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TEXTILE TREATMENT

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5 Claims. (Cl. 8—116.3)

This invention relates to a method of chemically treating cellulose fabrics to render them wrinkle-resistant and to improve several of their other characteristics and properties. Specifically, the invention deals with the process for treating cotton fabrics whereby they are rendered wrinkle-resistant, have an improved hand, and have an improved degree of lubricity.

For the past several years, intensive research has been conducted in an attempt to find chemical treatments for cellulose fabrics, particularly cotton cloths, which will impart to the fabric crease-resistant properties. The ultimate object of such treatments is to obtain a fabric which, on being formed into a garment and being laundered, will have the inherent characteristics of drip-drying without forming wrinkles of the type which are commonly removed by conventional ironing techniques. There have been several attempts to impart to cellulose fabrics these qualities by using amine formaldehyde resins and cyclic urea formaldehyde resins. While these treatments have provided wrinkle-resistant characteristics to cotton fabrics, they impart to the cellulose fiber certain disadvantages which make their use not entirely satisfactory from a commercial standpoint.

One of the chief drawbacks to the amine or urea type wrinkle-resistant resin treatments is that as the amount of resin placed into the fabric is increased, the fabrics tend to rapidly degrade upon being subjected to chlorine bleaches. This chlorine bleach degradation phenomenon may be mitigated to some extent by decreasing the amount of resin used to treat the fabric. As the chlorine degradation phenomenon is diminished by lowering the amount of resin placed into the fabric, there also occurs a lessening in the wrinkle-resistant characteristics. It, therefore, becomes necessary to critically adjust the amount of treatment to balance the wrinkle-resistance against the bleach susceptibility in the fabric.

Another disadvantage of many resin-treated cellulose fabrics is that the scorching characteristics of the fiber are such that the fabric will tend to yellow upon ironing. While ironing is not considered a necessity in truly wrinkle-resistant fabrics, many users of such fabrics find it necessary to use occasional ironing procedures for so-called "touch-up" jobs to improve the appearance of a particular garment.

One of the reasons advanced for the inadequacies of the prior art materials is that they do not sufficiently react with the fiber whereby an integral fiber resin bond is established in the form of a three-dimensional cross-link network. Furthermore, there is a progressive breakdown of these compounds on continued laundering.

It would be beneficial if a simple chemical treatment for cellulose fabrics were available which would impart a high degree of crease-resistance to such fabrics at low, economical dosages, yet would not possess the disadvantages of prior art treatments. Such a treatment should be capable of being applied to the cellulose fabric using simple operational techniques. It also should be capable of chemically combining with the cellulose molecule at a plurality of points, thereby forming an integral, three-dimensional cross-linked network.

In accordance with the invention, it has been found that the above objects may be accomplished by subjecting a cellulose fabric to a treatment with a specific group of N,N-dimethylol saturated fatty acid amides. In practice, the invention is performed by subjecting the cellulose

fabric to a polar liquid treating solution which contains amounts of formaldehyde and saturated fatty acid amide, the pH of the bath being acidic, and then drying and curing the fabrics at elevated temperatures, whereby the treatment is cross-linked and becomes an integral part of the fabric.

More specifically, the invention is conducted by first preparing a polar solvent solution or bath which contains the saturated fatty acid amide and formaldehyde in specific molar ratios. The ratio of formaldehyde to saturated fatty acid amide should be at least 3:1, and preferably in excess of 4:1, and may be as high as 10:1. As a general rule the treating bath should contain at least 2 moles of formaldehyde per mole of reactive hydrogen contained in the fatty acid amide grouping. The solvent for the bath may be water, or it may contain amounts of water and polar solvents, such as lower molecular weight water-soluble alcohols of which methanol, ethanol, normal propanol, isopropanol, butanol, and the like are exemplary. The reason for using blends of water and polar solvent alcohols is that certain of the amides used in the present invention are somewhat insoluble in water at use concentrations; hence, the alcohol is used to increase the solubility of the chemicals in the treating bath.

The pH of the bath is adjusted to between 2 and 7, and preferably to between 4.5 and 6.5, with any suitable acidic reagent such as, for instance, phosphoric acid, zinc sulfate, zinc nitrate, zinc chloride, magnesium chloride, triethylamine hydrochloride, citric acid, tartaric acid, and the well-known strong mineral acids, hydrochloric acid and sulfuric acid. In the case of the strong mineral acids, alkaline buffering agents are used so that better pH control is maintained.

The ingredients may be mixed without using any particular order of addition, although it is desirable to first make up the formaldehyde solution, adjust the pH, and then add thereto the saturated fatty acid amide. The temperature of the bath to form the methylol derivatives should be elevated to beween 80° and 160° F., with a preferred temperature being at about 125° F. At this point the bath is ready for use in the treatment of cellulose fabrics.

The above shows one method of preparing these compounds. The preferred method of making the N,N-dimethylol amides of the invention involves warming commercial aqueous or alcoholic formaldehyde solutions with the particular saturated fatty acid amide at temperatures between 80° and 160° F. for the requisite length of time and then diluting the resulting N,N-dimethylol saturated fatty acid amide to the use concentration with water, or with water and polar solvents, as previously described.

At this point the bath is ready for use in the treatment of cellulose fabrics. The fabric may contact the bath for a period of time as little as 1 minute to 5 minutes, with good results being obtained with a typical preparation of the invention in a period of time as little as 2 minutes.

The temperature of the finished treating bath, when used to treat the cellulose fabrics, may be varied considerably, although satisfactory results are obtained at room temperature, viz. 72±5° F. Good results may be obtained using temperatures as high as between 60° and 100° F.

After the fabric has been subjected to the treating bath which contains the N,N-dimethylol saturated fatty acid amide compound, it is then cured to form a three-dimensional cross-link network to bond the treatment to the fiber. This curing step is preferably conducted at a temperature of at least 140° C. to as high as 190° C. The time at which the fabric is elevated to these temperatures may vary from a period of time as long as 8 to

9 minutes to as short a period of time as a few seconds. The preferred drying temperatures range between 150° and 160° C.

To generally illustrate the curing step in relation to temperature, the following table is presented:

TABLE I

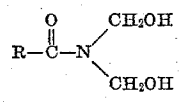
Temperature in °/C.:	Time in minutes
140	9
150	6
160	4
170	2
180	1
190	0.4

The particular saturated fatty acid amides which have shown good results in the invention may be any saturated fatty acid amide which contains from 2 carbon atoms to as many as 20 carbon atoms. It may be either straight or branched chain, and may contain minor amounts of such substituents as hydroxyl, keto groupings, and the like, although for the most part amides composed exclusively of hydrocarbons are preferred.

In a preferred embodiment of the invention, the saturated fatty acid amides should contain between 12 and 18 carbon atoms, with the most outstanding material of this particular class being stearamide.

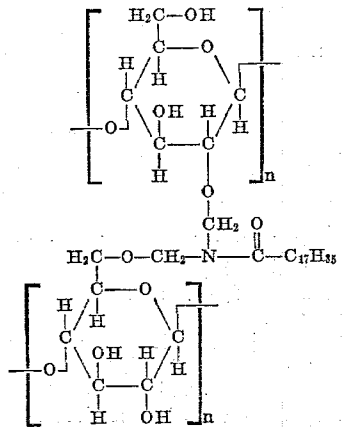
Although it is usually preferred to use pure fatty acid amides, amides prepared from mixed fatty acid amides of the type commonly obtained from vegetable and animal fats and oils may be used. In the case of amides derived from vegetable oils where degrees of unsaturation are present, it is desirable to hydrogenate the product to make it saturated.

The higher fatty acid amide methylol materials of the invention may be considered as being new composition of matter, which may be described as having the formula:



where R in the above formula is a saturated aliphatic group of from 11 to 17 carbon atoms in chain length. The most useful compound of the invention which gives results far superior to any of the amides that may be used is N,N-dimethylol stearamide. Preparation of these new compounds will be fully demonstrated hereinafter.

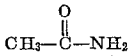
It is believed that the compositions of the invention are so advantageous when used to treat cellulose fabrics in accordance with the methods previously described, since they form an integrated cross-link network with the cellulose molecule. This phenomenon is set forth below in the following general formula, which is presented as being merely illustrative of the principles involved:



For purposes of completeness, and to illustrate saturated fatty acid amides that may be used in the practice of the invention, Table II below lists several saturated fatty acid amides as well as a few unsaturated fatty acid amides which will be presented for comparison in a later portion of this description of the invention.

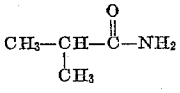
TABLE II

(1)



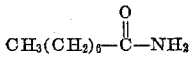
Acetamide

(2)



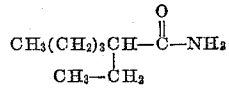
Isobutyrylamide

(3)



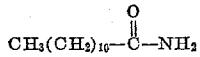
Caprylamide

(4)



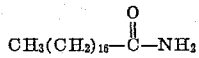
2-ethyl caproamide

(5)



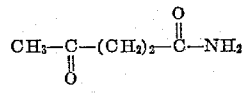
Lauramide

(6)



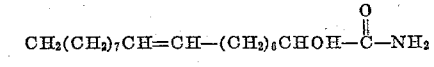
Stearamide

(7)



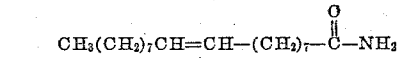
Levulinamide

(8)



2-hydroxy, octadecen-9-yl amide

(9)



Oleamide

Evaluation of the invention

By using the general procedure for making the treating solutions of the invention, several typical treating baths were prepared and were evaluated in their efficacy treatments for modifying cellulose fabrics. All the test baths were maintained at temperatures of 72±5° F. The contact time of the fabric with each bath was approximately 2 minutes. After the treatment bath, but before curing, the fabrics were padded onto a hand laundry roller, which exerted an approximate pressure of 40 pounds per square inch. The fabric leaving the roller was slightly damp to the touch, and was then inserted into a laboratory circulating-air oven, the temperature of which was regulated to 155° C.

The treated fabrics were tested for their crease-resistant properties in the Monsanto wrinkle recovery tester, which is described in the Technical Handbook and Yearbook of the American Association of Textile Chemists and Colorers, vol. 32, 1956 (tentative test method 66–56).

The chlorine retention properties of the treated and untreated fabrics were determined in accordance with AATCC tentative test method 69–52, which is described in the Technical Handbook and Yearbook of the American Association of Textile Chemists and Colorers, vol. 28, 1952. The particular fabric used in the test was a commercial grade of unbleached shirt cotton having an

approximate weave of 80 x 80. The results of these tests are presented below in Table III.

TABLE III

Test No.	Amide Compound [1]	Percent Amide	Percent CH_2O	Molar Ratio, Amide: CH_2O	Solvent [3]	Catalyst	pH	Reaction Temp., °F.	Time, Minutes	Warp	Fill	Discoloration
1										68	[2] 71(2)	
2	4	13.8	9.3	1:2.9	H_2O	$Zn(NO_3)_2$	3.5	73	2	126	126(4)	No.
3	4	6.9	9.3	1:1.6	H_2O	$Zn(NO_3)_2$	3.5	73	2	122	123(3)	No.
4	5	10.5	6.6	1:4.4	H_2O/i-PrOH 70:30	$MgCl_2$	4.2	75	2	126	131(5)	No.
5	5	5.3	6.6	1:8.5	H_2O/i-PrOH 70:30	$MgCl_2$	4.2	80	2	128	128(4)	No.
6	3	14.3	9.0	1:3.7	H_2O	$Zn(NO_3)_2$	4.0	80	2	136	129(1)	Slight.
7	1	12.0	15.0	1:2.5	H_2O	$Zn(NO_3)_2$	3.5	72	2	113	118(2)	No.
8	9	4.9	7.8	1:10.0	H_2O/EtOH 50:50	$ZnCl_2$	4.0	82	2	132	134(2)	Yes.
9	6	6.8	3.7	1:2.6	H_2O/EtOH 50:50	$ZnCl_2$	4.0	77	2	124	120(3)	No.
10	6	13.6	3.7	1:1.4	H_2O/EtOH 50:50	$ZnCl_2$	4.0	77	2	94	82(2)	No.
11	6	6.2	6.8	1:5.1	H_2O/EtOH 50:50	$Zn(NO_3)_2$	3.5	75	2	136	158(6)	No.
12	6	3.1	6.8	1:10.0	H_2O/EtOH 50:50	$Zn(NO_3)_2$	3.5	75	2	140	152(6)	No.
13	6	0.3	0.4	1:5.2	H_2O/EtOH 50:50	$Zn(NO_3)_2$	3.5	75	2	107	100(1)	No.
14	6	0.6	0.4	1:2.6	H_2O/EtOH 50:50	$Zn(NO_3)_2$	3.5	75	2	110	119(2)	No.

[1] See Table II.
[2] Number of trials run. Values given represent averages for trials run.
[3] Solvent ratios are by volume.

From the above table, it is readily observed that the dimethylol saturated amides gave satisfactory performance, whereas unsaturated fatty acids, such as N,N-dimethylololeamide, gave poor results since the fabrics treated discolor badly during the curing operation.

The above fabrics treated in accordance with the invention showed no degradation when treated in accordance with the chlorine test method above. Additionally, the preferred treated fabrics of the invention were sent to a commercial laundry, where they were laundered successively 7 to 9 times, after which they were tested to determine if any wrinkle-resistant diminution had occurred. In no case was there any decrease in the wrinkle-resistance of the fabrics so commercially laundered. No discoloration or degradation of the fabrics due to commercial bleaching was noted.

The finished product of the invention may be considered as a cellulose fabric having improved crease-resistance with such cellulose fabric containing from .5% to 3% by weight of a cured alkyl amide formaldehyde copolymer which is chemically bonded to the fabric through a plurality of ether linkages. The amounts of formaldehyde combined with the saturated fatty acid amide in a finished cotton may be expressed in terms of a formaldehyde-saturated fatty acid amide molar ratio of at least 1:1. It will be apparent by studying the various structural formulas that the amount of formaldehyde which combines with the saturated fatty acid molecule will be somewhat less than the quantity used in the treating bath. The excess of formaldehyde used in the bath probably acts as a driving force to make the reaction go to completion more readily under the conditions used. The amounts of formaldehyde in the bath specified are critical, and lesser amounts afford poor results.

The finished fabrics of the invention, in addition to having the wrinkle-resistant finish imparted to them, also have several other properties which are not achieved by use of prior art materials. In the case of white goods, the wearing quality of the cloth is in no way diminished and in some instances it is improved, and bleached fabrics have improved whiteness.

The treated fabrics can be given any degree of waterproofing by proper choice of the N,N-dimethylol saturated fatty acid amide bonded to them and by the concentration of active material in the treatment bath. In addition, the fabric can be given permanent softening by a similar selection of amide and concentration of treatment bath. This should not be taken to mean that wrinkle-resistance depends on the water proofing or softening properties which can be obtained as added features in the finished fabrics. A high degree of wrinkle-resistance can be imparted to a fabric without waterproofing or softening the finished fabric.

While the invention is primarily concerned with treating cellulose fabrics which are composed exclusively of cotton, it will be apparent that the invention applies to fabrics which are blends of cellulose fibers and synthetic or modified fibers. The invention, therefore, is designed to treat cotton-containing fabrics which contain at least 40% by weight of cotton fibers. Such fibers as cellulose acetates of the rayon type, nylon, polyamide type fibers, polyester fibers, vinyl acetate, acrylonitrile fibers, vinylidene chloride, vinyl chloride, vinylidene cyanide, copolymers of acrylonitrile and other vinyl monomers may all be suitably blended with cotton which, when treated in accordance with the invention, will show improved results.

As previously stated, several of the N,N-dimethylol saturated fatty acid amides are believed to be new compositions of matter. These compositions were, for the most part, prepared in accordance with the conditions set forth in Table III. The products were concentrated by precipitation from the solution. Several of these new compounds, which are white, waxy solids, are presented below in Table IV.

TABLE IV

Compound	Experimental Melting Point, ° C.	Reported Melting Point of Amide [1]
1. Dimethylol caprylamide	99–101	105–110
2. Dimethylol oleamide	84–86	76
3. Dimethylol lauramide	97–99	102
4. Dimethylol stearamide	95.5–96.5	108–109
5. Bis methylene stearamide	132	
6. Mixed #4 and #5	114–125	

[1] Lange's Handbook of Chemistry, 8th edition; and Handbook of Chemistry and Physics, 39th edition (1957–1958).

The invention is hereby claimed as follows:

1. The process of rendering cellulose fabrics wrinkle-resistant and imparting other improved properties to such fabrics which consists essentially of treating such fabrics at an acidic pH with a polar solvent solution consisting essentially of at least 1% by weight of an N,N-dimethylol monoamide of a saturated fatty acid solubilized in said polar solvent, said fatty acid amide without the methylol groups containing from 12 to 22 carbon atoms in chain length, and then dry curing the treated fabric at a temperature of between 140° C. to 190° C.

2. The process of claim 1 where the cellulose fabric is treated with N,N-dimethylol stearamide.

3. The process of rendering cellulose fabrics wrinkle-resistant and imparting other improved properties to such fabrics which consists essentially of treating such fabrics with an acidic polar solvent solution consisting essentially of an N,N-dimethylolamide compound prepared by reacting at a pH of 2–7 formaldehyde and a saturated fatty acid monoamide of from 12 to 22 carbon atoms in chain length combined in a molar ratio of at least 3 moles of

formaldehyde per mole of said monoamide, said solution containing at least 1% by weight of said N,N-dimethylolamide of said saturated fatty acid, and then dry curing the treated fabric at a temperature of between 140° C. and 190° C.

4. The process of claim 3 where the temperature of the treating solution is between 60° F. and 100° F., the pH of said reaction solution is between 4.5 and 6.5 before the formaldehyde and said amide are reacted, the molar ratio of formaldehyde to saturated fatty acid amide is at least 4 moles of formaldehyde per mole of said fatty acid amide, and the treated cellulose fabric is dry cured at a temperature between 150° C. and 180° C.

5. The process of claim 4 where the saturated fatty acid monoamide is stearamide.

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