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CREASE-PROOFING CELLULOSIC FABRICS, THE FABRICS OBTAINED AND METHODS OF MAKING THEM

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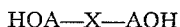
The present invention relates to a novel process for the treatment of cellulosic fabrics, especially cotton and rayon, for the purpose of increasing resistance to creasing, to crushing, wrinkling, and of reducing the tendency to shrinkage on laundering. The invention is particularly concerned with the process of crease-proofing cellulosic fabrics or other textile materials of cellulosic type and to the improved products obtained. The invention also comprises a process for stabilizing cellulosic fabrics against shrinkage on washing.

It is an object of the present invention to provide a process for increasing the resistance of cellulosic fabrics to creasing, crushing, and wrinkling by means of a cross-linking agent, which, in reacting with the cellulosic materials, does not form a resin on the textile materials so that it effects the crease-proofing and so on without essentially modifying the feel or appearance of the textile material. Another object of the present invention is to provide a cross-linking agent which does not cause retention of chlorine in the treated cellulosic fabric, whereby chlorine damage is avoided. Another object of the invention is to provide improved modified cellulosic textiles including such fabrics stabilized against shrinkage on washing. Other objects and advantages of the invention will be apparent from the description thereof hereinafter.

The use of thermosetting resin-forming condensates, such as those of formaldehyde with urea, melamine, or other nitrogen-containing compounds, for the purpose of increasing the resistance of cellulosic fabrics to creasing and the like is known. These resin-forming materials, however, are frequently characterized by the deposition of a substantial amount of resin on the surface of the fibers of the textile material which modifies the hand, frequently in a disadvantageous manner, as by harshening the hand or feel of the textile material. These resin-forming materials are also generally associated with chlorine-retention so that the cellulosic fabric is damaged, either in respect to its strength or its color or both after bleaching and ironing.

The Schoene and Chambers United States Patent 2,524,399 discloses the treatment of cellulosic fabrics with di-vinyl sulfone to reduce shrinkage and to improve resistance to creasing. However, the lachrymatory and vesicant properties of divinyl sulfone necessitate special precautions to protect the operators from poisoning thereby.

In accordance with the present invention, cellulosic fabrics are improved in their resistance to creasing, crushing, wrinkling, and tendency to shrink on washing by reaction with a di(2-hydroxyalkyl) sulfoxo compound of the formula



in which A is an alkylene group having 2 to 3 carbon atoms, namely ethylene $-\text{CH}_2\text{CH}_2-$, and propylene $-\text{CH}(\text{CH}_3)\text{CH}_2-$, with the hydroxyl groups bonded to β -carbon atoms, and X is selected from the group consisting of the sulfone group $-\text{SO}_2-$, the sulfoxide group $-\text{SO}-$, and groups of the class $-\text{SO}-\text{R}-\text{SO}-$ and $-\text{SO}_2-\text{R}-\text{SO}_2-$, where R is selected from the group

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consisting of C_1-C_6 alkylene groups, arylene groups such as o-phenylene, m-phenylene, and p-phenylene, and alkylarylene groups such as $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$ in which the CH_2 groups are in ortho, meta, or para positions on the benzene nucleus. The β -dihydroxyethyl sulfone is the preferred compound.

It is believed that these di(hydroxyalkyl) sulfoxo compounds react exclusively with the hydroxyl groups of the cellulosic molecules in the textile material. In any event, they do not form a resin deposit on the surface of such fibers or in or on the textile fabric.

The di(hydroxyalkyl) sulfoxo compounds of the invention may be applied to the textile material in any suitable way. Thus, an aqueous solution thereof having any desired concentration may be prepared and the textile material may be treated with such solution by dipping, spraying, brushing, by transfer rollers, by the use of a textile pad or any other suitable and conventional equipment or system. Generally, after the solution is applied, excess may be removed as by squeezing, centrifuging, or squeegeeing. When application is by a procedure where approximately 100% wet pick-up occurs, the concentration of the sulfoxo compound may be from 2 to 20% for most purposes. Optimum crushproofing and resilience are generally obtained when 12 to 15% concentration of the sulfoxo compound in the aqueous system is applied at about 100% wet pick-up, but good stabilization to washing shrinkage may be obtained with 2 to 5% of the sulfoxo compound.

An alkaline catalyst is needed to effect or assist the reaction of the di(hydroxyalkyl) sulfoxo compound with the fabric. This alkaline catalyst may be a fixed alkali or it may be a salt of a weak acid with a strong base. Besides the inorganic alkaline materials, quaternary ammonium hydroxides may be employed. Examples of suitable catalysts include the alkali metal carbonates and bicarbonates, such as sodium or potassium carbonate and sodium or potassium bicarbonate, alkali metal hydroxides, alkali metal acetates, and alkali metal phosphates and metasilicates such as trisodium phosphate, or sodium metasilicate. Benzyltrimethylammonium hydroxide is an example of a suitable quaternary ammonium base suitable for use as a catalyst. The amount of catalyst may range from 0.5 up to 5% concentration in the aqueous solution thereof by which it is applied to the fabric when the application is controlled to provide approximately 100% wet pick-up on the fabric. Adjustments of the upper or lower limits of the range may accordingly be made when different wet pick-up ratios are employed. The catalyst may be applied as a component of the impregnating solution used to apply the di(hydroxyalkyl) sulfoxo compound to the fabric. Generally, a 2% concentration of the catalyst is optimum when 100% wet pick-up is used.

After application and any desired removal of excess of the sulfoxo compound, the textile material is dried. This may be effected simply by drying in ambient air or by the application of heated air, by infrared heat, or by high frequency electric induction procedures. The particular equipment employed may be selected depending upon the particular type of textile material treated. It is essential that the reaction between the sulfoxo compound and the fabric be substantially completed by suitably heating the fabric either during the drying or thereafter. This heating operation which may be termed a curing or baking operation may be effected at a temperature in the range of about 250° to 450° F. The time of heating may vary from about $\frac{1}{2}$ to 2 minutes at the upper portion of the temperature range or as much as 1 to 2 hours in the lower portion of the range. A preferred practical condition is to employ 5 to 15 minutes at tem-

peratures of about 325° to 360° F. In any case, the upper limit of temperature should not be so high as to damage the fibers in the fabric by thermal decomposition.

The treatment of the present invention may be applied to any textile material containing cellulosic fibers or yarns and the textile material may be in the form of woven or knitted fabrics, "non-woven" fabrics derived from carded webs or from fibrous or filamentous webs obtained in any suitable fashion, such as air-deposition, wherein the fibers or filaments are distributed in a random array. The treatment may also be applied to yarns, threads, or other plied structures, or it may be applied to fibers or filaments in the form of loose or bulk masses or in the form of more or less compacted webbing, matting, or batting. In all fibrous structures having the fibers in heterogeneous array, the treatment renders the textile more resilient.

The fabrics or fibrous masses that may be treated are those which contain a predominant proportion of cellulosic fibers and/or filaments, by which is meant that the cellulosic fibers constitute more than 50% of the total fibers by weight. It is particularly useful with textile materials of cotton, viscose rayon, cuprammonium cellulose rayon, linen, ramine, as well as textile materials comprising fibers and filaments of two or more of such cellulosic materials. At the time of treatment with the cross-linking agent of the present invention, the fabric may be in the greige state or it may have been previously bleached, dyed, and/or printed or otherwise finished.

The cross-linking agents of the present invention do not appreciably modify the hand or feel of the textile material. The cross-linked textiles are quite resistant to acid materials and, on being subjected to heat, they undergo substantially no loss in strength even when such heat is elevated to a scorching temperature where discoloration is effected.

In some cases the treatment tends to cause a discoloration of the fabric, apparently because of the alkaline catalyst. However, this discoloration is easily removed by the usual bleaching operations making use of hypochlorites. As stated heretofore, employment of such chlorine-containing bleaching agents is not accompanied by the retention of chlorine in the treated fabrics so that the fabrics which have been bleached are not subject to chlorine damage.

If desired, the treatment with the sulfoxo compound may be supplemented by a treatment with a hand modifier or builder, softener, water-repellent agents, or materials which enhance the crease-resistance that can be obtained by means of the cross-linking agent. Such modifying agents may be applied simultaneously by way of the same aqueous solution of the sulfoxo compound (which is the generally preferred procedure) or they may be applied to the fabric before or after the application of the sulfoxo compound by means of a separate operation.

As water-repellent materials which also serve to soften the textile material, there may be used those quaternary ammonium compounds having a long-chain hydrocarbon group, such as stearamidomethylpyridinium chloride, stearyl pyridinium chloride, octadecyloxymethylpyridinium chloride, and the various quaternary ammonium salts described in United States Patent 2,351,581. The amount of water-repellent or softener may be as much as 5% and is preferably in the range of about 1 to 3% in the aqueous medium by which it is applied, assuming 100% wet pick-up. When it is applied solely for the purpose of softening, there may be employed as little as 0.1%.

Examples of auxiliary agents for enhancing the crease-resistance, for hand-building, for increasing tear strength, or for improving abrasion-resistance which can be applied in aqueous media include aqueous dispersions of water-insoluble linear addition polymers of one or more monoethylenically unsaturated monomeric compounds.

Examples include water-insoluble copolymers of 0.5 to 8% by weight of acrylic acid, methacrylic acid, and itaconic acid. Any one or more of these monoethylenically unsaturated acids may be copolymerized with one or more other copolymerizable compounds containing a single vinylidene group, such as esters of acrylic acid or methacrylic acid and monohydric alcohols such as methyl, ethyl, butyl, octyl, dodecyl, cyclohexyl, cyanoethyl, aminoethyl, and the like; esters of itaconic acid and the above alcohols; esters from maleic, fumaric, or citraconic acids, and the above alcohols; vinyl esters of carboxylic acids such as acetic, propionic, butyric, and the like; vinyloxyalkyl esters such as vinyloxyethyl acetate, etc.; vinyl ethers such as ethyl vinyl ether, butyl vinyl ether, octyl vinyl ether, hydroxyethyl vinyl ether, aminoethyl vinyl ether, aminopropyl vinyl ether, dimethylaminoethyl vinyl ether, vinyloxyethoxyethanol, vinyloxypropoxyethanol; methacrylonitrile or acrylonitrile; acrylamide, or methacrylamide, and N-substituted amides of these types; vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene fluoride, vinylidene cyanide, 1-chloro-1-fluoroethylene, ethylene, styrene, 2-vinylpyridine, 4-vinylpyridine, 2-methyl-5-vinylpyridine. These water-insoluble copolymers may be dispersed by means of non-ionic dispersing agents, such as alkylphenoxypolyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and six to sixty or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, methyloctylphenoxypolyethoxyethanols, nonylphenoxypolyethoxyethanols, dodecylphenoxypolyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene linked alkyl phenols; sulfur-containing agents such as those made by condensing six to sixty or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, and the like or mixtures of acids such as found in tall oil containing six to sixty oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan monostearate containing six to sixty oxyethylene units, etc.; block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections. The concentration of the water-insoluble polymers may be from ½ to 5% in the aqueous medium by which it is applied, either simultaneously with the sulfoxo compound or before or after the application of the sulfoxo compound. These auxiliary agents may be used in amounts which serve to modify the hand from a soft to a firm or stiff hand depending upon what is desired and depending upon the selection of comonomers used in any copolymer thus applied.

The fabric treated in accordance with the present invention may be a dyed fabric but, if not, pigments and/or dyes may be included in the aqueous solution used to apply the cross-linking agent or any other auxiliary treating agent. A dye or pigment may be applied by printing or dyeing the fabric after the completion of the crease-proofing treatment of the present invention.

In the following examples, which are illustrative of the present invention, the parts and percentages are by weight unless otherwise indicated. The tests whose results are given in the examples are performed on the treated fabric after being conditioned at 70° F. and 65% relative humidity. The crease-recovery angle is the angle obtained by the standard method of testing therefor. In all cases, unless otherwise indicated, the values given for the test are for the warp direction.

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Example 1

(a) A cotton print cloth is passed through a textile pad containing an aqueous dispersion containing 8% of di(2-hydroxyethyl) sulfone and 2% of sodium carbonate. The squeeze rolls are adjusted to provide for 100% wet pick-up and the fabric discharged from the nip of the squeeze rolls is heated in an oven at 325° F. for 15 minutes. The treatment increases the crease recovery from an angle of 70° to 127°, and the fact that the cellulose in the fabric is cross-linked is established by testing for solubility in cuprammonium hydroxide. The treated fabric is not soluble in the latter solution.

(b) In the same way improved crease-resistance is obtained by the treatment of a cotton print cloth with a 8% solution of di(2-hydroxypropyl) sulfone and 2% of potassium carbonate in water.

Example 2

The procedure of Example 1 is repeated except that the concentration of the di(2-hydroxyethyl) sulfone is raised to 15%. The crease-recovery angle is 132°. After six washes by the procedure given in Method 5550 of Federal Spec. CCC-T-191b, the crease recovery is 126°.

Example 3

The procedure of Example 1 is repeated except that the concentration of the sulfone is increased to 18% and the concentration of the sodium carbonate is increased to 4%. The crease-recovery angle obtained is 142°.

Example 4

The procedure of Example 1 is repeated except that the catalyst is replaced with 2% of sodium bicarbonate and the concentration of the sulfone is increased to 10%. The crease-recovery angle is 130°.

Example 5

A sample of 80 x 80 4-oz. cotton printcloth is impregnated with an aqueous solution containing 14.5% di(2-hydroxyethyl) sulfone, 1% of a copolymer of ethyl acrylate, methyl methacrylate, and about 3% of itaconic acid, and 1.7% sodium bicarbonate under conditions such that the fabric absorbs 100% of its own weight of the solution. It is then cured for 10 minutes at 340° F. The crease recovery of the treated fabric is 136°, while that of a water-treated control is 78°.

Example 6

Samples of a 120 x 60 cotton broadcloth and a 107 x 97 cotton lawn are treated with a solution containing 14% di(2-hydroxyethyl) sulfone and 4% sodium carbonate so that 100% wet pick-up of the solution is obtained. They are cured for 15 minutes at 340° F., rinsed in water, and redried. The crease-recovery angle of the broadcloth is increased by the treatment from 63° to 126°; that of the lawn, from 59° to 123°.

Example 7

A viscose rayon challis having a thread count of 84 x 64 is impregnated with a solution containing 20% di(2-hydroxyethyl) sulfone and 3% sodium metasilicate so that 100% wet pick-up is obtained. The impregnated fabric is cured for 10 minutes at 325° F., rinsed in water, and dried. The crease-recovery angle was 89° before treatment and becomes 119° afterwards.

Example 8

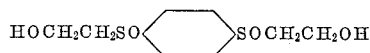
A sample of 80 x 80 cotton printcloth is impregnated with an aqueous solution of di(2-hydroxyethyl) sulfoxide and sodium carbonate under such conditions that the amount of sulfoxide applied is 17.2% of the weight of the fabric and the carbonate is 4% of the fabric weight. The fabric is then baked at 340° F. for 20 minutes, rinsed in water, and dried. The crease-recovery is increased from 58° to 107°.

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Example 9

(a) An 80 x 80 cotton printcloth is impregnated with a treating solution containing 11.2% 1,2-bis(2-hydroxyethylsulfonyl) ethane and 3.3% sodium bicarbonate under conditions such that the cloth picks up its own weight of the solution. The fabric is cured for 10 minutes at 350° F., rinsed in water, and redried. The treatment improves the crease-recovery of the fabric from 81° to 113°.

(b) Similar improvement in crease-recovery is obtained when the procedure of part (a) is repeated substituting 1,4-bis(2-hydroxyethylsulfoxy) benzene of the formula

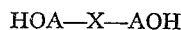


in the same amount for the disulfone therein used.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. A process of crease-proofing a fabric of cellulose fibers which comprises impregnating the fabric with an alkaline aqueous solution of a di(2-hydroxyalkyl) sulfoxo compound of the formula



wherein A is an alkylene group having 2 to 3 carbon atoms and the hydroxyl groups are attached to the β -carbon atom of the alkylene groups and X is a member selected from the group consisting of $-\text{SO}_2-$, $-\text{SO}-$, $-\text{SO}-\text{R}-\text{SO}-$, and $-\text{SO}_2-\text{R}-\text{SO}_2-$ wherein R is a member selected from the group consisting of alkylene groups having 1 to 6 carbon atoms, unsubstituted phenylene groups and alkylarylene groups of the formula $-\text{CH}_2\phi\text{CH}_2-$ in which ϕ is an unsubstituted phenylene group, and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

2. A process as defined in claim 1 in which the aqueous solution contains about 2 to 20% by weight of the di(2-hydroxyalkyl) sulfoxo compound.

3. A process as defined in claim 2 in which the fabric is a cotton fabric.

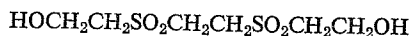
4. A process as defined in claim 2 in which the fabric is a regenerated cellulose fabric.

5. A process of crease-proofing a cellulosic fabric which comprises treating a fabric of cellulose fibers with an aqueous alkaline solution containing about 2 to 20% of di(2-hydroxyethyl) sulfone and subsequently drying and heating the fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

6. A process of crease-proofing a cellulosic fabric which comprises treating a fabric of cellulose fibers with an aqueous alkaline solution containing about 2 to 20% of di(2-hydroxypropyl) sulfone and subsequently drying and heating the fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

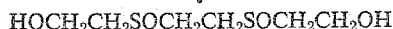
7. A process of crease-proofing a cellulosic fabric which comprises treating a fabric of cellulose fibers with an aqueous alkaline solution containing about 2 to 20% of di(2-hydroxyethyl) sulfoxide and subsequently drying and heating the fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

8. A process of crease-proofing a cellulosic fabric which comprises treating a fabric of cellulose fibers with an aqueous alkaline solution containing about 2 to 20% of a sulfone of the formula



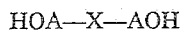
and subsequently drying and heating the fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

9. A process of crease-proofing a cellulosic fabric which comprises treating a fabric of cellulose fibers with an aqueous alkaline solution containing about 2 to 20% of a sulfoxide of the formula



and subsequently drying and heating the fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

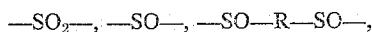
10. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of a di(2-hydroxyalkyl) sulfoxo compound of the formula



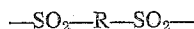
where

A in an alkylene group having 2 to 3 carbon atoms and the hydroxyl groups are attached to the β -carbon atom of the alkylene groups, and

X is a member selected from the group consisting of



and



wherein R is a member selected from the group consisting of alkylene groups having 1 to 6 carbon atoms, unsubstituted phenylene groups and alkylarylene groups of the formula $-\text{CH}_2\phi\text{CH}_2-$ in which ϕ is an unsubstituted phenylene group, and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

11. An article of manufacture as defined in claim 10 in which the cellulose fibers are cotton fibers.

12. An article of manufacture as defined in claim 10 in which the cellulose fibers are regenerated cellulose fibers.

13. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of di(2-hydroxyethyl) sulfone and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

14. As an article of manufacture, a crease-resistant textile material comprising cotton fibers cross-linked by impregnating the material with an aqueous alkaline solution of di(2-hydroxyethyl) sulfone and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

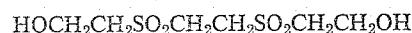
15. As an article of manufacture, a crease-resistant textile material comprising regenerated cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of di(2-hydroxyethyl) sulfone and subsequently drying and heating the impregnated fabric

at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

16. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of di(2-hydroxypropyl) sulfone and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

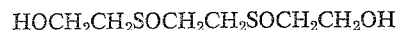
17. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of di(2-hydroxyethyl) sulfoxide and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° until cross-linking of the cellulose is obtained.

18. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of a sulfoxide of the formula



and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

19. As an article of manufacture, a crease-resistant textile material comprising cellulose fibers cross-linked by impregnating the material with an aqueous alkaline solution of a sulfoxide of the formula



and subsequently drying and heating the impregnated fabric at a temperature of about 250° to 450° F. until cross-linking of the cellulose is obtained.

20. A process which comprises impregnating a cellulosic textile material containing cellulosic hydroxyl groups with an aqueous solution of an alkaline catalyst and bis(beta-hydroxyethyl) sulfone, drying the impregnated material and heating to react the bis(beta-hydroxyethyl) sulfone with the cellulosic textile material.

References Cited by the Examiner

UNITED STATES PATENTS

2,474,808	7/1949	Schoene	260—207
2,524,399	10/1950	Schoene	8—116
2,670,265	2/1954	Heyna	8—120 XR

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