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PROCESS OF PRODUCING WRINKLE RESISTANT CELLULOSE FABRICS OF RELATIVELY HIGH MOISTURE REGAIN

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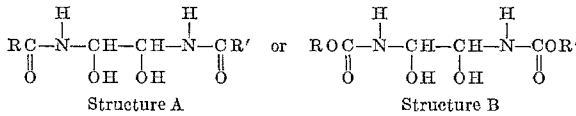
This invention relates to the treatment of cellulosic textile materials, particularly cellulose fabrics, to produce textiles having improved properties. In this invention and in copending application Serial No. 204,013, filed June 20, 1962, now U.S. Patent 3,198,660 of Sidney L. Vail, John G. Frick, Jr., and Wilson A. Reeves and copending application Serial No. 211,141, filed July 19, 1962, now U.S. Patent 3,160,469 of Sidney L. Vail, Clifford M. Moran, and John D. Reid, new textile treating agents and their use are described. The fabrics produced in these inventions are resistant to wrinkling, have improved resiliency, and possess wash-wear properties. For convenience, such fabrics are referred to in this application as wrinkle resistant, or as possessing wrinkle resistance properties. Moreover, the finishes produced from the new textile treating agents of these inventions were found to be extremely durable to acid hydrolysis. More specifically, the present invention relates to production of durable, wrinkle resistant cellulosic fabrics, whereby these treated cellulosic fabrics possess, in addition, the property of moisture regain to an extent equal to or slightly less than the cellulosic fabric prior to treatment.

The production of commercial, wrinkle resistant cellulosic fabrics (cotton cellulose for the most part) is generally accomplished by the use of di- and polyfunctional N-methylolamide reactants which are considered to crosslink cellulose. The cellulosic fabrics produced by this process generally have significantly lower moisture regain than the cellulosic fabrics before treatment. That is, cellulosic fabrics treated to impart wrinkle resistance, when dried to remove essentially all the water, will regain less moisture than the same cellulosic fabric that has not been treated when both fabrics are exposed to normal moisture in the atmosphere. Standard atmospheric conditions of 65% relative humidity and 70° F. are often used for the purpose of determining moisture regain.

It is desirable for several reasons that a wrinkle resistant cellulosic textile have moisture regain values approximately equivalent to or higher than that of the same textile before treatment. First, the "comfort factor" of cellulosic fabrics is related directly to moisture regain. Any reduction in moisture regain of a cellulosic fabric due to a wrinkle resistance finish would therefore reduce the "comfort factor." Secondly, undesirable generation of static electricity is related inversely to the hygroscopic nature of the elements comprising the fabric. Thus, it is desirable to avoid loss in moisture regain when a wrinkle resistant fabric is produced. Presumably, other factors such as dyeability, soiling, etc. are also affected by the property of moisture regain.

A primary object of the invention is to provide a process for the treatment of cellulose fabrics with amide-type compounds and the N-methylol derivatives of these amide-type compounds, whereby the fabric acquires the properties of increased resiliency and wrinkle resistance without sacrificing excessive loss of moisture regain. It is, furthermore, an object of this invention to provide such a treatment whereby the finish produced is resistant to harsh conditions of acidic hydrolysis. Also, the modified fabrics may be laundered repeatedly by ordinary procedures, which procedures may include the use of hypochlorite bleaching agents, without suffering discoloration. It is a further object to produce a finish which is not susceptible to chlorine damage from ironing after the modified fabric has been treated with hypochlorite bleaching agents.

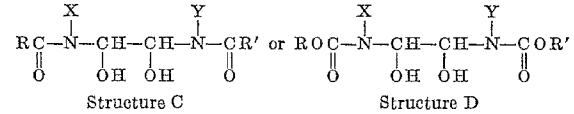
In general, these and other objects of the invention are accomplished by treating, as by impregnation, the cellulosic textile material, particularly a cellulose fabric, with an aqueous solution containing (a) about from 5 to 20 weight percent of an amide-type compound having the following structure:



Structure A

Structure B

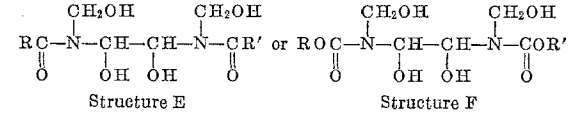
wherein R and R′ are the same or different alkyl groups containing from 1 to 4 carbon atoms; or the mono-N-methylol derivatives of these amide-type compounds having the structures:



Structure C

Structure D

wherein R and R′ have the same significance as above and X and Y are unlike members of the group consisting of hydrogen and —CH_2OH; or the di-N-methylol derivatives of these amide-type compounds having the structures:



Structure E

Structure F

wherein R and R′ have the same significance as above, and (b) from about 0.5 to 5 weight percent of an acidic catalyst, such as magnesium chloride, zinc fluoborate, zinc nitrate, and a mixture consisting of 60 weight percent of citric acid and 40 weight percent of magnesium chloride hexahydrate, and dry curing the treated cellulosic textile material with heat.

From prior work disclosed in the aforementioned applications it was indicated that the finish derived from compounds of Structure A would be susceptible to chlorine damage on ironing, whereas the finish derived from Structure B would not. As shown in Example 2 of this application, this was shown to be true and limits the use of derivatives of compounds of Structure A to treatment of fabrics where susceptibility to chlorine damage on ironing is not critical.

The compounds of Structures A and B, without methylolation, contain two N-methylol groups and, therefore, should theoretically be difunctional. However, it was found that a more effective agent was obtained by reacting the compounds with formaldehyde to obtain the N-methylolated derivatives designated by Structures C, D, E, and F.

The N-methylolated derivatives used for the treatment of the cellulosic textile in the process of this invention can be obtained by the reaction of the compounds of the above-described Structures A and B and formaldehyde in aqueous media under alkaline conditions. It is preferable with compounds of Structure B to use an excess of formaldehyde in this reaction, the excess being about one to two molar equivalents of "free" formaldehyde based on the presumption that all amido NH groups will methyl-

olate to form N-methylol groups. Thus, although two molar equivalents of formaldehyde could theoretically fully methylolate the compounds of the above-described structures, it is preferable to have about three to four molar equivalents of formaldehyde for the reaction with the compound. The chemical effect of the excess formaldehyde is not definitely known; however, in general, it appears that some formaldehyde is reacting with the cellulose to form methylene ether crosslinks in addition to the crosslinking through the nitrogenous agent. An amount of formaldehyde significantly in excess of the four to one ratio can also be employed, but it is inefficient and uneconomical to use such a large excess. With compounds of Structure A only an equimolar ratio of formaldehyde to the bisamide is required. The other conditions of this reaction are well-known in the trade. Generally, heating the alkaline, aqueous solution of the compounds of the above-described Structures A and B and formaldehyde at 60° C. for 30 minutes or allowing the solution to stand at room temperature (20–25° C.) for 18–24 hours is sufficient to achieve formation of the N-methylol derivatives. The reaction products thus produced are water soluble. The solution can be used as is or can be diluted with water for treatment of the cellulosic material.

Prior to application of the agent to fabric, an acidic substance or a substance producing acidity at elevated temperatures is added to the diluted solution to serve as a catalyst. The concentration of the reactants, i.e., the formaldehyde adducts of compounds of Structure A or B plus the excess or unreacted formaldehyde, can be varied depending on the particular textile processing conditions used, the type of textile being treated, and the properties desired in the finished textile. Generally, it is preferred to use from about 5% to 20% by weight of the reactants in the diluted treating solution. The catalysts which may be used are well-known in the trade. Magnesium chloride, zinc fluoborate, and zinc nitrate are examples of particularly suitable catalysts. Another such catalyst consists of 60 weight percent of citric acid and 40 weight percent of magnesium chloride hexahydrate. From about 0.5% to about 5% by weight of the acidic catalyst is generally preferred.

Treatment of the cellulosic textile material is carried out by standard procedure. The textile is thoroughly wetted with the above-described treating solution; the excess liquid is mechanically removed, and the wetted textile is dried and cured. Following the curing operation, it is preferable but not absolutely necessary, to water-wash the treated textile in an alkaline solution to remove any unreacted materials.

The processes of this invention can be used to treat substantially any hydrophilic fibrous cellulosic material such as cotton, rayon, ramie, jute and the like which can be impregnated with a liquid, dried, and cured.

The following examples are given by way of illustration and not by way of limitation of the invention. The detailed procedures given below in the examples are illustrative, and are not the only or specific conditions for the production of an acceptable finished textile. Many variations or additions within these procedures can be made, as will be readily apparent to those skilled in the art. In the examples, all parts and percentages are by weight. The fabrics were tested by the following methods: Wrinkle recovery angle, Monsanto method, American Society for Testing Materials (ASTM) test D 1295–53T; breaking strength, ASTM test D 39–49; damage caused by retained chlorine, American Association of Textile Chemists and Colorists tentative test method 92–1958T. All textile data were obtained on the warp threads only.

EXAMPLE 1

A weighed portion of the appropriate compound as listed below was dissolved in a 1:1 mixture of water and dimethylformamide. The pH of the solution was checked, and, when necessary, aqueous sodium hydroxide was added to adjust the pH to a value of about 7. Then a weighed portion of zinc fluoborate was added such that its final concentration in the padding solution was about 1%. Concentration of the crosslinking reactant in the padding solution was about 7.5%. Using this general procedure, the following compounds were used to prepare padding solutions:

Solution 1. Dihydroxyethylene bisacetamide
Solution 2. Dihydroxyethylene bisurethane

A sample of 80 x 80 cotton print fabric, scoured, desized, and bleached, was dipped in the treating solution and padded between rollers to give a 70 to 80% increase in the weight of the fabric. The wet fabric was pinned to original dimensions, dried for 10 minutes at 60° C. and cured for 3 minutes at 160° C. This treatment was followed by a wash in warm, alkaline water with a nonionic detergent added, and then the fabric was tumble dried.

Also, a 5% aqueous solution of dihydroxyethylene bisacetamide (Solution 1A) and a 5% aqueous solution of dihydroxyethylene bisurethane (Solution 2A), each containing 1.2% citric acid and 0.8% magnesium chloride hexahydrate as catalyst, were prepared. It was necessary to warm the water to dissolve the bisamides. However, once dissolved, the bisamides remained in solution until after the fabrics were treated. Using conditions similar to the above, treated fabrics were obtained from Solution 1A with a wrinkle recovery angle (warp only) of 131°. In a similar manner, Solution 2A produced a treated fabric with a wrinkle recovery angle (warp only) of 118°.

EXAMPLE 2

A weighed portion of the appropriate compound as listed below was dissolved in an alkaline, aqueous solution of formaldehyde, such that the molar ratio of formaldehyde to the bisamide was 3:1 or as noted otherwise. The pH of the solution was checked, and, when necessary, aqueous sodium hydroxide was added to adjust the pH to a value of about 8. The solution was allowed to stand for 24 hours at 20–25° C. or heated for one hour at 60° C. Then a weighed portion of magnesium chloride hexahydrate was added such that its final concentration in the padding solution was about 4%. Concentration of the unmethylolated, nitrogenous agent in the padding solution was about 5%. Using this general procedure, with variations noted where appropriate, the following compounds were used to prepare various padding solutions:

Solution 3. Dihydroxyethylene bisacetamide.
Solution 4. Dihydroxyethylene bisacetamide with a catalyst of 1% zinc fluoborate.
Solution 5. Dihydroxyethylene bisurethane.
Solution 6. A 10% concentration of dihydroxyethylene bisurethane.
Solution 7. Dihydroxyethylene bisacetamide with a molar ratio of formaldehyde to bisamide of 1:1.
Solution 8. Dihydroxyethylene bisurethane with a molar ratio of formaldehyde to the bisamide of 1:1.

A sample of 80 x 80 cotton print fabric was treated as described in Example 1, except that the fabric was dried for seven minutes at 60° C. The properties of the treated fabrics are shown in Table I.

EXAMPLE 3

The durability of some of the finishes to acidic hydrolysis was tested by treating the fabrics for thirty minutes at 80° C. in a solution containing 1.5% phosphoric acid and 5% urea. Also, a fabric prepared in the usual manner from a dimethylolurea (DMU) solution was hydrolyzed for comparison purposes. The results of this hydrolysis on properties of the treated fabrics are given in Table II.

Table I

PROPERTIES OF TREATED FABRICS

Fabrics from Solution	Wrinkle Recovery Angle (warp only)	Breaking Strength Retained after Scorch Test, Percent
1	105°	22
2	99°	70
3	138°	34
4	128°	21
5	136°	100
6	127°	90
7	130°	26
8	112°	73
Untreated	75°	95

Table II

ACID HYDROLYSIS OF TREATED FABRICS

Fabrics from Solution	Percent of Original Nitrogen Retained After Hydrolysis	Wrinkle Recovery Angle after Hydrolysis
1	77	102°
2	63	89°
3	80	133°
4	61	110°
5	68	140°
6	46	117°
7	79	124°
8	61	112°
DMU	5	89°

EXAMPLE 4

The moisture regain of some of the treated fabrics was determined in the following manner: (1) the sample was heated to 100° C. for 15 minutes (2) then placed in a conditioning atmosphere of 70° F. and 65% relative humidity for 72 hours (3) the sample was weighed (4) then dried in oven at 100° C. for 4 hours (5) and reweighed.

$$\text{Percent moisture regain} = \frac{\text{Conditioned weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

For comparison purposes, the moisture regains of a sample of dimethylolurea (DMU) treated fabric and an untreated fabric were determined.

The results are shown in Table III.

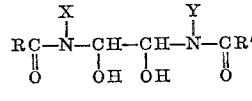
Table III

MOISTURE REGAIN OF TREATED FABRICS

Fabrics from solution:	Moisture regain, percent
Solution 3	6.7
Solution 5	6.2
Solution 7	6.7
Solution 8	6.9
DMU	5.2
Untreated fabric	6.7

We claim:

1. The process comprising impregnating a cellulose fabric with an aqueous solution containing about from 5 to 20 weight percent of a compound of the formula



wherein R and R′ are alkyl groups containing from 1 to 4 carbon atoms and X and Y are unlike members selected from the group consisting of hydrogen and —CH_2OH, and from 0.5 to 5 weight percent of an acidic catalyst, and dry curing the impregnated cellulose fabric with heat.

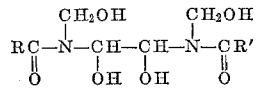
2. The process of claim 1 wherein R and R′ are different alkyl groups.

3. The process of claim 1 wherein R and R′ are the same alkyl group.

4. The process of claim 3 wherein R and R′ are methyl and the acidic catalyst in $Zn(BF_4)_2$.

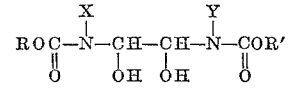
5. The process of claim 3 wherein R and R′ are methyl and the acidic catalyst is $MgCl_2$.

6. The process comprising impregnating a cellulose fabric with an aqueous solution containing about from 5 to 20 weight percent of a compound of the formula



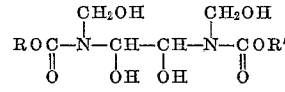
wherein R and R′ are alkyl groups containing from 1 to 4 carbon atoms, and from 0.5 to 5 weight percent of an acidic catalyst, and dry curing the impregnated cellulose fabric with heat.

7. The process comprising impregnating a cellulose fabric with an aqueous solution containing about from 5 to 20 weight percent of a compound of the formula



wherein R and R′ are alkyl groups containing from 1 to 4 carbon atoms and X and Y are unlike members selected from the group consisting of hydrogen and —CH_2OH, and from 0.5 to 5 weight percent of an acidic catalyst, and dry curing the impregnated cellulose fabric with heat.

8. The process comprising impregnating a cellulose fabric with an aqueous solution containing about from 5 to 20 weight percent of a compound of the formula



wherein R and R′ are alkyl groups containing from 1 to 4 carbon atoms, and from 0.5 to 5 weight percent of an acidic catalyst, and dry curing the impregnated cellulose fabric with heat.

9. The process of claim 8 wherein R and R′ are different alkyl groups.

10. The process of claim 8 wherein R and R′ are the same alkyl group.

11. The process of claim 10 wherein R and R′ are ethyl and the acidic catalyst is $Zn(BF_4)_2$.

12. The process of claim 10 wherein R and R′ are ethyl and the acidic catalyst is $MgCl_2$.

13. The process comprising impregnating a cellulose fabric with an aqueous solution containing about from 1 to 5 weight percent of dihydroxyethylene bisurethane and from 0.5 to 5 weight percent of an acidic catalyst, and dry curing the impregnated cellulose fabric with heat.

14. The process of claim 13 wherein the acidic catalyst consists of 60 weight percent of citric acid and 40 weight percent of magnesium chloride hexahydrate.

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