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CELLULOSIC TEXTILES REACTED WITH
ALDEHYDES IN AN AZEOTROPIC ME-
DIUMJoseph W. Schappel, Morton, Pa., assignor to
American Viscose Corporation, Wilmington,
Del., a corporation of DelawareNo Drawing. Original application December 16,
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11 Claims. (Cl. 8-116.4)

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This invention relates to the treatment of hydroxylated textile materials such as regenerated cellulose with aldehydes which react with the hydroxyl groups of the textile to form acetal-type bridges between the hydroxyl groups. The invention is of particular advantage in the modification of textiles composed of or comprising regenerated cellulose with formaldehyde and will be described more in detail in connection with that embodiment. This is a continuation of my application Serial No. 65,741, filed December 16, 1948, now abandoned.

The term "textile material" includes filaments, fibers, staple or yarns, whether in the finished condition or at some intermediate stage in their production, as well as fabrics, such as knitted, woven or felted fabrics, and garments or other articles made from them.

It has been proposed heretofore to react textile materials with aldehydes, and especially formaldehyde, for increasing the strength, especially the wet strength, of the textile, or to improve its resilience, crease resistance, and/or resistance to shrinkage, and to reduce the extent to which the materials are swollen by water. However, in spite of the fact that formaldehyde is known to improve various properties of the textile, the formaldehyde treatment has not been used commercially except in a few isolated instances, apparently because of the difficulty of insuring uniform reaction of the hydroxyls of the textile with the formaldehyde and of obtaining predictable, reproducible results.

The uniformity of the aldehyde-modified textile is determined by the number and distribution of the acetal bridges between the hydroxyl groups of the textile, which in turn depends on the extent to which the textile is swollen during the reaction of the hydroxyls and the aldehyde, and the uniformity of distribution of the aldehyde on the textile when the latter is heated to bring about the chemical reaction resulting in the formation of the acetal bridges.

The method generally proposed in the prior art for modifying regenerated cellulose textiles or the like with formaldehyde has involved treating the textile with an aqueous medium containing the formaldehyde and an acid catalyst, drying the impregnated textile, and finally heating it to baking temperature to complete the chemical reaction. A proposed variation from that method involved impregnating the textile with the aqueous medium containing the aldehyde and catalyst, at least partially drying the impregnated material, and then immersing the textile

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in an inert liquid heated to the elevated temperature required to complete the chemical reaction. It is impossible to produce a uniformly formalized textile or to duplicate results from batch to batch by these procedures because of variables which cannot be controlled.

When the textile impregnated with the aqueous treating liquid is dried before it is heated to the elevated temperature at which the chemical reaction is completed, it shrinks progressively as the amount of water present in or on the yarns is reduced. Some acetal bridges are formed during the drying, and since the textile changes from a more highly swollen condition to a less highly swollen condition as the drying proceeds, those acetal bridges formed during the drying are formed while the textile is swollen to an extent which is different from one end of the drying period to the other, and also different from the extent to which the textile is swollen when it is heated to the elevated temperature for completing the reaction. As a consequence, and since uniformity of cross-linking in the treated textile depends on uniformity of swelling of the textile when the cross-links (acetal bridges) are formed, a uniformly modified textile in which the acetal bridges are uniformly distributed along the cellulose chains is not obtained.

A further difficulty encountered with those prior art method is that when the impregnated textile is dried or partially dried between the impregnation with the aqueous treating solution and heating or baking thereof at the elevated temperature, some of the formaldehyde present in or on the impregnated textile is lost by evaporation. The amount of formaldehyde carried by the dried fabric is less than the amount applied to it by treatment with the aqueous treating solution, and as the amount lost by evaporation may vary from batch to batch, and, moreover, is not uniform at all portions of the textile in any batch, it is difficult to control the amount of formaldehyde carried by the textile when it is heated to complete the reaction and insolubilize the formaldehyde in situ on the textile. These difficulties exist whether the chemical reaction is brought about by subjecting the impregnated, dried textile to dry heat or by heating it while it is immersed in an inert liquid. Even when the impregnated textile is not dried before it is immersed in a heated inert liquid for completing the chemical reaction, the results are not reproducible under the conditions which have been heretofore suggested for effecting the reaction.

The primary object of this invention is to pro-

vide a process for modifying hydroxylated textile materials, specifically regenerated cellulose textile material, with an aldehyde, such as formaldehyde, whereby a uniformly modified textile is obtained and the results are always reproducible. A further object is to provide a process in which all of the acetal bridges formed by reaction between the hydroxyls of a regenerated cellulose textile and the aldehyde are formed while the textile is in a uniformly swollen condition. Other objects of the invention will appear hereinafter.

The objects of this invention are achieved by immersing a dry or substantially dry textile comprising yarns or fibers of a hydrophilic hydroxyl-containing fiber-forming material, such as a regenerated cellulose textile containing at most its normal moisture of regain, in a liquid bath comprising water, a cross-linking agent, an acid catalyst, and a water-miscible liquid which is not itself a swelling agent for the textile material or reactive with the aldehyde at acid pH, which bath is preheated to the temperature at which the chemical reaction between the hydroxyls of the textile material and the aldehyde is to take place but below its boiling point under the pressure conditions prevailing during the reaction, whereby the textile is impregnated with the bath and the reaction between the textile and the aldehyde is completed between the time the textile is immersed in the bath and its removal from the bath, a substantial reaction product of the textile material and cross-linking agent being formed in situ in the fibers of the textile material. The aldehyde cross-linking agents of the present invention which react chemically with the hydroxyls of the textile are formaldehyde, glyoxal, and pyruvic aldehyde.

The textile to be modified is hydrophilic and readily swollen by the water present in the bath. In order to provide a flexible, predictable process adapted to the production of textiles the properties of which are modified to the desired extent, which can be predetermined, it is important to regulate the extent to which the textile is swollen during the reaction between the hydroxyls and the cross-linking agent.

In the present method, the swelling effect of the water on the textile is regulated by the non-swelling agent present with the water in the bath, the extent to which the textile is swollen being controlled by the relative proportions of the water and non-swelling agent.

Examples of the non-swelling agents, which must be water-miscible but which must be free from any substantial swelling effect on the textile and must not react with the aldehyde at acid pH include water-miscible ethers such as diethylene glycol diethyl ether, dimethoxy tetraethylene glycol, and 1,4-dioxane, and water-miscible ketones such as acetonyl acetone. These particular water-miscible ethers and ketones are generally characterized by the fact that they form azeotropes with water having a boiling point of at least 80° C., specifically in the range of 80 to 110° C., do not swell the cellulose or other hydrophilic textile, have an affinity or attraction for water which is greater than that of cellulose, and function, in the present process, to control the extent to which the textile is swollen by the water used in making up the bath or split off in the reaction of the hydroxyls and the aldehyde.

The concentration of the water-miscible non-swelling agent in the treating bath may be between 70 and 95% by volume, based on the total volume of the bath. The amount of aldehyde

present in the bath varies inversely with the amount of non-swelling agent between 10 and 2.5%. Generally, the amount of fixed formaldehyde required to modify the properties of regenerated cellulose is in the range of 0.5 to 2% on the weight of the textile.

In one preferred embodiment of the invention the liquid treating bath or solution has the following composition: from 80 to 90% by volume of non-swelling agent, from 7.2 to 3.6% by weight of aldehyde (20 to 10% by volume of 36-38% formalin), from 0.01 to 1.5% by weight of the acid-reacting catalyst, and the balance water. Any water-soluble acid or acid-liberating salt which catalyzes the reaction between cellulose and formaldehyde can be used.

The textile is entered into the treating bath at a temperature below the boiling point of the treating solution, preferably about 2° C. below the boiling point, under the existing pressure conditions and the temperature of the bath is maintained constant throughout the treatment so that the temperature is uniform at all portions of the textile during the entire process. This is in marked contrast to the variations in temperature at different portions of the textile which occur when it is impregnated with the treating bath in one stage and then transferred to another stage for heating to cure the aldehyde. The fabric or other textile may be preheated to the temperature of the bath before it is entered in the heated bath if desired.

By controlling the relative proportions of the water and water-miscible non-swelling agent and the proportion of aldehyde in the bath, the extent of swelling of the textile and the number of acetal bridges introduced are predetermined and controlled. The results can be reliably reproduced for textile material of a given kind by preselection of these conditions within the broad and specific ranges indicated.

By the present method, in which the regenerated cellulose or the like is reacted with the aldehyde while it is in a condition of uniform swelling controlled by the proportion of water to water-miscible, non-swelling agent throughout both the impregnating and "curing" stages, the acetal bridges formed are all formed while the cellulose is swollen to the same extent. Therefore, the acetal bridges are distributed through the cellulose uniformly or substantially uniformly, and the textile is uniformly modified. The desired modifications of the textile, such as the decrease in the water retention capacity and stabilization of the textile against progressive dimensional shrinkage on repeated laundering, improvement in crease resistance, etc. can be and are obtained without prohibitive loss of other good properties such as tensile strength and elongation and, in the case of discontinuous fibers, without loss of cardability of the fibers.

The following examples, in which the non-swelling agent is by volume and the aldehyde and catalyst are by weight, illustrate specific embodiments of the invention.

EXAMPLE I

Ten pounds of dry regenerated cellulose staple fibers were entered into a preheated bath consisting of an aqueous solution of 1,4-dioxane, formaldehyde (added as a 36% formalin solution), and hydrochloric acid as catalyst in the amounts shown in Table I. The baths were preheated to and maintained at the temperatures shown in the table. The staple was held in the preheated

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solution for the periods of time shown in the table, removed from the bath, flushed with cold water, and washed for 5 minutes in a 1% Na_2SO_3 solution to remove excess unreacted formaldehyde. It was then rinsed in water, given a soft finish by treatment with a dilute aqueous medium containing sorbitol monopalmitate, and dried at 85° C. Results of the treatments are summarized in Table I.

Table I

	Percent 1, 4-Di- oxane	Percent HCHO	Percent HCl	Time, min.	Temp., ° C.	Percent H ₂ O Reten- tion
Control.....	81.0	6.4	0.0222	7	84	112.0
A.....	80.9	6.0	0.0254	10	85	58.0
B.....	81.0	5.9	0.0263	12	85	47.1
C.....	81.0	5.8	0.0285	14	86	47.4
D.....	80.0					40.8

The "water retention" denotes the amount of water retained by a textile material after it is thoroughly wet out and centrifuged under specified conditions. As long as the conditions of the test are held constant, the percent water retention is a direct indication of the extent to which the fiber swells in water. It corresponds to the results obtained by the microscope technique according to which the cross-sections of the fibers are photographed dry and wet and the area is measured by the planimeter. Thus, in Example I, the conditions for all of the tests were the same and the percent water retention for the treated samples (A to D, inclusive) as compared to that for the control, is a measurement of the extent to which the textile material was modified by the treatment.

The modified staple fibers were spun into a 30/1 yarn and woven into fabrics having the construction 72 warp x 64 filling. The greige fabrics were then: (1) desized by washing, dried relaxed, and measured for shrinkage; (2) subjected to the CCC-T-191 treatment described in Federal Standards Stock Catalog, Section 4, Part 5 (Supplement to Federal Specifications for Textiles), dried relaxed, and measured for shrinkage; and (3) again thoroughly wet out and washed in warm water, whizzed to remove excess moisture, ironed on a flat bed press, and again measured for shrinkage. These fabrics were compared with a greige fabric woven from untreated regenerated cellulose staple which was wet out, dried, and measured for shrinkage in the same manner as the fabric woven from the formalized staple. The results of these treatments (1), (2) and (3) are shown in Table II below:

Table II

	(1)		(2)		(3)	
	Warp	Fill	Warp	Fill	Warp	Fill
Control.....	16.8	9.3	18.5	12.1	14.1	8.4
A.....	11.4	4.1	13.9	7.6	11.0	6.1
B.....	9.2	3.1	11.6	6.2	9.1	4.6
C.....	8.9	2.4	11.1	4.8	8.9	2.7
D.....	9.6	1.3	12.1	3.7	8.8	2.4

As will be obvious, the fabrics woven from yarns spun from the formalized staple fibers are characterized by increased resistance to progressive dimensional shrinkage on repeated laundering as compared to fabrics made from yarns of the untreated staple fibers. For this purpose of stabilizing regenerated cellulose fabrics against

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progressive dimensional shrinkage on repeated laundering, or for any other modification of the fabric, the treatment may be performed on the fibers, yarns, or on the fabric as such.

Regenerated cellulose textile materials treated in accordance with the present invention are no longer soluble in cuprammonium solution.

EXAMPLE II

- 10 An aqueous solution containing 3.6% of formaldehyde, 0.3% of hydrochloric acid and 90% of acetyl acetone was preheated to 84° C. Skeins of 150 denier, 30 filament, 3 turns per in. twist viscose rayon yarn were immersed in the solution for 5 minutes at 84° C., withdrawn, washed with cold water, soaked for 5 minutes in a 1% Na_2SO_3 solution, rinsed with water, given a soft finish, and dried at 85° C. The yarns were impregnated with the solution and the formaldehyde was reacted with the regenerated cellulose while they were immersed in the solution.

PROPERTIES

	Percent H ₂ O Retention	Tensile, Dry	Strength, g./denier Wet
Control.....	86	2.3	1.2
Treated.....	44	2.1	1.2

EXAMPLE III

- 35 An aqueous solution containing 4.8% of formaldehyde, 88% of 1,4-dioxane, and 0.021% hydrochloric acid was heated to 100° C. Skeins of 300 denier, 80 filament, 3 turns per inch twist viscose rayon yarn were immersed in the solution for 3 minutes at 100° C., withdrawn, washed with cold, then hot, water, soaked for 5 minutes in 1% Na_2SO_3 solution, rinsed in water, and dried.

PROPERTIES

	Percent H ₂ O Retention	Tensile, g./d.		Elongation at break		Percent Fixed CH ₂ O
		Dry	Wet	Dry	Wet	
Control.....	85.0	2.3	1.2	19.0	29.5	0
Treated.....	46.0	2.0	1.2	13.4	14.5	1.1

EXAMPLE IV

- 55 An aqueous solution containing 4.7% of formaldehyde, 0.021% of hydrochloric acid, and 87% of dimethoxytetraethylene glycol was heated to 81° C. Skeins of 300 denier, 80 filament, 3 turns per inch twist viscose rayon yarn were immersed in the bath for 10 minutes at 81° C. The yarn was then withdrawn and after-treated as in Example I.

PROPERTIES

	Percent H ₂ O Retention	Tensile Strength, g./d.	
		Dry	Wet
Control.....	85.0	2.3	1.2
Treated.....	47.8	2.0	1.0

- 75 In all cases it was found that the cross-sectional swelling of the regenerated cellulose fibers on exposure to moisture was reduced, and this reduction was not accompanied by prohibitive deterioration of the other properties of the fibers, such as tensile strength, extensibility, etc. The

cardability of staple fibers treated in accordance with the invention was satisfactory.

EXAMPLE V

An aqueous solution containing 35% of dioxane, 4% glyoxal, and about 0.03% of hydrochloric acid was heated to 85° C. Skeins of 300 denier, 80 filament, 3 turns per inch twist yarns of regenerated cellulose from viscose were immersed in the solution at 85° C. for ten minutes, withdrawn, and after-treated as in Example I. They were insoluble in cuprammonium solution.

PROPERTIES

Percent H ₂ O Retention	Tensile, g./d.	
	Dry	Wet
61.0.....	1.8	1.0

The invention is particularly advantageous when the hydroxylated textile material to be modified is regenerated cellulose. However, other textile materials containing available hydroxyl groups can be modified uniformly by the treatment, including cotton, low-substituted (substitution less than 1) cellulose ethers which are hydrophilic and water-swellaable but insoluble in water, and cellulose esters which are hydrophilic and water-swellaable, but insoluble in water. Such cellulose esters or ethers as may be soluble in the ketones or ethers used in the treating bath are excluded.

The water-miscible, non-swelling agent for the textile predominates in the treating liquid for the textile.

The outstanding advantages of the invention are: (a) the extent to which the textile is modified can be predetermined; (b) the conditions can be easily controlled for predetermined results; (c) the results can be reliably reproduced from lot to lot.

Some changes and modifications can be made in the above described details without departing from the nature and spirit of the present invention, and it is to be understood that the invention is not to be limited except as defined by the appended claims.

I claim:

1. A method comprising the step of introducing a hydrophilic, water-swellaable, water-insoluble cellulosic textile material containing free hydroxyl groups in the molecule into a heated reaction medium which exerts a controlled swelling action on the textile and contains water, between 2.5% and 10% by weight of an aldehyde selected from the group consisting of formaldehyde, glyoxal, and pyruvic aldehyde, from 0.01 to 1.5% by weight of an acid-reacting catalyst, and between 70 and 95% by volume of a water-miscible liquid which is free from any substantial swelling effect on the textile and does not react with the aldehyde under acid conditions, said water-miscible liquid having an affinity for water greater than that of cellulose and forming an azeotrope with water boiling in the range of 80° to 110° C., the temperature of said medium being

maintained substantially constant from the time of introduction throughout the reaction at a point raised sufficiently to effect reaction between the textile material and the aldehyde but below the boiling point of the medium under the pressure prevailing during the reaction.

2. The method of claim 1, wherein the aqueous medium is preheated to and maintained during the reaction at a temperature about 2° C. below its boiling point.

3. The method of claim 1, wherein the water-miscible liquid is an ether.

4. The method of claim 1, wherein the water-miscible liquid is a ketone.

5. The method of claim 1, wherein the textile material is of regenerated cellulose and the aldehyde is formaldehyde.

6. The method of claim 5, wherein the water-miscible liquid is 1,4-dioxane.

7. The method of claim 5, wherein the water-miscible liquid is acetonyl acetone.

8. The method of claim 5, wherein the water-miscible liquid is diethylene glycol diethyl ether.

9. The method of claim 5, wherein the water-miscible liquid is dimethoxy tetraethylene glycol.

10. A method comprising the step of introducing a hydrophilic, water-swellaable, water-insoluble cellulosic textile material containing free hydroxyl groups in the molecule into a heated reaction medium which exerts a controlled swelling action on the textile and contains water, between 2.5% and 10% by weight of an aldehyde selected from the group consisting of formaldehyde, glyoxal, and pyruvic aldehyde, from 0.01 to 1.5% by weight of an acid-reacting catalyst, and between 70 and 95% by volume of a water-miscible liquid which is substantially free from any swelling effect on textile and does not react with the aldehyde under acid conditions, said water-miscible liquid being selected from the group consisting of 1,4-dioxane, acetonyl acetone, diethylene glycol diethyl ether and dimethoxy tetraethylene glycol, the temperature of said medium being maintained substantially constant from the time of introduction throughout the reaction at a point raised sufficiently to effect reaction between the textile material and the aldehyde but below the boiling point of the medium under the pressure prevailing during the reaction.

11. A method as defined in claim 10 in which the textile material is of regenerated cellulose.

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