

1

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CHEMICALLY MODIFIED TEXTILES

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

The invention relates to improvements in processes for producing partial ethers and esters of cellulose of a relatively high degree of chemical modification while retaining desirable fabric properties.

One of the barriers to attaining a high degree of substitution in chemically modified cotton fabrics is the excessive stiffness imparted to the fabrics. When a high degree of substitution is reached during chemical processing, the fabric swells, weakens, gelatinizes, or may even dissolve. When such a fabric is dried, it becomes stiff, boardy, brittle and weak. This tendency for cellulose to swell, gelatinize, or dissolve during chemical modification is also a barrier to attaining a high degree of substitution in the chemical modification of cotton fibers, yarns and fabrics.

We have discovered that cross-linking the cellulose, prior to or during the process of chemical modification, provides a way of breaking through this barrier and obtaining chemically modified cellulosic textile products with a relatively high degree of substitution. Although in this one important aspect, the invention provides processes for the chemical modification of cellulosic textile materials such as cotton, regenerated cellulose in the form of rayon, linen or ramie, with suitable changes that do not depart from the principles of the invention, it will also provide improved processes for the chemical modification of other cellulosic materials, such as cotton linters, wood pulp, or regenerated cellulose fibers.

A preferred way of practicing the invention consists of reacting a cross-linking agent with the cellulose of a cotton textile to form chemical bridges between the cellulose chains and then chemically modifying this cross-linked cotton textile with a process that does not cross link the cellulose, but which unites a desired chemical group with the cellulose by reaction with some of the remaining hydroxyl groups. The cross-linking step and the further chemical modification step are usually performed separately, but in certain instances where the reagents used are compatible, both the cross-linking and non-cross-linking phases of the process may be performed at the same time by putting the cross-linking agent and the non-cross-linking agent into the same treating solution. The cross-linking reaction may be carried out in the presence of a catalyst. A base such as sodium hydroxide is preferred for certain polyfunctional etherifying cross-linking reagents. With other cross-linking agents, such as formaldehyde or other aldehydes, an acidic catalyst is preferred. Both the cross-linking agent and the catalyst, if required, are ordinarily dissolved in the same solution, although in certain instances they may be applied separately. The preferred solvent is water, but organic solvents may be required in certain instances.

2

Application to the fabric is usually by padding, that is, by passing the fabric through the solution of reagents and then through squeeze rolls. Reaction with the cellulose may be initiated or completed by heating the impregnated fabric at an elevated temperature, after which it may be washed and dried. The cross-linked fabric is then subjected to chemical modification by a non-cross-linking process. In most instances processes known to the art are used for the non-cross-linking step, but it is obvious that many new chemical modifications will be found to which the principle of this invention will be applicable.

Although the reaction with the cross-linking agent may be carried out by padding and curing as described above, it may also be done by immersion of the cellulosic material in a solution which contains the reactants. Immersion is preferred with fibers and yarns and with fibrous materials such as cotton linters or wood pulp. In most instances an elevated temperature is required to carry out the cross-linking reaction, but with certain cross-linking reagents the reaction is sufficiently rapid at room temperature. Thus the cross-linking reaction is carried out at temperatures selected from the range of about 20° to about 160° C., depending on the cross-linking reagent used. Similarly, the time of reaction may be varied widely, depending on the cross-linking agent and on the temperature at which it is reacted with the material. Thus the time of reaction may vary from about 30 seconds to 24 hours. The choice of details for performing the cross-linking step may be readily made by chemists versed in the art of chemical modification of cellulose.

Cross-linking agents that fall within the scope of this invention are defined as follows:

(1) Polyfunctional compounds that react with cotton cellulose to make it less soluble in cuprammonium hydroxide solution, these compounds being active in this respect at a degree of substitution of the cellulose of 0.05 or less, calculated on the number of glucose units combined with a cross-linking bridge per total number of glucose units. Such compounds, ways of cross-linking cotton cellulose with them, and methods for determining their effect on cuprammonium solubility of cellulose are described in Textile Research Journal 25, 41-46, and 27, 324-6.

(2) Polyfunctional compounds that react under suitable conditions with the hydroxyl groups of low viscosity carboxymethyl cellulose to make non-dispersible gels or films.

Compounds that come under category No. 2 above give evidence of cross-linking in the test described as follows:

500 mg. of low viscosity sodium carboxymethyl cellulose are placed in a 30 ml. beaker and mixed with 3 ml. of 5% aqueous sodium hydroxide solution, using a small stainless steel spatula. The compound to be tested, usually 100 mg. or about 6 drops, if a liquid, is then mixed thoroughly with the viscous sirup. A portion of the mixture is spread on the surface of an inverted beaker and placed in an oven at 120° C. for 30 minutes. After removal from the oven and cooling, the film is removed from the surface of the beaker by peeling off, adding a little water to loosen it if necessary, and placed in 50 ml. of water. If cross-linking has occurred, the film does not disperse or dissolve after standing in the water for several hours. The portion of the mixture remaining in the 30 ml. beaker is observed over a period of 2 days. If cross-linking in the cold occurs, this is shown by the formation of a gel that swells, but does not dissolve when placed in water.

This test may be modified by using 3 ml. of water in place of the 5% sodium hydroxide solution. Cross-link-

ing agents that are active under neutral conditions give positive results in the test modified in this manner. Similarly, the test may be modified by mixing the carboxymethyl cellulose with 3 ml. of water and 0.2 ml. of 6 N aqueous sulfuric acid solution. Compounds, such as aldehydes, which cross-link under acid conditions, give positive result in the test modified in this manner. In certain instances, especially with pyridine complexes like the pyridine complex of 1,2-dichloroethane, the test is modified by replacing the 3 ml. of 5% aqueous sodium hydroxide solution with 3 ml. of water and 200 mg. of crystalline sodium acetate. Curing of the film with compounds of this type is at 140° C.

In the modified forms of the test, the cured film, or the gel formed on standing, should be placed in 2% aqueous sodium hydroxide solution instead of in water, to determine whether cross-linking has occurred, as indicated by failing to disperse in this solution.

Without limiting the scope of the invention to the compounds named, since many other compounds will be found to be effective cross-linking agents for cellulose, compounds that have been found to give positive results in the test, or modified tests, described above include the following.

(1) Cross-linking under alkaline conditions:

A. Cold—

Epichlorohydrin
Butadiene dioxide
1,3-dichloropropanol-2
1,3-dichloro-2-methylpropanol-2
2,3-dibromopropanol-1
N,N'-methylenebisacrylamide
Bis(chloromethyl)sulfide
Cyanuric chloride
Divinyl sulfone

B. Heat cure—

Epichlorohydrin
Butadiene dioxide
Vinyl cyclohexene dioxide
1,4-dichloro-2,3-epoxybutane
1,3-dichloropropanol-2
1,3-dichloro-2-methylpropanol-2
2,3-dibromopropanol-1
2,2'-dichloroethyl ether
2,3-dibromopropionic acid
Dibromosuccinic acid
Dichloromaleic anhydride
Dichloroacetic acid
Mucochloric acid
1,2-dichloroethane, pyridine complex
1,2-disulfato ethane
1,4-disulfato butane
1-chloro-2-sulfato ethane
Bis(2-sulfatoethyl)amine
Propargyl bromide
Cyanuric chloride
Tris(aziridinyl)phosphine oxide
Tris(aziridinyl)phosphine sulfide
Carbonylbisaziridine
Tris(2-chloroethyl)vinyl phosphonate
Bis(2-chloroethyl)2-chloroethyl phosphonate
Tetrakis(bromomethyl)phosphonium bromide

(2) Cross-linking under acid conditions:

Formaldehyde
Glutaraldehyde
Tetrakis(hydroxymethyl)phosphonium chloride

Although the principle of this invention in its broadest aspects, that is, cross-linking prior to or during chemical modification of the fibrous cellulosic material, is applicable to any chemical modification involving the remaining hydroxyl groups of the fibrous cellulosic material, it is particularly valuable with chemical modifications that introduce hydrophilic, solubilizing or ionic groups. Examples of such chemical modifications are: aminization,

carboxymethylation, sulfoethylation, phosphatoethylation, phosphorylation, phosphonomethylation, and sulfation. Details of some of these chemical modification processes are given in the following references:

- 5 Industrial and Engineering Chemistry 44, 2187-2189.
Textile Research Journal, 23, 522-527.
Textile Research Journal, 17, 554-561.
Textile Research Journal, 18, 551-556.
U.S. Patents 2,743,232; 2,459,222; 2,681,846.

10 The following examples, in which parts and percentages are by weight unless otherwise indicated, are illustrative of the invention.

Example 1

15 A sample of 48² cotton sheeting was cross-linked by padding it to a wet pickup of about 155% with a solution containing 10 parts of potassium di(2-sulfatoethyl) amine monohydrate [DSA], 25 parts sodium hydroxide and 65 parts water and then curing in an oven at 110°-120° C. for 45 minutes. After this cross-linked sample was washed free of caustic and dried, it was found to be 90% insoluble in cuprammonium hydroxide solution made to A.S.T.M. specifications [A.S.T.M. Designation: D539-48T(3)-].

25 This cross-linked sample was then aminized once, twice, and three times, removing a portion after each aminization for test purposes. The aminization was effected by the method of Reeves and Guthrie (Textile Research Journal, 23, 522-527), using a solution containing 20% 2-aminoethyl sulfuric acid, 30% sodium hydroxide and 50% water and cured for 45 minutes at 110-120° C.

A control was prepared at the same time from plain cotton sheeting by using the same aminizing solutions and curing conditions as for the cross-linked sample. Some properties of the cross-linked samples and the control samples are reported in the following table.

Sample	Percent Nitrogen	Stiffness (in. lbs. $\times 10^{-4}$)	Warp Breaking Strength (lbs.)	Percent Elongation at Break
40 Cross-linked only	0.34	70.4	43.5	22.7
Cross-linked—aminized once	1.10	70.0	41.5	25.7
Cross-linked—aminized twice	1.82	94.8	40.0	30.9
45 Cross-linked—aminized three times	2.45	80.8	34.6	32.9
Control—aminized once	0.82	130.4	47.6	34.9
Control—aminized twice	1.49	996.2	37.1	36.9
Control—aminized three times	1.81	(¹)	(¹)	(¹)

50 ¹ Fabric properties completely destroyed.

This table shows the following advantages of cross-linking prior to aminization: (1) a higher nitrogen content may be obtained; (2) much less stiffness results from progressive aminization; and (3) loss in breaking strength is less at the higher levels of reaction.

Example 2

A sample of 48² cotton sheeting was padded with a solution containing 25% sodium hydroxide, 20% 2-aminoethyl sulfuric acid, 5% di(2-sulfatoethyl) amine and 50% water. The wet fabric was then placed in an oven and cured at 110° C. for 30 minutes. After washing free of sodium hydroxide and drying, the treatment was repeated until the final product had a nitrogen content of 1.65%. A control was aminized with a solution from which the cross-linking agent was omitted, using the same procedure, to give a product containing 1.60% nitrogen. The cross-linked aminized sample was less stiff, had a higher breaking strength and better crease resistance than the control.

Example 3

A sample of 48 by 48 cotton sheeting was cross-linked exactly as described in Example 1 and then carboxymethylated by padding with an aqueous solution con-

5

taining 30% monochloroacetic acid and 0.5% of a suitable wetting agent, partially drying in air at room temperature (about 27° C.), padding with 48% sodium hydroxide solution, drying for 10 minutes at about 110° C. in an oven, washing free of caustic and drying.

This cross-linked carboxymethylated sample, which was insoluble in cuprammonium hydroxide solution, was much less stiff than was a control of plain cotton sheeting carboxymethylated at the same time and in the same manner.

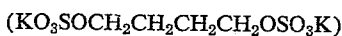
Example 4

A sample of 48 by 48 cotton sheeting was cross-linked by padding it through a solution containing 83.5 parts of 36% aqueous formaldehyde, 1.3 parts of ammonium chloride and 215 parts of water and curing it for 5 minutes in an oven at 120° C. After washing thoroughly and drying, this cross-linked sample was found to be 91% insoluble in cuprammonium hydroxide solution.

This cross-linked sample and a control of plain cotton sheeting were then carboxymethylated exactly as described in Example 3. The stiffness of the cross-linked carboxymethylated sample was 85.6×10^{-4} in.-lbs. while that of the control was 918.0×10^{-4} in.-lbs. The cross-linked carboxymethylated sample showed, in addition, greater crease resistance than the control.

Example 5

A sample of 48 by 48 cotton sheeting was cross-linked by padding it with a solution containing 7 parts of the dipotassium salt of butane disulfuric acid



20 parts of sodium hydroxide and 73 parts of water, and then curing in a steamheated oven at 110° C. for 45 minutes. After washing the cross-linked sample free of caustic and drying, it was found to be 86.7% insoluble in cuprammonium hydroxide solution.

A control sample treated in the same way except that the cross-linking reagent was omitted was completely soluble in the cuprammonium hydroxide solution.

Both the cross-linked sample and the control sample were then aminized once, twice and three times exactly as described in Example 1. Some properties of these samples are reported in the following table.

Sample	Percent Nitrogen	Stiffness (in.-lbs. $\times 10^{-4}$)	Warp Breaking Strength (lbs.)
Cross-linked only.....	0	41.8	52.7
Cross-linked—aminized once.....	0.83	100.0	44.7
Cross-linked—aminized twice.....	1.60	161.6	39.1
Cross-linked—aminized three times.....	2.16	285.0	33.8
Treated with NaOH only.....	0	21.0	60.8
NaOH treated—aminized once.....	0.85	98.0	52.0
NaOH treated—aminized twice.....	1.60	296.0	45.4
NaOH treated—aminized three times.....	2.90	528.0	32.7

It is seen from this table that at equal nitrogen values, the samples cross-linked prior to aminization were less stiff than the control samples, especially so for those having the higher nitrogen values. It is also seen that this is done without any greater loss of breaking strength than that of the control samples.

Example 6

A sample of 48 x 48 cotton sheeting was cross-linked and phosphonomethylated at the same time by treating it as follows. The fabric was padded so as to obtain a maximum pickup with a solution containing 25% sodium hydroxide, 10% butane disulfate sodium salt, 15% chloromethyl phosphonic acid sodium salt, and 50% water. It was then cured in an oven at 140° C. for 30 minutes, washed free of caustic and dried. The resulting cross-linked phosphonomethylated fabric was a useful ion exchange fabric having an ion exchange capacity of 1.09 milliequivalents per gram.

6

Another sample of the original cotton sheeting treated in exactly the same manner as described above, except that the cross-linking reagent was replaced with water, went into solution when the attempt was made to wash it free of caustic and was therefore useless as an ion exchange fabric.

Example 7

A sample of 48 by 48 cotton sheeting was cross-linked by padding it first through a saturated aqueous solution of 1,3-dichloropropanol-2 and then, without drying, through a solution containing 40 parts of sodium hydroxide in 60 parts of water. The cross-linked sample was then washed free of caustic and dried. A control sample was made at the same time, using the same solutions but omitting the cross-linking reagent. The samples were then aminized three times as described in Example 1. Some properties of the samples thus prepared are given in the following table:

Sample	Percent Nitrogen	Stiffness (in.-lbs. $\times 10^{-4}$)	Warp Breaking Strength (lbs.)
Cross-linked only.....	0	45.3	48.8
Cross-linked—aminized three times.....	2.20	522.8	31.3
NaOH treated only.....	0	22.6	62.1
NaOH treated—aminized three times.....	2.08	859.5	31.4

This table shows that cross-linking prior to aminization has permitted the preparation of a highly aminized fabric with less stiffness and with no greater loss of breaking strength than was obtained from the fabric which had not been cross-linked.

Example 8

A cross-linked sample and a sodium hydroxide treated control sample were prepared as described in Example 7. Both samples were then cyanoethylated by padding with a 2% sodium hydroxide solution, placing in a reaction tube and pumping acrylonitrile through them at 60–65° C. for 3½ hours. The samples were then washed with 5% acetic acid, then with water and dried. The cross-linked sample was found to have a nitrogen content of 8.47% and a stiffness of 54.4×10^{-4} in.-lbs. while the caustic control sample had a nitrogen content of 8.23% and a stiffness of 161.6×10^{-4} in.-lbs. The cross-linked sample also had higher crease resistance and tear strength than the caustic treated control.

Example 9

A cross-linked sample and a sodium hydroxide treated control sample prepared as in Example 7 were phosphonomethylated by padding with a solution containing 12 parts of chloromethyl phosphonic acid, 25 parts of sodium hydroxide and 63 parts of water and then curing for 30 minutes in an oven at 140° C. After washing the chemically modified samples free of caustic and drying, the cross-linked sample was found to contain 2.45% phosphorus and the control sample contained 2.07% phosphorus. Test results have showed that the stiffness, crease resistance, tear strength, breaking strength and elongation at break of the cross-linked phosphonomethylated sample were all equal to or better than the same properties of the control sample. Thus the cross-linking permitted a higher phosphorus content while maintaining as good or better fabric properties.

Example 10

A sample of 48 x 48 cotton sheeting was cross-linked by padding it through an aqueous solution containing 10% divinyl sulfone and then, without drying, padding it with a second aqueous solution containing 0.5% sodium hydroxide and 20% sodium sulfate. The wet fabric was allowed to remain at room temperature for 30 minutes. It was then soaked for a few minutes in 5% acetic acid solution, washed in running tapwater for 30 min-

utes and dried. This cross-linked fabric, which was insoluble to the extent of 89.8% in cuprammonium hydroxide solution, was aminized three times as described in Example 1. The cross-linked aminized fabric had a stiffness of 251×10^{-4} in.-lbs. while a plain cotton fabric aminized in exactly the same way had a stiffness of 616×10^{-4} in.-lbs. The cross-linked aminized sample also had greater crease resistance than did the plain cotton-aminized control sample.

Example 11

A sample of purified cotton linters was cross-linked by wetting with a 10% aqueous solution of 1,3-dichloropropanol-2 and then covering the wet sample with 50% sodium hydroxide. After a few minutes the sample was washed free of caustic and dried. Five parts of the cross-linked linters, which were not soluble in cuprammonium hydroxide solution, were then sulfated by adding them to a solution containing 57.5 parts of chlorosulfonic acid in 134.5 parts of pyridine and heating the mixture for 1.5 hours on the steam cone with occasional stirring. Two hundred parts water was then added and the sulfated linters filtered off, soaked in 5% sodium hydroxide solution for about 10 minutes, washed free of caustic and dried. These cross-linked sulfated linters were found to contain 15.27% sulfur and to be useful as an ion exchange material.

When plain cotton linters were sulfated in the same manner, they dissolved on the addition of water to the sulfation mixture, and consequently had no value as an ion-exchange material.

We claim:

1. A process comprising impregnating a cotton fabric with an aqueous solution containing 5 to 15% potassium di(2-sulfatoethyl)amine monohydrate and 15 to 30% sodium hydroxide, heating the impregnated fabric at 90° to 150° C. for 5 to 60 minutes, then washing and drying said fabric, then aminizing the fabric by impregnating it with an aqueous solution containing 5 to 20% of 2-aminoethyl sulfuric acid and 20 to 30% sodium hydroxide, heating the impregnated fabric at 100° to 140° C. for 5 to 45 minutes, and then washing and drying said fabric.

2. A process comprising impregnating a cotton fabric with an aqueous solution containing 5 to 15% potassium di(2-sulfatoethyl)amine monohydrate and 15 to 30% sodium hydroxide, heating the impregnated fabric at 90° to 150° C. for 5 to 60 minutes, then washing and drying said fabric, then carboxymethylating the fabric by impregnating it with a 20 to 40% aqueous solution of monochloroacetic acid, partially drying in air at room temperature, then passing the fabric through a 25 to 50% aqueous solution of sodium hydroxide, heating the sodium hydroxide treated fabric at about 90° to 120° C., then washing said fabric free of sodium hydroxide and finally drying said fabric.

3. A process comprising impregnating a cotton fabric with an aqueous solution containing 5 to 20% formaldehyde and 0.1 to 1.0% of an acid catalyst, heating for 2 to 10 minutes at 90° to 130° C., washing and drying the heated fabric, then carboxymethylating the fabric by impregnating it with a 20 to 40% aqueous solution of monochloroacetic acid, partially drying in air at room temperature, passing the partially dried fabric through a 25 to 50% aqueous solution of sodium hydroxide, then heating said sodium hydroxide treated fabric at about 90° to 120° C., washing said fabric free of sodium hydroxide, and finally drying said fabric.

4. A process comprising impregnating a cotton fabric with an aqueous solution containing 4 to 10% of the dipotassium salt of butane disulfuric acid and 15 to 30% of sodium hydroxide, heating the impregnated fabric at 100° to 150° C. for 3 to 60 minutes, then washing and drying said heated fabric, then aminizing the fabric by impregnating it with an aqueous solution containing 5 to 20% of 2-aminoethyl sulfuric acid and 20 to 30% sodium hydroxide, heating the impregnated fabric at 100°

to 140° C. for 5 to 45 minutes and then washing and drying said fabric.

5. A process comprising impregnating a cotton fabric with a saturated aqueous solution of a member of the group consisting of 1,3-dichloropropanol-2, 2,3-dichloropropanol-1, and a mixture thereof, then passing the fabric through a 25 to 50% aqueous solution of sodium hydroxide, then washing and drying said fabric, then aminizing the fabric by impregnating it with an aqueous solution containing 5 to 20% of 2-aminoethyl sulfuric acid and 20 to 30% sodium hydroxide, heating the impregnated fabric at 100° to 140° C. for 5 to 45 minutes, and then washing and drying said fabric.

6. A process comprising impregnating a cotton fabric with a saturated aqueous solution of a member of the group consisting of 1,3-dichloropropanol-2, 2,3-dichloropropanol-1, and a mixture thereof, then passing the fabric through a 25 to 50% aqueous solution of sodium hydroxide, then washing and drying said fabric, then cyanomethylating the fabric by impregnating it with a 2 to 5% aqueous solution of sodium hydroxide, reacting the impregnated fabric with acrylonitrile for 2 to 5 hours at 50° to 70° C., and then washing and drying said fabric.

7. A process comprising impregnating a cotton fabric with a saturated aqueous solution of a member of the group consisting of 1,3-dichloropropanol-2, 2,3-dichloropropanol-1, and a mixture thereof, passing the fabric through a 25 to 50% aqueous solution of sodium hydroxide, washing and drying the fabric, then phosphonemethylating by impregnating with an aqueous solution containing 5 to 15% of chloromethyl phosphonic acid and 15 to 30% sodium hydroxide, heating the impregnated fabric in an oven at 100° to 150° C. for 10 to 60 minutes, and then washing and drying said fabric.

8. A process comprising impregnating a cotton fabric with an aqueous solution containing 10 to 30% 2-aminoethyl sulfuric acid, 3 to 10% di(2-sulfatoethyl)amine and 20 to 30% sodium hydroxide, and then heating the impregnated fabric at 90° to 150° C. for 5 to 60 minutes.

9. A process comprising wetting cotton linters with a 2 to 15% aqueous solution of a member of the group consisting of 1,3-dichloropropanol-2, or of 2,3-dichloropropanol-1, and a mixture thereof, adding an excess of 25 to 50% aqueous sodium hydroxide to the wetted linters, washing and drying said linters, and then sulfating the linters with the pyridine complex of chlorosulfonic acid.

10. A process for chemically modifying fibrous cellulosic materials while preserving their fibrous form which comprises reacting a fibrous cellulosic material containing free hydroxyl groups with a cross linking agent which is a member of the group consisting of polyfunctional cellulose etherifying and esterifying agents and with a member of the group consisting of monofunctional cellulose etherifying and esterifying agents.

11. The process of claim 10 wherein the fibrous cellulosic material is a member of the group consisting of cotton fiber, linen, ramie, wood pulp, and regenerated cellulose fibers.

12. The process of claim 10 wherein the fibrous cellulosic material is first reacted with the polyfunctional agent and then with the monofunctional agent.

13. The process of claim 10 wherein the fibrous cellulosic material is simultaneously reacted with the polyfunctional agent and the monofunctional agent.

References Cited in the file of this patent

UNITED STATES PATENTS

2,148,951	Maxwell	Feb. 28, 1939
2,451,686	Moller et al.	Oct. 19, 1948
2,588,463	Balassa	Mar. 11, 1952
2,729,535	Balassa	Jan. 3, 1956
2,730,427	Suen	Jan. 10, 1956
2,842,541	Journey	July 8, 1958
2,860,946	Belt	Nov. 18, 1958