United States Patent Office

3,676,053
Patented July 11, 1972

3,676,053

METHOD OF MODIFYING FIBROUS MATERIALS

Yasuhiko Miyake, Nobara, and Eifu Takayanagi, Shigeo Narita, Masaaki Shin, Toshio Hayashi, and Koichi Sakurai, Kanakawa-Prefecture, Japan, assignors to Mitsui Toatsu Chemicals, Incorporated, Tokyo, Japan

No Drawing. Filed Sept. 4, 1969, Ser. No. 855,411
Claims priority, application Japan, Sept. 26, 1968, 43/69,106; Jan. 14, 1969, 44/2,333; Jan. 31, 1969, 44/6,665; Mar. 14, 1969, 44/18,850; Mar. 26, 1969, 44/22,309
Int. Cl. D06m *13/14, 13/18, 13/40*
U.S. Cl. 8—116 **10 Claims**

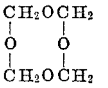
ABSTRACT OF THE DISCLOSURE

The present invention is a method of modifying cellulosic fibrous materials characterized by impregnating a cellulosic fibrous material with a modifier containing tetraoxane and/or pentaoxane and heat-treating it at an elevated temperature preferably above at least about 100° C. in the presence of an acid substance. Also covered are novel modifier compositions containing tetraoxane and/or pentaoxane and an acid catalyst.

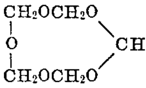
This invention relates to novel methods and modifier compositions for modifying fibrous materials consisting of or containing cellulosic fibers.

Heretofore, cellulosic fibrous materials have been modified by using as modifiers an N-methylolated derivative and/or alkylated N-methylol derivatives of amino compounds having active nitrogen, such as, urea, melamine, ethylene-urea or glyoxal monourein in order to improve their crease resistance and smooth drying property. Derivatives of this kind shall be briefly called N-methylol substances hereinafter. As typical examples of such modifiers, there are urea-formaldehyde resins, melamine-formaldehyde resins, dimethylol ethylene urea resins and methylol glyoxal monourein resins, e.g., 1,3-dimethylol-4,5-dihydroxy-2-imidazolidinone.

We have conducted extensive research on the modification of cellulosic fibrous materials with tetraoxane and pentaoxane which are cyclic compounds having the below-mentioned structures:



Tetraoxane



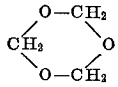
Pentaoxane

These materials are not believed to have been heretofore in modifying fibers. We have discovered a method whereby cellulosic fibrous materials can be modified to impart higher crease resistance and smooth drying properties (appearance ratings) than obtained when the above-mentioned N-methylol substances are used. We have also found that the durability to laundering of the novel modifications is very excellent and that there is no chlorine damage which is a defect likely to occur through the use of the above mentioned N-methylol substances.

The present invention includes methods of modifying cellulosic fibrous materials characterized by impregnating such material with a modifier containing at least one of tetraoxane and pentaoxane and heating the impregnated fibrous material at a temperature preferably above at least about 100° C. in the presence of an acid substance. The present invention also includes novel compositions for treating cellulosic fibrous materials and containing tetraoxane and/or pentaoxane and a catalyst of acid substance.

In spite of the fact that the tetraoxane and/or pentaoxane used in the present invention are themselves cyclic compounds having directly no reactivity for cellulosic fibrous materials, it is believed that the rings of these compounds are opened by the action of acid substances and elevated temperatures during the above-mentioned heat treatment and that the resulting product reacts with the cellulosic fibrous material.

A well known conventional compound which is a cyclic compound similar to tetraoxane or pentaoxane, is trioxane having the structure



This compound has been used as an additive to N-methylol substances in the treatment of cellulosic fibrous materials for enhancing wet and dry crease angles and other properties of the treated fibrous material (see British Pat. 1,081,039). However, according to our investigations, when a cellulosic fibrous material is impregnated with trioxane in the absence of any N-methylol substance and heated in the presence of an acid substance, the increase, if any, in crease resistance and smooth drying properties of the treated cellulosic fibrous material is very low and insufficient from a practical standpoint, irrespective of the amount of the trioxane used.

The reasons for this are not clear. However, as a possible explanation, it is believed that the lack of effect of trioxane in modifying cellulosic fibrous materials is due (1) to the far lower reactivity of trioxane, particularly to the far lower velocity of ring-opening and reaction of trioxane when heated in the presence of an acid substance, and (2) the excessively higher volatility of trioxane such that, during heat-treatment, it volatilizes by sublimation and evaporation from the cellulosic fibrous material.

The acid substances or acid catalysts used in the method of the present invention are any substances which show acidity at the time of the above-mentioned heating treatment and include, for example, such inorganic acids as hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid and others; such organic acids are formic acid, acetic acid, oxalic acid, tartaric acid, citric acid, benzene sulfonic acid and others; ammonium salts and amine salts of the above-mentioned inorganic acids and organic acids; such metallic salts of the above-mentioned acids, preferably magnesium and zinc salts, such as, magnesium chloride, zinc chloride, zinc nitrate, magnesium fluoborate, zinc fluoborate and others. Any acidic catalyst employed heretofore in modifying cellulosic materials with N-methylol substances as mentioned above, can be used in the present invention. Single catalysts or mixtures of two or more can be used. The amount of catalyst used can be varied over wide ranges depending on the kind of acid substance (or catalyst) and is usually 0.01 to 1000, preferably 0.1 to 1000, more preferably 0.1 to 100, parts by weight per 100 parts by weight of the total modifier, e.g., tetraoxane and/or pentaoxane used.

The cellulosic fibrous material which can be used in the present invention is any material in which at least a part, for example 10 to 100 weight percent, of the component fibers consists of cellulosic fibers. Examples of cellulosic fibers include natural fibers as cotton, linen and ramie, and staple fibers or filaments of such regenerated fibers as viscose rayon and cupra rayon.

These cellulosic fibrous materials can comprise cellulosic fibers only or as mixed with one or more other types of staple fibers or filaments, for example, synthetic fibers such as of the polyamide, polyester, polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, polyvinyl alcohol, polyolefin and polyether types, protein fibers such as wool and silk, and/or inorganic fibers such as glass fibers, graphite fibers and asbestos fibers. The term "cellulosic fibrous materials" as used herein includes all materials containing cellulosic fibers of the types described above with or without other fibers as described above and can be treated according to this invention in the form of staple fibers or filaments or in woven, nonwoven (bonded) or knitted form or in the form of yarns. Cellulosic textiles are the preferred fibrous material.

The modifier used in the present invention contains either tetraoxane or pentaoxane individually or both together. Tetraoxane used in the present invention can be produced by any suitable method, several of which are well known. For example, it can be produced by decomposing polyoxymethylene in which the terminal group is stabilized (for example, a polyoxymethylene in which the terminal hydroxyl group is acetylated, alkylated or urethanated), the decomposition being carried out at a temperature above at least 100° C. under a reduced pressure in the presence of a catalyst selected from alkali metal salts of persulfuric acid, alkali metal salts of acid sulfuric acid, zinc chloride or picric acid (see Japanese Pat. No. 500,317).

Pentaoxane used in the present invention can be produced by any suitable method, several of which are well known. For example, it can be isolated from the residue resulting from the polymerizing reaction of trioxane or from the thermodecomposition product (in the presence of an acid substance or catalyst) of said trioxane polymer (see K. H. Burg et al. Die Makromolekular Chemie 111, 181–193 (1968)).

The modifier used in the present invention can contain one or more of the N-methylol substances described above and previously used as modifiers for cellulosic fibrous materials, amino type compounds and/or trioxane, together with the tetraoxane and/or pentaoxane.

Typical examples of the above-mentioned N-methylol substances include the urea-formaldehyde resins such as dimethylol urea, precondensates and the like, melamine-formaldehyde resin, dimethylol ethylene urea and dimethylol glyoxal monourein and alkylated derivatives thereof. The ratio of N-methylol substance to the total of tetraoxane and/or pentaoxane is in a range of 50:1 to 1:50 by weight. Preferably the weight amount of tetraoxane and/or pentaoxane is greater than that of the N-methylol substance. For example, the total amount of tetraoxane and/or pentaoxane is 50 to 100% based on the weight of N-methylol substance, tetraoxane and pentaoxane.

The above-mentioned amino type compounds which can be used in the present invention are compounds containing at least one HN< group such as the amino group, imino group, amido group and/or the imido group.

Typical examples of suitable amino type compounds include aminotriazines such as melamine; guanidine compounds such as dicyandiamide and guanidine; urea compounds such as urea, thiourea and N,N′-dialkyl urea; cyclic urea compounds, such as, ethylene urea, propylene urea, 4,5-dihydroxyethylene urea, 5-hydroxypropylene urea, acetylenediurein, uron, 5-alkyltriazone and 5-hydroxyalkyltriazone; carbamate compounds, such as, methyl carbamate, ethyl carbamate, isopropyl carbamate, butyl carbamate, hydroxyethyl carbamate, methoxyethyl carbamate, 2-hydroxypropyl carbamate and ethylene glycol dicarbamate and their alkylated derivatives, i.e., their N- or N,N′-alkyl substituted derivatives; hydantoin type compounds such as hydantoin and 5,5-dimethylhydantoin; carbamoyl ethyl type compounds such as tris-(2-carbamoyl ethyl) amine and bis-(2-carbamoyl ethyl) alkylamine; amide type compounds of unsaturated organic acids such as acrylamide and methacrylamide.

Reaction products of the above-mentioned amino type compounds form N-methylol substances and thus the formaldehyde reaction products of each of the above-mentioned amino type compounds can be used as the N-methylol substance in the manner described above. Moreover, alkylated derivatives, i.e., the reaction products of an alkanol with the N-methylol substance can be used as the N-methylol substance in the manner described above.

The ratio of the amino type compound to the total of tetraoxane and/or pentaoxane is generally 1 to 100 parts by weight per 100 parts by weight of the total of tetraoxane and/or pentaoxane.

One mode of working the present invention is explained as follows. A cellulosic fibrous material is impregnated with the modifier and acid substance simultaneously or one after the other. It is necessary that the modifier and acid substance be simultaneously held in the cellulosic fibrous material at the time that it is heat-treated.

Both the modifier and acid substance can be contained in the cellulosic fibrous material before the heat-treatment or a part of either one or both of them can be contained in the cellulosic fibrous material before the above-mentioned heat-treatment and the remainder can be applied to the cellulosic fibrous material simultaneously with the heat-treatment. Also, both of them can be applied to the cellulosic fibrous material simultaneously with the above-mentioned heat-treatment.

In impregnating the cellulosic fibrous material with the modifier and heat-treating it in the presence of the acid substance, the heat-treating temperature is preferably above at least about 100° C. because, when the heat-treatment is carried out at a temperature below about 100° C., the improvement in crease resistance and smooth drying properties of the cellulosic fibrous material may not be fully realized, a long time may be required to develop such effects, and the reproduceability of such effects may be poor and thus is less satisfactory in practice.

To avoid such degradative influences on the cellulosic fibrous material itself as, for example, discoloration and strength reduction, the temperature used in the heat-treatment is generally substantially below about 230° C. and is usually preferably in the range of about 130 to about 180° C.

Further, in working the present invention, the cellulosic fibrous materials are impregnated with the modifier and acid substance simultaneously, or one after the other as described above, or in any other manner. A method of impregnation which is practical and convenient is as follows.

Either one or both of the modifier and acid substance (catalyst) is or are dissolved or dispersed in a suitable solvent to form a treating bath and the cellulosic fibrous material is impregnated with the obtained treating bath by a suitable method such as padding, dipping, coating or spraying.

As solvents suitable for use in preparing the treating bath, there are, for example, water; such aliphatic alcohols as methanol, ethanol and isopropyl alcohol, such aromatic hydrocarbons as benzene, toluene and xylene; such aliphatic and aromatic nitrohydrocarbons as nitromethane, nitroethane, nitropropane and nitrobenzene; such aliphatic halogenohydrocarbons as trichloroethylene, tetrachloroethylene, dichloroethane, tetrachloroethane and chloroform; such aliphatic, and alicyclic ethers as diethyl ether and dioxane; such ketones as acetone, methyl ethyl ketone and methyl isobutyl ketone; such acetic esters as methyl acetate and ethyl acetate and mixtures of two or more of these solvents.

The concentration of the total of tetraoxane and pentaoxane in the solvent or liquid phase is not narrowly critical and can vary from about 0.1 to about 90%, preferably about 0.5 to about 30%, based on the total weight of the solution or dispersion. The total amount of tetraoxane and/or pentaoxane applied to the cellulosic fibrous material is not narrowly critical and can be varied over wide ranges, e.g., about 0.1 to about 50%, preferably about 0.5 to about 15%, based on the total weight of cellulose or cellulosic derivative in said material.

Further, heretofore there has been used a method of modifying cellulosic fibrous materials with formaldehyde alone by using (1) formalin, (2) gaseous formaldehyde or (3) paraformaldehyde or trioxane as a formaldehyde generating substance. However, in such prior modifying treatments the pungent smell of formaldehyde emanates during the treating step and from the finished cellulosic fibrous material after the treating step. The workability of such prior treatments is so poor from an industrial standpoint since formaldehyde is a gaseous substance, it is very difficult to reproduceably develop the same levels of crease resistance and smooth drying properties and the strength of the treated cellulosic fibrous material is very low. Thus, such prior methods have not yet been substantially accepted commercially.

In the method of modifying cellulosic fibrous materials according to the present invention, when at least one of tetraoxane and pentaoxane is used as a modifying agent, no formaldehyde smell issues at all out of the cellulosic fibrous material during or after treatment and there is no defect at all in workability.

Further, according to our investigations, cellulosic fibrous materials modified by the method of the present invention are more than twice as high in formaldehyde content as materials modified with the above-mentioned prior formaldehyde treating process. Thus, it is believed that the cross-links between the modified cellulose molecules are longer as a result of the method of the present invention than by the prior method using formaldehyde.

By the process of the present invention, the rings of the tetraoxane and pentaoxane are believed to open and react instantly with cellulose molecules, without decomposing into formaldehyde, to give crosslinks between cellulose molecules. It has been found that the difference in the length of the crosslinks can have a great influence on the strength of the treated cellulosic fibrous material.

It is believed that the crosslinks formed in the cellulose fiber composing cellulosic fibrous material by the present invention are longer and thus the cellulose molecules which compose the cellulose fiber have a larger degree of freedom of movement and there results a higher strength in the treated cellulosic fibrous material than obtained with formaldehyde or the like by the use of formalin, gaseous formaldehyde or paraformaldehyde or trioxane as a formaldehyde generating substance.

In the method of the present invention, when at least one of tetraoxane and pentaoxane and an N-methylol substance are simultaneously used, at the time of the heat-treatment, it is believed that the rings of at least one of tetraoxane and pentaoxane open and the product of ring opening modifies the cellulosic fibrous materials while reacting with the N-methylol substance. As a result, the improvements of the crease resistance and smooth drying properties of said cellulosic fibrous material is remarkably greater than in the case of using the N-methylol substance in the conventional method. Moreover, the defect of chlorine damage is avoided and the amount of and the degree of methylolation of the N-methylol substance used can be substantially reduced to avoid the generation of formaldehyde odor during and after the modifying treatment.

In the method of the present invention, when the above-mentioned amino type compound is also used together with at least one of tetraoxane and pentoxane, at the time of the heat-treatment, the rings of at least one of tetraoxane and pentaoxane open and the product of ring opening modifies the cellulosic fibrous materials while reacting with the amino type compound which shows a buffer action toward the acid catalyst. Therefore, the present invention is particularly advantageous when such buffer action is needed in order to prevent the color or whiteness of the cellulosic fibrous material from being changed. With the simultaneous use of the amino type compound, the crease resistance and smooth drying properties of said cellulosic fibrous material are improved to a commercially acceptable degree.

In the method of the present invention, when trioxane is used together with at least one of tetraoxane and pentaxoxane, the ring opening of the trioxane is accelerated by the tetraoxane or pentaoxane, the rings of which are far more likely to be opened than those of the trioxane and, as a result, the crease resistance and smooth drying properties of said cellulosic fibrous material is improved to a degree which is satisfactory from the practical viewpoint as compared with the modification of the cellulosic fibrous material by using trioxane alone. However, even when the same modifying treatment as in the method of the present invention is carried out by using only trioxane as a modifier instead of at least one of tetraoxane and pentaoxane, as described above, the remarkable effects of the crease resistance and smooth drying properties of the present invention are not obtained.

Additives which are conventionally used in the modification of cellulosic fibrous materials such as softeners, strength loss reducing agents, water-repellents, water- and oil-repellents, hand builders, anti-static agents, wetting agents and pH adjusting agents may be simultaneously used with the modifiers of this invention for example in the treating baths containing the modifiers.

The residual acid catalyst and the unreacted substances remaining in the cellulosic fibrous material after heat-treatment can be removed in the same manner as in conventional treatments, e.g., by soaping with an aqueous solution containing an anionic surface active agent, nonionic surface active agent or alkaline substance and washing. But, on the other hand, when the present invention is used in such methods as, for example, post-curing methods in the manufacture of permanent press garments, such soaping and washing need not be carried out.

In the present invention, when mechanical shaping such as embossing, calendering or pleating is applied to a cellulosic fibrous material before the completion of the heat-treatment, there is obtained a secondary effect that such mechanical shaping has durability after the completion of the heat-treatment. Moreover, the methods and modifiers of the present invention can be used in permanent press methods such as the post-cure method where the heat-treatment is completed after carrying out mechanical shaping together with cutting and sewing. For example, cellulosic fabrics can be impregnated with modifiers of this invention, the impregnated fabrics can then be dried, the dried fabric can then be cut and sewn into a garment, the garment can then be pressed and cured to form a durably shaped garment.

The following examples are presented in which, unless otherwise specified, parts and percentages are on a weight basis and temperatures are on the centigrade scale.

EXAMPLES 1–10

Aqueous solutions containing the types and amounts of modifiers set forth in Table I were prepared and used as treating baths in the following manner. In each case, 1.2% $Zn(NO_3)_2 \cdot 6H_2O$ catalyst based on the weight of treating bath was used.

Ordinary desized, scoured, bleached and mercerized cotton broadcloth was dipped in each treating bath, squeezed to a pick-up of 70% by pressing rolls, dried with hot air at 80° C. for 4 minutes, further heat-treated at 150° C. for 4 minutes in a pin-tenter frame type of oven, then soaped at 50° C. with water containing 0.2% soda ash and 0.2% neutral detergent for 1 minute and then thoroughly rinsed with water and dried to obtain a finished broadcloth.

For each resulting cloth, the crease resistance (see the column headed "Initial" in Table I) was measured by the Monsanto method and the smooth drying properties (appearance ratings) after 5 home launderings were measured by the method of A.A.T.C.C. 88 A 1964 T. Also, the crease resistance after the above-mentioned 5 home launderings was also measured by the Monstanto method. Also, the initial finished broadcloth was soaped at 100° C. for 40 minutes with an aqueous solution containing 0.05% soap powder, was then rinsed with water at 60° C., was dried and was then chlorinated and scorched by the method of A.A.T.C.C. 92–1967 and the level of chlorine resistance, if any, was observed by the degree of discoloration. The results of these tests are given in Table I.

TABLE I

Ex. No.	Modifiers (content in percent by weight of the treating bath): Tetra-oxane	Penta-oxane	Tri-oxane	(*)	Propylene urea	Properties of finished broadcloth: Crease resistance (in degrees): Initial	After 5 home launderings	Smooth drying properties (rating)	Chlorine resistance	Remarks
1	4					301	297	5	Did not discolor	Examples of the present invention.
2		4				299	292	5	do	Do.
3	3	1				303	296	5	do	Do.
4	1	1	2			295	289	5	do	Do.
5		2	2			291	285	4	do	Do.
6			4			193	187	1	do	Comparative example.
7	3			1		292	288	4	do	Example of the present invention.
8			3	1		218	199	2	Discolored to be brown	Comparative examples.
9				4		276	262	4	do	Do.
10	4				0.4	297	292	5	Did not discolor	Example of the present invention.

*1,3-dimethylol-4,5-dihydroxy-2-imidazolidinone.

EXAMPLES 11–18

Aqueous solutions containing the types and amount of modifiers and acid substances (catalyst) set forth in Table II were used as treating baths. Ordinary desized, scoured, bleached and mercerized cotton twill fabric was dipped in the treating bath, squeezed to a pick-up of 65% in the same manner as in Examples 1–10, dried with hot air at 80° C. for 4 minutes and was cut and sewn into a pant leg. Each pant leg was steamed for 3 seconds, then pressed at a head temperature of 150° C. under a pressure of 1 kg./cm.^{2} for 10 seconds to provide creases. Each pressed pant leg was suspended in an oven so that the creases were vertical and then heat-treated at 160° C. for 5 minutes. The smooth drying properties and crease retention of each pant leg were measured by using the methods of A.A.T.C.C. 88A and 88C, respectively. Also, the crease resistance and chlorine resistance were investigated by the same methods as described in Examples 1–10. The smooth drying properties and the crease retention ratings were 5 in each case. In the chlorine resistance test, none of the treated fabrics discolored. The values of the crease resistance are given in Table II.

TABLE II

Ex. No.	Content in percent by weight of the treating bath: Modifier: Penta-oxane	Tetra-oxane	Acid substance: $MgCl_2\cdot 6H_2O$	$ZnCl_2$	$Mg(BF_4)_2\cdot 6H_2O$	$Al_2(SO_4)_3\cdot 18H_2O$	Crease resistance (in degrees): Initial	After 5 home launderings
11	3		4				292	288
12	3			2			289	284
13	3				1		296	291
14	3					0.4	294	290
15		3	4				293	289
16		3		2			288	285
17		3			1		293	288
18		3				0.4	295	289

EXAMPLES 19–21

Aqueous solutions containing 4% by weight tetraoxane and 1.2% by weight magnesium fluoborate hexahydrate were used as the treating baths. Cotton broadcloth as described in Examples 1–10 was dipped in each treating bath, squeezed and dried in the same manner as described in Examples 1–10 and was then divided into three sections and the three kinds of heat-treatment as are shown in the following Table III were applied to them in a pin-tenter frame type oven. After the heat-treatment, crease resistance and smooth drying properties (appearance) of each of these sections of each cloth were measured in the same manner as described in Examples 1–10 and are given in Table III.

TABLE III

Ex. No.	Heat-treating conditions: Temperature (in ° C.)	Time (in min.)	Crease resistance (in degrees): Initial	After 5 home launderings	Smooth drying properties (rating)	Remarks
19	90	5	188	179	1	Comparative example.
20	140	5	289	277	4	Examples of the present invention.
21	180	1.5	311	302	5	Do.

EXAMPLES 22–25

Aqueous solutions containing the types and amounts of modifiers set forth in Table IV were used as treating baths. In each case, the treating bath contained 4% $MgCl_2\cdot 6H_2O$ catalyst based on the weight of bath. Ordinary desized, scoured and bleached cotton broadcloth was treated with the treating liquid in the same manner as described in Examples 1–10. The crease resistance and smooth drying properties of the treated cloths were measured in the same manner as described in Examples 1–10 and the tear strength was measured with an Elmendorf type tearing tester. The measured values are given in Table IV. The chlorine resistance was also observed in the manner as described in Examples 1–10 and it was found that the treated broadcloth did not discolor at all. In Examples 24 and 25, in which formaldehyde was used as a modifier, the operation was very difficult due to the pungent odor of formaldehyde throughout the respective steps of preparing the treating bath and the dipping, squeezing, drying and heat-treating of the cloth. No such odor was observed in carrying out Examples 22 and 23.

TABLE IV

	Contents in percent by weight of the treating bath				Properties of finished broadcloth				
	Modifier				Crease recovery angle (in degrees)				
Ex. No.	Tetraoxane	Pentaoxane	Formaldehyde	Acid substance, $MgCl_2 \cdot 6H_2O$	Initial	After 5 home launderings	Smooth drying properties (Rating)	Tear strength (ing.)	Remarks
22	4			4	295	288	5	634	Examples of the present invention.
23		4		4	296	288	5	629	Do.
24			4	4	277	264	4	603	Comparative examples.
25*			4	4	284	276	4	582	Do.

* Repetition of Example 24.

EXAMPLE 26

An aqueous solution containing 10% by weight tetraoxane and 3% zinc nitrate hexahydrate was used as a treating bath. The ordinary desized and scoured, dyed, blended tropical fabric consisting of 35% viscose rayon and 65% polyester was dipped in the treating bath, was squeezed to a pick-up of 75% and was dried, heat-treated and soaped in the same manner as described in Examples 1–10. When the crease resistance and smooth drying properties (appearance) of the treated fabric were measured in the same manner as described in Examples 1–10, it was found that the initial crease resistance was 305 degrees and the appearance rating was 5.

The crease resistance and appearance rating of the untreated fabric were, respectively, 273 degrees and 4. Since it was a dyed fabric, the chlorine resistance was not tested.

EXAMPLE 27

An aqueous solution containing 10% by weight tetraoxane and 3% by weight zinc nitrate hexahydrate was used as a treating bath. Ordinary desized, scoured and bleached cupra rayon taffeta fabric was dipped in the treating bath, was squeezed to a pick-up of 130% and was dried, heat-treated and soaped in the same manner as described in Examples 1–10. The crease resistance and appearance rating of the treated fabric were measured in the same manner as described in Examples 1–10 and were found to be, respectively, 264 degrees and 4. When the chlorine resistance was tested in the same manner as described in Example 1, the treated fabric did not discolor at all.

The crease resistance and appearance rating of the untreated fabric were measured and found to be, respectively, 123 degrees and 1. The chlorine resistance was the same for the untreated fabric as for the treated fabric. Furthermore, it was noted that the untreated fabric shrank to a much greater degree than the treated fabric during the home launderings conducted in conjunction with the appearance rating tests.

What is claimed is:

1. Method of modifying cellulosic fibrous material in the form of staple fibers, yarns, filaments, woven fabrics, non-woven (bonded) fabrics or knitted fabrics comprising impregnating said material with a modifier composition containing a compound selected from the class consisting of tetraoxane, pentaoxane and mixtures thereof and heating the resulting impregnated material in the presence of an acidic catalyst at a temperature and for a time sufficient to react said compound and provide cross-links in said fibrous material.

2. Method as claimed in claim **1** wherein said temperature is at least about 100° C.

3. Method as claimed in claim **2** wherein said cellulosic fibrous material is a cellulosic textile and said modifier composition is an aqueous solution or dispersion.

4. Method as claimed in claim **3** wherein said modifier composition also contains trioxane.

5. Method as claimed in claim **3** wherein said modifier composition also contains at least one substance selected from the class consisting of organic compounds containing at least one HN< group selected from the class consisting of melamine, guanidine, dicyandiamide, urea, thiourea, N,N′-dialkyl urea, ethylene urea, propylene urea, 4,5-dihydroxyethylene urea, 5-hydroxypropylene urea, acetylenediurein, uron, 5-alkyltriazone and 5-hydroxyalkyltriazone, methyl carbamate, ethyl carbamate, isopropyl carbamate, butyl carbamate, hydroxyethyl carbamate, methoxyethyl carbamate, 2-hydroxypropyl carbamate, ethylene glycol dicarbamate, hydantoin, 5,5-dimethylhydantoin, tris-(2-carbamoyl ethyl) amine, bis-(2-carbamoyl ethyl) alkylamine, acrylamide and methacrylamide, N-methylol derivatives thereof and alkylated derivatives of said N-methylol derivatives.

6. Method as claimed in claim **1** wherein said cellulosic fibrous material is a fabric and the resulting impregnated fabric is dried and cut, sewed and shaped into an article prior to said heating step.

7. Method as claimed in claim **3** wherein said acidic catalyst is selected from the class consisting of zinc nitrate, magnesium chloride, zinc chloride, magnesium fluoborate, zinc fluoborate and aluminum sulfate.

8. Method as claimed in claim **5** wherein said substance is dimethylol glyoxal monourein.

9. Cellulosic fibrous material produced by the method claimed in claim **1**.

10. Cellulosic fibrous material produced by the method claimed in claim **6**.

References Cited

UNITED STATES PATENTS

2,233,402	3/1941	Cresswell	8—116.4
3,268,915	8/1966	Warnock et al.	8—116.3 X
3,426,041	2/1969	Miyake et al.	260—340

FOREIGN PATENTS

1,081,039	8/1967	Great Britain	8—116.4

GEORGE F. LESMES, Primary Examiner

H. WOLMAN, Assistant Examiner

U.S. Cl. X.R.

8—115.5, 116.3, 116.4, 120, 127.6, 128; 117—139.4