METHOD OF MODIFYING FIBROUS MATERIALS

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ABSTRACT

The present invention is a method of modifying cellulosic fibrous materials characterized by impregnating a cellulosic fibrous material with a modifier containing a polyoxymethylene dialkyl diether diether having at least three oxymethylene groups per molecule and reacting same with the fibrous material in the presence of an acid substance. Also covered are novel modifier compositions containing a polyoxymethylene dialkyl diether of the type described above and an acid catalyst.

18 Claims, No Drawings
METHOD OF MODIFYING FIBROUS MATERIALS

This invention relates to novel methods and modifier compositions for modifying fibrous materials consisting of or containing cellulosic fiber. Such materials shall be briefly called cellulosic fibrous materials hereinafter.

Heretofore, cellulosic fibrous materials have been modified by using as modifiers N-methylolated derivatives and/or alkylated N-methylol derivatives of amino compounds, such as, urea, melamine, ethylene urea, propylene urea, glyoxal monourein, carbamic acid esters and the like, in order to improve their crease-resistance and smooth drying property.

Derivatives of this kind shall be briefly called N-methylol substances hereinafter. However, the cellulosic fibrous materials modified by such modifiers as these N-methylol substances have the defects of rough and stiff hand and are susceptible to chlorine damage on account of the amino group contained in the N-methylol substances.

Methods avoiding defects of this type have been disclosed heretofore and use formaldehyde or formalin, or use paraformaldehyde as a formaldehyde generating substance. However, these methods also have the defects of being inefficient, impractical and noxious because of the liberation, when carrying out the method, of large amounts of formaldehyde which is a gas of pungent and noxious smell. Also, the reproducibility of improved crease-resistance and smooth drying property is poor because the methods utilize formaldehyde which is a gaseous substance in normal form and thus difficult to control in reacting it with the cellulosic material which is a solid material.

We have conducted extensive research on the modification of cellulosic fibrous materials to find a novel method and modifier composition for modifying cellulosic fibrous materials without the defects hereinbefore mentioned resulting from methods using as modifiers N-methylol substances, or formaldehyde, or formalin, or paraformaldehyde.

The present invention includes methods of modifying cellulosic fibrous materials characterized by reacting such cellulosic fibrous materials in the presence of an acidic substance with a polyoxymethylene dialkyl diether of the formula R₁O(CH₂O)ₙR₂, wherein R₁ and R₂ are alkyl which may be the same or different in the same molecule, and n is an integer from 3 to 8, hereinafter called the reactant A.

Typical examples of reactant A used in the present invention include trioxymethylene dimethyl diether, trioxymethylene diethyl diether, trioxymethylene dibutyl diether, trioxymethylene dimethyl diether, tetraoxymethylene diethyl diether, pentaoxymethylene dimethyl diether, hexa oxymethylene dimethyl diether, heptaoxymethylene dimethyl diether, octaoxymethylene dimethyl diether, and mixtures of two or more of them. Preferably, the alkyl groups represented by R₁ and R₂ contain one to four carbon atoms, such as methyl, ethyl, isopropyl and butyl, inasmuch as such reactants are more easily and more economically obtained in industrial practice.

In the application of this method, the integer n in the above mentioned formula is required not more than 8 because of the necessary condition that the reactant A must be dissolved homogeneously into the solvents which are described later, and the integer n is also required not less than 3, taking into consideration of (1) the fact that the relative proportion of R₁ and R₂ in the reactant molecule, which are not substantially effective for improvement of cellulosic fibrous materials must be smaller, (2) the volatility of the reactant which affects the reproducibility of the resulting data of improving crease resistance and smooth drying property of the cellulosic fibrous materials, and (3) the necessity that the reactant A must remain in cellulosic fibrous materials after printing.

From above described reasons, the reactant A in the present invention is restricted to those polyoxymethylene dialkyl ethers having from three to eight oxymethylene groups in a molecule. The reactant A which contains more than eight or less than three oxymethylene groups in a molecule is, therefore, excluded from the claim of the present invention.

As typical examples of acid substances or catalysts in the present invention, there are the inorganic acids, such as hydrochloric acid, nitric acid, sulphuric acid, fluoboric acid and phosphoric acid, the organic acids, such as formic acid, acetic acid, oxalic acid, citric acid, benzene sulfonic acids and phytic acid, and the salts of the above-mentioned acids including the magnesium salts, such as magnesium chloride, magnesium nitrate, magnesium sulphate, magnesium fluoroborate, dibasic magnesium phosphate and magnesium acetate, the zinc salts, such as zinc chloride, zinc sulphate, zinc fluoroborate, zinc acetate and zinc oxide, and other metallic salts, such as calcium nitrate, strontium nitrate, cadmium fluoroborate and stannic chloride, the ammonium salts, such as ammonium chloride, ammonium nitrate, ammonium acetate and ammonium oxide, and the amine salts, such as 2-amino-2-methylpropanol hydrochloride and monoethanol amine hydrochloride. As typical examples of acid substances which may be applied in gaseous state to the cellulosic fibrous materials, there are boron trifluoride, hydrogen chloride and sulphur dioxide. Mixtures of two or more of the above-mentioned acid substances may be applied to the cellulosic fibrous material in the present invention.

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 500, parts by weight per 100 parts by weight of the total reactant A 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. The cellulosic fibrous materials which are advantageously modified by the method of the present invention, are, for example, fibrous materials comprising natural fibers such as cotton, flax and ramie; comprising staple fibers or filaments of regenerated fibers such as viscose rayon and cuprammonium rayon; and comprising blends of these cellulosic fibers with staple fibers or filaments of one or more other fibers such as cellulose diacetate, cellulose triacetate, polyamide, polyester, polycapro nitrite, polyvinylchloride, polyvinylidene chloride, polyvinylalcohol, polylefin and polyester type fiber, and silk, wool and glass 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, non-
woven (bonded) or knitted form or in the form of yarns, slivers or towels. Cellulosic textiles are the preferred fibrous materials.

The modifier used in the present invention contains a single reactant A or mixtures of two or more together. The reactant A 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 reacting formaldehyde on a polymer thereof with dicycloalkyl or dialkyl formalin in the presence of an acid reacting catalyst and subsequently adding a basic substance in an amount at least sufficient to neutralize the catalyst, as disclosed in British Pat. No. 603,872.

In the present invention, the means of impregnating the cellulosic fibrous materials with the reactant are not limited. However, it is particularly convenient to impregnate reactant A as part of a liquid body. In such a case, reactant A may be impregnated to cellulosic fibrous material by such means as dipping the cellulosic fibrous material in a liquid body containing reactant A and then squeezing, or by directly coating or spraying the liquid body onto the cellulosic fibrous material. When the liquid body is applied to the cellulosic fibrous material, the temperature of the liquid body may be at normal temperature, or at a temperature kept within the range where the liquid body does not volatilize and the fibers composing cellulosic fibrous material are not damaged, paying attention to the boiling point of the components of the liquid body. In this respect, impregnation is usually carried out at a temperature below 100°C, although higher temperatures can be used, if desired. When reactant A is liquid, it may be applied to the cellulosic fibrous material directly by means of dipping and squeezing, coating or spraying. Generally, however, it is better to apply reactant A as a part of a liquid body obtained by merely dissolving such as, water, aliphatic or acyclic saturated alcohols including methanol, ethanol, isopropanol, butanol, and cyclohexanol; aliphatic, alicyclic or aromatic saturated hydrocarbons including hexane, heptane, cyclohexene, benzene, toluene and xylene; hetenic hydrocarbons including chloroethylenes, chloroethylenes and tetrachloroethylenes; aliphatic or acyclic saturated ethers including diethyl ether and dioxane; ketones including acetone, methyl ethyl ketone and methyl isobutyl ketone; acetate esters including methyl acetate and ethyl acetate; and mixture of two or more of such liquid mediums. After reactant A is applied to the cellulosic fibrous material utilizing a vaporizable liquid medium as mentioned above, a drying step can be applied to the impregnated cellulosic fibrous material to remove the liquid medium. However, a separate drying step need not be used; drying and curing can be carried out in the same step. The acid substance employed in the present invention works as catalyst to aid in splitting the alkyl groups from reactant A and aid the reaction of the polyoxy-methylene moiety with the cellulose. The acid substance can be acidic in its normal state or can be a substance whose acidity can be utilized, for example, by causing the liberating of free acid by such means as heating. The acid substances can be applied to cellulosic fibrous materials in the same manner by which reactant A is applied as described above and can be accomplished by reactant A in the same liquid medium or not. When the acid substance is in gaseous form, it may be applied undiluted per se or diluted with such gas as air, nitrogen, steam and so on. In the method of the present invention, it is convenient to accelerate curing, i.e., the effect of the acid substance and the reaction of reactant A with the cellulose usually by heating at elevated temperatures which preferably do not exceed 230°C.

In the event there remain residues of reactant A, acid substance and/or additives such as those mentioned hereinafter, on the cellulosic fibrous material after curing such residues are readily removed by the usual treating process of after-washing or soaping. In such treating process, the cured cellulosic fibrous materials are treated with a solution containing a low concentration of detergent and/or alkaline substance such as, for example, soap and/or soda ash, respectively, and then rinsed and dried. The sequence of soaping and rinsing can be repeated as often as desired.

One mode of working the present invention is explained as follows. A cellulosic fibrous material is impregnated with the reactant A and acid substance simultaneously or one after the other. It is only necessary that the reactant A and acid substance be simultaneouly held in contact with the cellulosic fibrous material at the time that reactant A is reacted therewith. Both the reactant A and acid substance can be contained in the cellulosic fibrous material before the heat treatment or reactant A can be applied before curing and the acid substance added during curing, 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. Any suitable sequence and mode of application and curing can be used.

The curing temperature used can vary widely depending on the strength and amount of acid substance and the length of curing time that would be acceptable. When strong acids are used, e.g., hydrogen chloride, room temperatures, e.g., 20°C to 30°C, can be used. When less acidic substances, e.g., the acid salts are used, elevated temperatures such as those above 100°C are preferred. To avoid degradative influences on the cellulosic fibrous material itself such as, for example, discoloration and strength reduction, the temperature used in curing is preferably substantially below about 230°C; and is usually preferably in the range of about 100°C to about 180°C. An incense ordinary hot air type oven is utilized.

Further, in working the present invention, the cellulosic fibrous materials are impregnated with the reactant A 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 reactant A and acid substance (catalyst) is or are dissolved or dispersed in a suitable liquid medium 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. The concentration of the total of reactant A in the liquid medium is not narrowly critical and can vary from about 0.1 percent to about 90 percent, preferably about 0.1 percent to about 60 percent, based on the total weight of the solution or dispersion. The total amount of reac-
tant A applied to the cellulosic fibrous material is not narrowly critical and can be varied over wide ranges, e.g., about 0.01 percent to about 50 percent, preferably about 0.05 percent to about 15 percent, based on the total weight of cellulose or cellulosic derivative in said material.

In practicing the present invention, such N-methylol type agents, softeners, strength-loss-reducers, water-repellents, oil-repellents, hand-modifiers, antistatic agents, wetting agents, pH adjusting agents, buffers, optical brighteners and bluing agents as have been used heretofore in the conventional treatment of cellulosic fibrous materials may be utilized with reactant A as far as the use of them does not adversely affect the objects and effects of the present invention. Also, trioxane, tetraoxane and pentaoxane, each alone or in mixtures of two or more together, can also be used in combination with reactant A. Typical examples of the above-mentioned N-methylol type agents include the methylol ureas, methylol melamines, dimethylol ethylene urea and dimethylol glyoxal monourein and alkylated derivatives thereof. The ratio of N-methylol substance to the total of reactant A is in a range of 50:1 to 1:100 by weight. Preferably the weight amount of reactant A is greater than that of the N-methylol substance. For example, the total amount of reactant A is 50 to 100 percent based on the total weight of N-methylol substance and reactant A. Amino type compounds can be used with reactant A in the present invention. Such amino type compounds contain at least one

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group such as the amino group, imino group, amido group and/or the imido group. Typical examples of suitable amino type compounds include amidotriazines such as melamine; guanidine compounds such as dicyandiamide and guanidine; urea compounds such as urea, thiouria and N,N'-dialyl urea; cyclic urea compounds, such as, ethylene urea, propylene urea, 4,5-dihydroxyethylene urea, 5-hydroxypropylene urea, acetylenedienure, uron, 5-alkyltriazine and 5-hydroxyalkyltriazine; carbamate compounds, such as, methyl carbamate, ethyl carbamate, isopropyl carbamate, butyl carbamate, hydroxethyl 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; carbomoyl ethyl type compounds such as tris-(2-carbamoyl ethyl) amine and bis-(2-carbamoyl ethyl) alkyamine; amide type compounds of unsaturated organic acids such as acrylamide and methacrylamide. Reaction products of the above-mentioned amino type compounds form N-methylol type agents and thus the formaldehyde reaction products of each of the above-mentioned amino type compounds can be used as the N-methylol type agents in the manner described above. Moreover, alkylated derivatives, i.e., the reaction products of an alcanol with the N-methylol type agents can be used as the N-methylol type agents in the manner described above. The ratio of the amino type compound to the reactant A is generally 1 to 100 parts by weight per 100 parts by weight of the total of reactant A.

The cellulosic fibrous materials treated by the method of this invention are free of defects of rough and stiff hand and susceptibility to retained chlorine damage because reactant A only makes cross-links between cellulose molecules with no formation of any high molecular weight resins, and reactant A contains no amino groups in its chemical structure.

The method of the present invention is superior to such well known methods which use formaldehyde or formalin, or paraformaldehyde as a formaldehyde generating substance, in that there is no pungent odor of formaldehyde liberated before, during or after the modification treatment, and the reproducibility of improved crease- and shrink-resistance and smooth drying properties is considerably greater. In the method of the present invention as the modification of cellulosic fibrous materials is proceeding, i.e., as the cellulose fiber is cross-linked by reactant A, reactant A does not operate by first degrading into formaldehyde and then reacting with the cellulosic fibrous material, but it is split under the influence of the acid substance to lose the alkoxyethyl groups, and then it immediately reacts with the cellulosic fibrous material. Confronted with these facts, the method of the present invention is fundamentally different from the well known modification treatments of cellulosic fibrous materials. Also, owing to the reaction mechanism mentioned above, the method of the present invention provides the additional advantage of considerably less strength loss because of the greater freedom of motion which is the result of longer cross-links than the well known methods using formaldehyde or formaldehyde generating materials in which straight formaldehyde works upon the cellulose.

Furthermore, in case of applying the present invention, the end alkyl group in the reactant A is liberated as alkoxyethyl group and the alkoxyethyl group reacts directly with the cellulosic fibrous materials forming alkoxyethyl ether. On account of the fact, not only dry crease recovery but wet crease recovery of the treated cellulosic fibrous materials is also improved and the ratio wet/dry crease recovery more than unit. This characteristic indicates that the reactant A has the advantageous effect which can not be expected by applying usual reagents for treating cellulosic fibrous materials.

In the present invention, all of the reactants A are generally stable chemicals having no pungent odor such as formaldehyde, which is a great advantage in handling and applying it to the cellulosic material. In practicing the present invention and above all on the application of reactant A as a solution in water or other solvent, reactant A is dissolved without depolymerization and does not liberate formaldehyde odor. In contrast, paraformaldehyde which has been herein-above mentioned as a formaldehyde generating substance is comparatively unstable under normal conditions and liberates a pungent odor of formaldehyde as it gradually decomposes. Paraformaldehyde can be dissolved in water or polar solvents, but it cannot be dissolved without depolymerization down to formaldehyde to liberate the pungent odor of formaldehyde. From such a viewpoint, reactant A utilized in the present invention has the great advantage in workability and practical handling.

In the present invention, when mechanical shaping or treatment such as embossing, calendering, pleating and polishing is performed on the cellulosic fibrous materials before the completion of curing under the influence
of the acid substance during the modification process, there is a secondary effect that such mechanical shaping has durability after completion of curing. 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, cellulose 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, percentages of components in the treating baths or aqueous solutions are based on the total weight of the bath or solution, temperatures are on the centigrade scale and crease resistances are in degrees as the total of warp and filling crease recoveries. The temperatures of the treating baths in the following examples were, unless otherwise specified, at the normal temperature of about 20°-25°C.

**EXAMPLES 1-11**

11 treating baths were prepared each containing the polyoxymethylene dialkyl diether and acidic catalyst and other additives (if any) identified in Table I in the amounts also set forth in the Table in percentage. For Examples 2 and 3, mixtures of equal weight amounts of ethyl alcohol and water, and if isopropyl alcohol and water, respectively, were used as the liquid medium. Water was used in the other examples. Each treating bath was padded onto the untreated fabric in the usual manner using squeezing rolls to provide the following wet pick-ups. In Examples 1-8 and Control A, the fabric was a 100 percent cotton broadcloth and the wet pick-up was 73 percent in each case. In Example 9 and Control B, the fabric was spun rayon muslin which was desized and scoured in the usual way and, in each case, the wet pick-up was 100 percent. In Examples 10 and 11 and Control C, the fabric was a blend broadcloth containing 65 percent polyester and 35 percent cotton, and in each case the wet pick-up was 65 percent. The cotton broadcloth and the blend broadcloth fabrics used had been desized, scoured, bleached and mercerized in the usual manner. In Examples 4 and 5 the temperature of the treating baths was about 50°C.

Each fabric was dried with hot air at 80°C for 4 minutes to provide dry, curable fabrics and then further cured at 150°C for 4 minutes in a pintenter frame oven. Each cured fabric was then soaked at 50°C with water containing 0.2 percent soda ash and 0.2 percent neutral detergent for 1 minute and then thoroughly rinsed with water and dried to obtain the finished fabric.

For each finished fabric, the crease-resistance was measured by the Monsanto method and the smooth drying property (appearance rating) after 5 home launderings were measured by the method of A.A.T.C.C. 88A 1964T. The results of these tests are given in Table I.

Each of the finished fabrics showed better hand resilience and softness compared with control fabrics which were treated with water as the treating bath.

Also, each finished fabric showed no discoloration on scouring after chlorination by the method of A.A.T.C.C. 92-1967. Thus, each finished fabric was characterized by excellent chlorine resistance.

**TABLE I**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Diether, RO(CH₂)ₙR</th>
<th>Acidic Catalyst</th>
<th>Other Additive</th>
<th>Crease Recovery</th>
<th>Appearance Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>CH₃</td>
<td>Zn(NO₃)₂, 6H₂O</td>
<td>Do.</td>
<td>174</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>Zn(NO₃)₂, 6H₂O</td>
<td>Do.</td>
<td>293</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>CH₃</td>
<td>MgBF₄, 6H₂O</td>
<td>Do.</td>
<td>291</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>CH₃</td>
<td>MgCl₂, 6H₂O</td>
<td>Do.</td>
<td>288</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>CH₃</td>
<td>MgCl₂, 6H₂O</td>
<td>Do.</td>
<td>297</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>CH₃</td>
<td>MgCl₂, 6H₂O</td>
<td>Do.</td>
<td>310</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>CH₃</td>
<td>MgCl₂, 6H₂O</td>
<td>Do.</td>
<td>315</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>MgCl₂, 6H₂O</td>
<td>Do.</td>
<td>310</td>
<td>5</td>
</tr>
<tr>
<td>Control B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CH₃</td>
<td>Zn(BF₄)₂</td>
<td>Glyoxal</td>
<td>296</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>CH₃</td>
<td>ZnCl₂</td>
<td>Dimethylol</td>
<td>301</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>CH₃</td>
<td>ZnCl₂</td>
<td>Monomethylol</td>
<td>301</td>
<td>5</td>
</tr>
</tbody>
</table>

*"Amt." in Table I is the abbreviation of "amount".*
EXAMPLE 12

An aqueous solution containing CH₃OH(CH₂O)₁₂CH₃, CH₃O(CH₂O)₆CH₃, and CH₃O(CH₂O)₈CH₃ in the relative amounts of 1.2, 3.6 and 1.2 percent, respectively, and 1.5% Zn(BF₄)₂ was applied to a 100 percent cotton twill fabric which had been desized, scoured, bleached and mercerized in the usual manner to a wet pick-up of 75 percent. The resulting impregnated fabric was dried in the same manner as described in Examples 1-11. The resulting dried, curable fabric was sewn into a pant leg, pressed with a hand iron and a commercial side-press for pant legs to provide creases. The creased pant leg then was suspended in an oven so that the creases were vertical and cured at 160°C for 7 minutes. The smooth drying property (appearance rating) and crease-resistance of the pant leg were measured by the same methods as described in Examples 1-11 and found to be 5° and 298° respectively. The creases of the pant leg remained sharp after the five home launderings performed for the measurement of the smooth drying property.

A control fabric which was treated with water as the treating bath had a crease-resistance of 172° and a smooth drying property or appearance rating of 2. The creases of the pant leg disappeared after five home launderings. The fabric treated by the method of the present invention had a better hand than the control and its chlorine resistance (A.A.T.C.C. 92-1967) was excellent.

EXAMPLE 13

An aqueous solution containing 10 percent of a mixture of CH₃O(CH₂O)₆CH₃, CH₃O(CH₂O)₆CH₃, and CH₃O(CH₂O)₈CH₃ in the weight ratio of 1:6:3 was applied to the same cotton broadcloth as used in Examples 1-8 and dried to obtain a dried, curable fabric in the same manner as described in Examples 1-11. The wet pick-up was 74 percent.

A vessel separated by a horizontal plastic net into upper and lower parts, with a lid on the top of the upper part, and containing concentrated hydrochloric acid (35 percent) in the bottom of the lower part was prepared.

The dried, curable fabric was spread flat on the plastic net in the vessel and left for 20 minutes after the lid of the vessel had been shut (i.e., the fabric was subjected to hydrogen chloride gas from the hydrochloric acid). The temperature inside the vessel was kept at 21°C during the procedure. The fabric was then taken out of the vessel, washed with water, and then with 0.2 percent soda ash solution, neutralized with dilute acetic acid, and thoroughly rinsed with water and dried to obtain a finished fabric.

The crease-resistance and the smooth drying property of the finished and control fabrics (treated with water as the treating bath were measured by the same method as described in Examples 1-11. The crease-resistance was 287° and 175°, respectively, and smooth drying property or appearance rating was 5 and 1 respectively, for the finished and control fabrics.

The finished fabric treated by the method of the present invention had a better hand then the control and its chlorine resistance was excellent.

EXAMPLE 14

A water solution containing 6% CH₃O(C-}

H₂O)₆CH₃ and 2% Zn(BF₄)₂ was applied to the same type of cotton broadcloth as described in Examples 1-8 to obtain a finished fabric in the same manner as described in Examples 1-11 through padding, drying, curing, soaking, rinsing and drying. The wet pick-up was 80 percent. This part illustrates the present invention.

B. Part A was repeated except that CH₃O(C-H₂O)₆CH₃ was substituted on a weight for weight basis for CH₃O(CH₂O)₈CH₃. This part does not illustrate the present invention.

C. Part A was repeated except that only water was used as the treating bath or solution. This part represents a control fabric.

The crease-resistance and smooth drying properties of both fabrics were measured by the methods described in Examples 1-11 and the results set forth in Table II were obtained.

| TABLE II |
| A. Example of the present invention | B. Comparative Example | C. Control |
| Crease-resistance (degrees) | 298 | 174 | 176 |
| Smooth Drying Property (appearance rating) | 5 | 1 | 1 |

The hand of the fabric of comparative example B did not differ from that of the control fabric C. But the fabric of the present invention, fabric A, had a better hand than the control fabric and its chlorine resistance was excellent.

EXAMPLE 15

A. An aqueous solution containing 5% CH₃O(C-H₂O)₆CH₃ and 2% Zn(BF₄)₂ was applied to the same type of cotton broadcloth as described in Examples 1-8 in the same manner as described in Examples 1-11 except that the wet pick-up was 80 percent to obtain a finished fabric. This treatment and the finished fabric shall be briefly called hereinafter treatment A and fabric A, respectively.

B. The same treatment as treatment A was performed to obtain a finished fabric except that the dried, curable fabric, was stored before curing for 24 hours in a chamber in which the temperature and the relative humidity were kept at 20°C and 65 percent, respectively. This treatment and the finished fabric shall be briefly called hereinafter treatment B and fabric B.

C. The same treatments as treatment A and B were performed except that, in each case, formaldehyde (commercial 37 percent formalin as source) was substituted on a weight for weight basis for CH₃O(C-H₂O)₆CH₃ to obtain finished fabrics. These treatments and fabrics shall be briefly called hereinafter treatments A' and B', and fabrics A' and B' corresponding to treatments A and B, and fabrics A and B, respectively. The treatments A' and B' were different from the treatments A and B in that the operators suffered from the extremely pungent odor of formaldehyde during the preparation of the treating bath, dipping the fabrics in the bath, drying the impregnated fabric, storing in the case of treatment B and curing the dried, impregnated fabric.
The crease-resistance and smooth drying properties of all fabrics were measured by the methods described in Examples 1–11 and the results are set forth in Table III.

**TABLE III**

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Crease-Resistance (degrees)</th>
<th>Smooth Drying Property (appearance rating)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>291</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>294</td>
<td>5</td>
</tr>
<tr>
<td>A'</td>
<td>290</td>
<td>5</td>
</tr>
<tr>
<td>B'</td>
<td>211</td>
<td>1</td>
</tr>
<tr>
<td>Control</td>
<td>179</td>
<td>1</td>
</tr>
</tbody>
</table>

**EXAMPLE 16**

An aqueous solution containing 6 percent of a mixture of equal weight amounts of CH₂O(CH₂O)₅CH₃ and CH₂O(CH₂O)₅CH₃, and 2% ZnCl₂ and 0.2% CH₃COOH was prepared. The solution was applied, as a treating bath, to the same type of cotton broadcloth as used in Examples 1–8 in the same manner as Examples 1–11. The fabric was cured, without drying, at 170° C. for 2 minutes in a pin-tenter frame type of oven, and then soaped, rinsed and dried in the same manner as Examples 1–11 to obtain a finished fabric.

The crease-resistance and the smooth drying property of the finished fabric as measured in the same manner as Examples 1–11 were found to be 294° and Class 5, respectively. A control fabric treated in the same way with water as a treating bath was found to have a crease resistance of 177° and a smooth drying property appearance rating of 1.

What is claimed is:

1. Method of modifying cellulosic fibrous material comprising impregnating said material with a modifier composition containing a polyoxymethylene di-lower alkyl diether having the formula

\[ R_1O(CH₂O)ₙR_2 \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl and \( n \) is an integer from 3 to 8 and reacting said polyoxymethylene di-lower alkyl diether with said material in the presence of an acidic catalyst.

2. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is tetraoxymethylene diethyl diether.

3. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is tetraoxymethylene diethyl diether.

4. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is di-oxypropyl diether.

5. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is trioxymethylene dimethyl diether.

6. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is penta-oxymethylene dimethyl diether.

7. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is hexa-oxymethylene dimethyl diether.

8. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is heptaoxymethylene dimethyl diether.

9. Method as claimed in claim 1 wherein said polyoxymethylene di-lower alkyl diether is octa-oxymethylene dimethyl diether.

10. Method as claimed in claim 1 wherein said modifier composition also contains a material selected from the class consisting of tetraoxane, penta-oxane, mixtures thereof and mixtures of at least one of them with trioxane.

11. Method as claimed in claim 1 wherein said modifier composition also contains at least one substance selected from the class consisting of organic compounds containing at least one group and N-methylol derivatives thereof.

12. Method as claimed in claim 1 wherein said acidic catalyst is selected from the class consisting of zinc nitrate, magnesium chloride, zinc chloride, magnesium fluorate, zinc fluorate, hydrogen chloride, and mixtures thereof.

13. Composition for modifying cellulosic fibrous materials comprising a solution or dispersion of a polyoxymethylene di-lower alkyl diether having the formula

\[ R_1O(CH₂O)ₙR_2 \]

wherein \( R_1 \) and \( R_2 \) are lower alkyl and \( n \) is an integer from 3 to 8 and an acidic catalyst in a vaporizable inert liquid.

14. Composition as claimed in claim 13 wherein said polyoxymethylene di-lower alkyl diether is selected from the class consisting of tetraoxymethylene diethyl diether, tetraoxymethylene diethyl diether, tetraoxymethylene diisopropyl diether, trioxymethylene dimethyl diether, penta-oxymethylene dimethyl diether, hepta-oxymethylene diethyl diether, hepta-oxymethylene dimethyl diether, octa-oxymethylene dimethyl diether and mixtures thereof.

15. Composition as claimed in claim 14 wherein said solution or dispersion also contains at least one substance selected from the class consisting of organic compounds containing at least one group and N-methylol derivatives thereof.

16. Composition as claimed in claim 14 wherein said solution or dispersion also contains a material selected from the class consisting of tetraoxane, penta-oxane, mixtures thereof and mixtures of at least one of them with trioxane.

17. Composition as claimed in claim 14 wherein said acidic catalyst is selected from the class consisting of zinc nitrate, magnesium chloride, zinc chloride, magnesium fluorate, zinc fluorate, hydrogen chloride, and mixtures thereof.

18. Cellulosic fibrous material treated by the method claimed in claim 1.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,840,339
DATED : October 8, 1974
INVENTOR(S) : Kosuke YAMAMOTO et al.

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

Col. 3, line 50, "carbomoyl" should be --carbamoyl--
Col. 7, line 33, "if" should be --of--
Col. 9, line 28, "batter" should be --better--

Signed and sealed this
nineteenth Day of July 1977

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks