected from the group consisting of a monohydric alkanol containing 1 to 3 carbon atoms and a water soluble polyhydric alkanol, said base being selected from the group consisting of alkali metal hydroxides, alkali metal compounds which form alkali metal hydroxides in aqueous solution, and quaternary ammonium hydroxides, the amounts of water and alcohol being about 15 to 100% and 10 to 70% by weight respectively based on the cotton textile, and treating the cotton textile with a cross-linking agent selected from the group consisting of a dihalohydrin and an epoxyhalide having the following formulae:



wherein R is selected from the group consisting of hydrogen and an alkyl group containing 1 to 5 carbon atoms, and one X is a hydroxyl group and the remaining X's are selected from the group consisting of bromine and chlorine, and



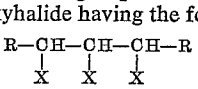
wherein R is selected from the group consisting of hydrogen and an alkyl group containing 1 to 5 carbon atoms, and X is selected from the group consisting of bromine and chlorine, the ratio of strong base to cross-linking agent being about 0.8 to 1.3 on a chemical equivalent basis, said reagents being present on the textile at the same time, and said process being continued until improved wet and dry crease recovery characteristics are imparted to the cotton textile.

2. The process of claim 1 in which the strong base is an alkali metal hydroxide.

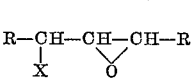
3. The process of claim 1 in which said base is present in an amount in the approximate range of from 4% to 20% based on the weight of the cotton textile.

4. The process of claim 3 in which the strong base is sodium hydroxide.

5. A process for imparting improved wet and dry crease recovery characteristics to a cotton textile comprising the steps of treating a cotton textile with a strong base in the presence of water and a monohydric alkanol containing 1 to 3 carbon atoms, said base being selected from the group consisting of alkali metal hydroxides, alkali metal compounds which form alkali metal hydroxides in aqueous solution, and quaternary ammonium hydroxides, the amounts of water and alkanol being about 15 to 100% and 10 to 70% by weight respectively based on the cotton textile, the amount of said strong base being in the range of about 4% to 20% based on the cotton textile, and treating the cotton textile with a cross-linking agent selected from the group consisting of a dihalohydrin and an epoxyhalide having the following formulae:



wherein R is selected from the group consisting of hydrogen and an alkyl group containing 1 to 5 carbon atoms, and one X is a hydroxyl group and the remaining X's are selected from the group consisting of bromine and chlorine, and



wherein R is selected from the group consisting of hydrogen and an alkyl group containing 1 to 5 carbon atoms, and X is selected from the group consisting of bromine and chlorine, the ratio of strong base to cross-linking

agent being about 0.8 to 1.3 on a chemical equivalent basis, said reagents being present on the textile at the same time, and said process being continued until improved wet and dry crease recovery characteristics are imparted to the cotton textile.

6. The process of claim 5 in which the said cross-linking agent is epichlorohydrin.

7. The process of claim 5 in which the cross-linking agent is dichloropropanol.

8. The process of claim 5 in which the alkanol is present in the range of from 20% to 55% based on the weight of the cotton textile.

9. The process of claim 5 in which the strong base is an alkali metal hydroxide.

10. The process of claim 5 in which the strong base is sodium hydroxide.

11. A process for imparting improved wet and dry crease recovery characteristics to a cotton textile comprising the steps of treating a cotton textile with sodium hydroxide in the presence of water and ethyl alcohol, said sodium hydroxide being present in an amount in the range from about 4% to 20%, the amount of water being about 15% to 100%, and the amount of ethyl alcohol being about 10% to 70%, all based on the weight of the cotton textile, and treating the cotton textile with dichloropropanol to impart improved dry and wet crease recovery characteristics, the ratio of sodium hydroxide to dichloropropanol being in the range of about 0.8 to 1.3 on a chemical equivalent basis, the chemical reagents being present on the textile at the same time.

References Cited in the file of this patent

UNITED STATES PATENTS

1,741,637	Lillienfeld	Dec. 31, 1929
2,524,399	Schoene	Oct. 3, 1950
2,731,323	Reinhardt	Jan. 17, 1956
2,904,386	Gagarine	Sept. 15, 1959
2,985,501	Gagarine	May 23, 1961

FOREIGN PATENTS

510,511	Great Britain	Aug. 2, 1939
543,301	Great Britain	Feb. 18, 1942
696,282	Great Britain	Aug. 26, 1953
698,135	Great Britain	Oct. 7, 1953
724,096	Great Britain	Feb. 16, 1955
727,889	Great Britain	Apr. 13, 1955

OTHER REFERENCES

Reeves: Textile Research Journal, January 1955, p. 44 (copy in P.O.S.L.).

Methods of Cellulose Chemistry, Charles Doree, 2nd edition, 1947, pp. 311–313 (copy in Div. 63).