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3,102,773

PROCESS FOR TREATING TEXTILES

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This invention relates to a method of chemically treating cellulose fabrics to improve their wash and wear characteristics. Specifically the invention deals with a process for treating cotton fabrics whereby the treated cotton is rendered crease-resistant.

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 properties of crease resistance. 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 laundry 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 of 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-linked 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 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

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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 obtained by subjecting a cellulose fabric to the following sequential treating steps:

CAUSTIC TREATMENT

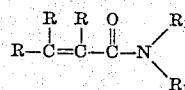
In this phase of the treatment the cellulose fabric is subjected to an aqueous bath which contains a minimum of at least 5% by weight of an alkali metal hydroxide. While sodium, potassium, lithium, cesium, and rubidium hydroxides may be used, from a commercial standpoint sodium hydroxide is preferred since it gives good results in the process and is relatively inexpensive. While the concentrations of the bath should be at least 5% by weight, it is advantageous to use between 5% and 20% by weight solutions, with 10% solutions giving the optimum results. The bath may be maintained at room temperature, viz. $72 \pm 5^\circ \text{F}$. Alternatively, it may be elevated to higher temperatures such as about 210°F ., depending upon the type of operation sought to be achieved. The contact time of the cellulose fiber with the bath may vary from as little time as 0.5 minute to 5.0 minutes, depending upon the concentration of the caustic and the temperature of the bath. If shirt grade cotton should be treated and a 10% caustic solution is to be used at room temperature, a typical contact time would be about 2.0 minutes.

The purpose of this step is to convert a portion of the hydroxyl groups in the cellulose molecule to the alkali metal alcoholate form, which is more commonly known as sodium cellulose. After the fabric has been converted to the sodium form, it is then preferably padded to remove the excess moisture from the cloth. At this point the fabric is then ready for the second step, which I prefer to call etherization.

ETHERIZATION

The padded alkali cellulose fabric is now immersed in an aqueous bath or solution which contains at least 1% by weight of a water-soluble acrylamide compound. The concentration of the acrylamide compound in this bath may be varied from a 1% by weight concentration up to the saturation solubility of the particular acrylamide compound used. Commercial expediency suggests as a useful range of concentration between 2% and 5% by weight solution, with 2% being the most preferred.

The particular acrylamides that are used in the invention must be water-soluble at use concentrations and they must contain at least one free amido hydrogen. To more clearly illustrate compounds of this type, the following structural formula is presented:



In the above formula R may be a radical selected from such groupings as hydrogen, methyl, ethyl, or propyl. R_1 is a radical that may be either hydrogen, methyl, ethyl, propyl, butyl, isobutyl, or isopropyl; with, in the above formula, at least one occurrence of R_1 being hydrogen.

The following list of acrylamide compounds of the type useful in the practice of the invention are presented below:

Table I

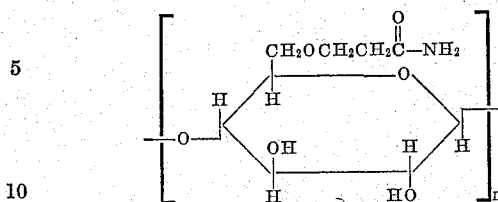
- (1)
$$\begin{array}{c} \text{H} & \text{H} & \text{O} & \text{H} \\ | & | & || & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{H} \end{array}$$
 Acrylamide
- (2)
$$\begin{array}{c} \text{H} & \text{H} & \text{O} & \text{H} \\ | & | & || & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{CH}_3 \end{array}$$
 N-methyl acrylamide
- (3)
$$\begin{array}{c} \text{H} & \text{CH}_3 & \text{O} & \text{H} \\ | & | & || & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{H} \end{array}$$
 Methacrylamide
- (4)
$$\begin{array}{c} \text{CH}_3 & \text{CH}_3 & \text{O} & \text{H} \\ | & | & || & | \\ \text{CH}_3-\text{C}=\text{C}-\text{C}-\text{N}-\text{H} \end{array}$$
 2,3-dimethyl buten-2-yl amide
- (5)
$$\begin{array}{c} \text{H} & \text{CH}_3 & \text{O} & \text{H} \\ | & | & || & | \\ \text{CH}_3-\text{CH}_2-\text{C}=\text{C}-\text{C}-\text{N}-\text{H} \end{array}$$
 2-methyl penten-2-yl amide
- (6)
$$\begin{array}{c} \text{H} & \text{H} & \text{O} & \text{H} & \text{CH}_3 \\ | & | & || & | & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{C}-\text{CH}_3 \\ & & & & | \\ & & & & \text{CH}_3 \end{array}$$
 N-t-butyl acrylamide
- (7)
$$\begin{array}{c} \text{H} & \text{CH}_3-\text{CH}_3 & \text{O} & \text{H} \\ | & | & || & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{CH}_3 \end{array}$$
 N-methyl,2-ethyl acrylamide
- (8)
$$\begin{array}{c} \text{CH}_3 & \text{H} & \text{O} & \text{H} \\ | & | & || & | \\ \text{CH}_3-\text{C}-\text{C}-\text{C}-\text{N}-\text{CH}_3 \end{array}$$
 N-methyl,3-methyl buten-2-yl amide
- (9)
$$\begin{array}{c} \text{H} & \text{H} & \text{O} & \text{H} \\ | & | & || & | \\ \text{CH}_3-\text{CH}_2-\text{C}=\text{C}-\text{C}-\text{N}-\text{H} \end{array}$$
 Penten-2-yl amide
- (10)
$$\begin{array}{c} \text{H} & \text{CH}_3 & \text{O} & \text{H} \\ | & | & || & | \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{N}-\text{CH}_2-\text{CH}_3 \end{array}$$
 N-ethyl methacrylamide

Of the above compounds by far the most preferred material is acrylamide itself.

As in the case of the alkali metal hydroxide bath, the acrylamide bath may be used at about room temperature or it may be heated to as high as 210° F. The contact time of the alkali hydroxide treated cellulose fabric with the bath will vary with the concentrations of the bath and the particular temperature employed. Here, as in the case of the caustic bath, the more concentrated the solution and the higher the temperature, the shorter will be the contact time of the fabric being treated. In a typical embodiment of the invention, the fabric would be immersed in the 2% acrylamide solution at 75° F. for a period of about 2.0 minutes.

What is believed to have been accomplished in this particular treatment step is to chemically link the acrylamide through the vinyl linkage to the cellulose molecule through the chemical process of what might be described as etherization. For purposes of illustrating what is be-

lieved to be the mechanism involved, the following structure is presented:



The above represents a segment of a cellulose chain showing the linkage of monomeric acrylamide. It will be understood that the above is presented for purposes of a clearer understanding of the invention, and it is not intended that the above is binding insofar as it relates to the inherent mode by which the invention operates.

Once again the fabric would be preferably padded to remove the excess liquid and the fabric would then be ready for the final treating process, which bath contains an acidic reagent and certain portions of formaldehyde.

ACIDIC FORMALDEHYDE TREATMENT

The padded fabric is immersed into or treated with an acidic aqueous solution of formaldehyde. The amount of formaldehyde contained in this bath is adjusted in proportion to the amount of acrylamide contained in the acrylamide bath, so that the molar ratio of formaldehyde to water-soluble acrylamide is at least 3:1. The molar ratio may be varied over a considerable range whereby ratios as high as 5:1 may be employed, although from an economic standpoint the molar ratio of the formaldehyde to water-soluble acrylamide is preferably maintained within the range of 3:1 to 4:1. The pH of the formaldehyde bath is adjusted with an acidic reagent to produce a pH within the range of 2.0 to 7.0. Preferably the pH is maintained within the range of 4.5 to 6.5.

The concentration of the acidic reagent may be varied over wide ranges which, of course, are dependent upon the pH range. The usual weight range of the acidic reagent is between 5% and 10% by weight. The acidity of the formaldehyde bath causes the amide grouping of the water-soluble acrylamide to react with the formaldehyde to form at least one methylol derivative. The acid reagent is also present in the bath to cause subsequent cross-linking of the methylol amide groups, which mechanism will be described more fully hereinafter.

The number of acidic reagents which may be used may be selected from a large number of chemical compounds of either the organic or inorganic type. Since the particular acidic material used is not critical, it is believed that any number of compounds may be used without departing from the spirit of the invention. For purposes of illustration, however, the following partial list of acidic compounds is presented: phosphoric acid, zinc sulfate, zinc nitrate, zinc chloride, magnesium chloride, triethylamine hydrochloride, citric acid, tartaric acid, and the well-known strong mineral acids, hydrochloric and sulfuric. In the case of the strong mineral acids, alkaline buffering agents are used so that better pH control is maintained.

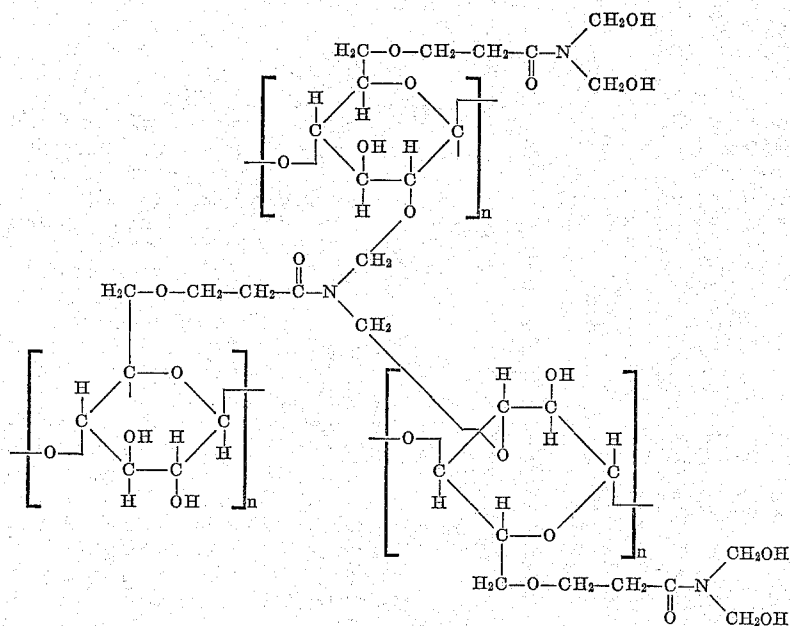
The temperature of the acidic formaldehyde treating bath may be varied from about room temperature to higher temperatures, although care must be exercised in order not to lose the formaldehyde by the use of excessive heat. The contact time of the treated fabric with the acidic formaldehyde bath will vary from 1.0 minute to 5.0 minutes, depending upon the concentrations and temperatures employed. A 5% formaldehyde solution, having a pH of 5.5 at room temperature, would be in contact with the treated fabric for 2.0 minutes in a typical embodiment of the invention.

CROSS-LINKING

After the fabric has been treated in the acidic formaldehyde bath, it is then subjected to a curing or heat treatment

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step which further reacts the methylol amide fabric linkage with the free hydroxyl positions of the cellulose to form a three-dimensional cross-linked network. A simplified illustration of this cross-linking phenomenon is presented below:



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of the invention. All the test baths were maintained at temperatures of $72 \pm 5^\circ \text{F}$. The contact time of the fabric with each bath was approximately 2.0 minutes. Between each bath the fabrics were padded on a hand laundry roller which exerted an approximate pressure of 40 pounds

It should be noted that the molecule is cross-linked through ether groups.

In this phase of the invention, the treated fabric is dried at a temperature between 140°C . and 190°C . for a period of time ranging from 8 to 9 minutes to a period of time as short as a few seconds. The preferred drying temperatures are between 150°C . and 160°C .

To generally illustrate the drying times in relation to temperature, the following table is presented:

Table II

Temperature in $^\circ \text{C}$..	Time in minutes
140	9
150	6
160	4
170	2
180	1
190	0.4

The fabric leaving the roller was slightly damp to the touch. The treated fabrics were tested for their crease-resistant properties on the Monsanto Wrinkle Recovery Tester, which is described in the Technical Manual and Yearbook of the American Association of Textile Chemists and Colorists, 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 Manual and Yearbook of the American Association of Textile Chemists and Colorists, vol. 28, 1952.

The padded fabric used in the tests was a commercial grade of unbleached shirt type cotton lawn having an 80 x 80 weave.

The results of these tests are presented below in Table III:

Table III

Test No.	Percent NaOH	Acrylamide compound ¹	Percent acrylamide compound	Percent HCHO	Molar ratio, HCHO: Acrylamide compound	Catalyst	pH	Warp angle average ²	Fill angle average ²
I									
II		1	2	5.5	6.5	Zn(NO ₃) ₂ ...	7.5	68(4)	66(4)
III		1	4	5.5	3.3	Zn(NO ₃) ₂ ...	3.5	78(4)	77(4)
IV	10	1	2	5.5	6.5	Zn(NO ₃) ₂ ...	3.5	75(4)	76(4)
V	10	3	2	5.5	7.8	MgCl ₂ ...	3.5	137(4)	140(4)
VI	5	1	2	5.5	6.5	ZnCl ₂ ...	4.8	125(4)	129(4)
VII	5	1	1	3.0	3.3	Zn(NO ₃) ₂ ...	5.3	143(2)	132(2)
VIII	10	1	1	3.0	3.3	Zn(NO ₃) ₂ ...	3.8	143(3)	141(3)
IX	10	1	2	1.0	1.2	Zn(NO ₃) ₂ ...	3.8	142(1)	126(1)
X	1	1	0.5	3.0	1.6	Zn(NO ₃) ₂ ...	3.8	69(4)	89(4)
XI	10	6	2	6.0	7.0	Zn(NO ₃) ₂ ...	3.5	83(3)	87(3)
							3.8	132(4)	128(4)

¹ See Table I.

² Figure in brackets is number of tests run.

EVALUATION OF THE INVENTION

By the general procedures outlined above, the following tests were conducted to demonstrate the efficacy

The above fabrics treated in accordance with the invention showed no degradation nor appreciable chlorine pick-up. Additionally, the preferred treated fabrics of the

invention were sent to a commercial laundry, where they were laundered successively 7-9 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 containing from .5% to 3% by weight of a cured acrylamide formaldehyde copolymer which is chemically bonded to the fabric through a plurality of ether linkages. The amounts of formaldehyde combined with acrylamide in a finished cotton copolymer combination may be expressed in terms of a formaldehyde-acrylamide 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 acrylamide 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.

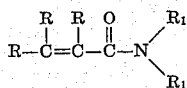
The finished fabrics of the invention, in addition to having the wrinkle-resistant finish imparted to them, also have several other properties which are not achieved by use of prior art materials. In the case of white goods, the wearing quality of the cloth is in no way diminished and in some instances it is improved, and bleached fabrics have improved whiteness. Since several improved properties are imparted to the fabric, I prefer to term my treated fabrics as having improved shape-holding qualities, which term is intended to mean that the fabric has all or several of the above qualities in addition to that of wrinkle-resistance.

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, vinyl chloride, copolymers of acrylonitrile, vinylidene cyanide, and other vinyl monomers may all be suitably blended with cotton which, when treated in accordance with the invention, will show improved results.

It will also be apparent to those skilled in the art that the invention may be advantageously combined with other textile treatments and reagents, such as softening and bleaching agents, to combine their effects and reduce the amount of processing equipment necessary to produce a suitable fabric. When used in conjunction with softening reagents, it is preferred to use the saturated di-fatty quaternary ammonium compounds of which dioctadecyl-diethyl-ammonium chloride is exemplary. Another useful group of fatty-containing textile softeners are those described in Johnson U.S. Patent 2,874,074.

The invention is hereby claimed as follows:

1. The process of treating cellulose fabrics to improve their shape holding qualities which comprises the sequential steps of contacting said fabrics with an aqueous bath containing from 5% to 20% by weight of sodium hydroxide, contacting the alkali-treated fabric with an aqueous solution containing from 1% to the saturation solubility of an acrylamide of the formula:



where R is from the group consisting of hydrogen, methyl,

and ethyl, and R₁ is from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, butyl, and isobutyl, with the proviso that at least one occurrence of R₁ is hydrogen, and then subjecting the acrylamide treated fabric to an aqueous acidic bath which contains an amount of formaldehyde calculated to give a formaldehyde to water-soluble acrylamide molar ratio of from 3:1 to 4:1, said bath containing from 3% to 10% by weight of water soluble chemical which gives said bath a pH of from 4.5 to 6.5, and finally curing the treated fabric at a temperature between 150° C. to 180° C.

2. The process of claim 1 where the cellulose fabric is predominantly garment grade cotton, the sodium hydroxide bath has a concentration of from 5% to 10% by weight and the water-soluble acrylamide is acrylamide.

3. The process of treating cellulose fabrics to improve their shape-holding qualities which comprises the sequential steps of contacting said fabrics with an aqueous bath containing from 5% to 20% by weight of an alkali metal hydroxide, contacting the alkali-treated fabric with an aqueous bath which contains from at least 1% by weight to the saturation solubility of a water soluble acrylamide compound, said acrylamide compound containing at least 1 reactive amido hydrogen, then contacting the acrylamide compound-treated fabric with an aqueous acidic bath which contains an amount of formaldehyde calculated to give a formaldehyde to water-soluble acrylamide compound molar ratio of at least 3:1, with the pH of said bath having been adjusted within the range of from 2 to 7, by the addition of a water soluble acidic reagent, and finally curing the treated fabric at a temperature between 140° C. and 190° C.

4. The process of claim 3 where the water soluble acidic reagent used to adjust the pH of the aqueous acidic formaldehyde bath, is an acidic zinc salt.

5. The process of claim 3 where the water soluble acidic reagent used to adjust the pH of the aqueous acidic formaldehyde bath, is zinc chloride.

6. The process of claim 3 where the water soluble acidic reagent used to adjust the pH of the aqueous acidic formaldehyde bath, is zinc nitrate.

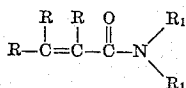
7. The process in accordance with claim 3 where the acrylamide compound is methacrylamide.

8. The process of claim 3 where the acrylamide compound is N-t-butyl acrylamide.

9. The process of treating of cellulose fabrics to improve their shape-holding qualities which comprises the sequential steps of contacting said fabrics with an aqueous bath containing from 5% to 20% by weight of an alkali metal hydroxide, contacting the alkali-treated fabric with an aqueous solution containing from between 1% to 5% by weight of an acrylamide compound from the group consisting of acrylamide, methacrylamide, and N-t-butyl acrylamide, and then contacting the acrylamide compound treated fabric with an aqueous acidic bath which contains an amount of formaldehyde calculated to give a formaldehyde to acrylamide compound molar ratio of from 3:1 to 4:1, said bath containing a sufficient quantity of an acidic salt from the group consisting of the acidic salts of zinc and magnesium to adjust the pH of said bath to between the ranges of from 4.5 to 6.5, and finally curing the treated fabric at a temperature between 150° C. and 180° C.

10. A cellulose fabric having improved shape-holding qualities which comprises a major portion of cellulose fabric and from .5% to 3% by weight of the products of the sequential reaction of the fabric with a water soluble acrylamide compound and formaldehyde, said reaction products being chemically bonded to the fabrics through at least 2 ether linkages, with the amount of formaldehyde which was sequentially combined with acrylamide being in a molar ratio of at least 1:1.

11. The cellulose fabric of claim 10 where the starting acrylamide compound has the formula:



where R is a member of the class from the group consisting of hydrogen, methyl, and ethyl and R₁ is from the group consisting of hydrogen, methyl, ethyl, butyl, isobutyl, propyl, and isopropyl, with the proviso that at least one occurrence of R₁ is hydrogen.

12. The cellulose fabric of claim 11 where the sequentially reacted acrylamide-formaldehyde product was formed from acrylamide.

13. The cellulose fabric of claim 11 where the sequentially reacted acrylamide-formaldehyde reaction product was formed from methacrylamide.

14. The cellulose fabric of claim 11 where the sequen-

tially reacted acrylamide-formaldehyde reaction product was formed from N-t-butyl acrylamide.

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