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MODIFICATION OF CELLULOSIC TEXTILES WITH METHYLOLATED HYDROXYALKYL CARBAMATES

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ABSTRACT OF THE DISCLOSURE

Methylol derivatives of hydroxaylkyl carbamates, produced by reacting a hydroxyalkyl carbamate with at least two molar equivalents of formaldehyde in aqueous alkaline solution, may be used as new finishing agents for cotton to produce wrinkle-resistant and wash-wear fabric. These agents have little or no adverse effect on color-fastness-to-light of dyed fabric. Hydroxyethyl carbamate is a typical example of a useful compound for making this type of agent. These finishes are very durable and cellulosic materials treated therewith may be held for substantial periods of time during which the fabrics may be converted into garments prior to the heat-setting operation.

This application is a division of application bearing Ser. No. 403,668, filed Oct. 13, 1964.

This invention relates to new finishing agents, to treating baths containing these finishing agents, and to the application of these treating baths to cellulosic fibrous materials. More specifically, it relates to wash-wear cellulosic fabrics which are not only resistant to wrinkling but are also resistant to chlorine damage and which exhibit outstanding durability to removal of these properties by laundering. Most important, dyed fabrics when treated with these novel finishing agents and then exposed to actinic light are characterized by their superior resistance to fading.

Textiles composed of cellulosic fibers such as cotton and rayon, are commonly finished by a wrinkle-resistant or wash-wear treatment. Such treatments improve the appearance of the textile by preventing the formation of wrinkles or mussiness while the textile is in use. The treatments, also, can give the textiles the ability to dry smoothly after washing and thereby reduce, or eliminate, the need for pressing. In these treatments an agent called a crosslinking agent or resin-former is applied to the textile under conditions that promote reaction of the agent with cellulose, or with itself. The agents used for this purpose are most commonly monomeric, or low-molecular weight condensates, or addition products of formaldehyde and an organic amide, such as dimethylol urea, dimethylol ethyleneurea, and trimethylol melamine. Less commonly used are other classes of agents, such as acetals and diepoxides. Preference for the formaldehyde-amide condensates is due to their economy, their effectiveness, and their ease of application.

The benefits derived from wrinkle-resistance and wash-wear treatments of cellulosic fabrics are obvious and undoubted. With the benefits however, a number of adverse effects are produced. Four serious drawbacks are: Loss of fabric strength; susceptibility to damage by chlorine bleach; loss of wrinkle-resistance or wash-wear properties on repeated laundering; and increased fading of dyed fabrics on exposure to sunlight. The first defect, loss of fabric strength, seems independent of the finishing agent employed. The magnitude of the other defects does vary with the agent employed. It has proven difficult, however, to minimize all these defects by selection of one finishing agent. In fact, selection of an agent to minimize one defect often increases the severity of another defect. For instance, it has been possible to obtain treated textiles with good durability of fabric properties and freedom from damage by chlorine bleaches by use of condensates of alkyl carbamates and formaldehyde as finishing agents. But, if applied to dyed goods, these agents cause the colors to fade more rapidly on exposure to sunlight or other active (actinic) light. On the other hand, condensates from formaldehyde and urea, or certain substituted ethyleneureas, can be applied to dyed cellulosic fabrics without greatly increasing the rate of color fading due to light exposure. The fabric so treated, however, can lose the wrinkle-resistance or wash-wear properties in relatively few launderings and can be severely weakened by the action of chlorine bleaches.

It is the purpose of this invention to provide a new class of agents for use in the treatment of cellulosic textiles to render them wrinkle-resistant or smooth-drying. The agents are economical, effective, and can be easily applied by conventional equipment and methods commonly used in textile finishing. Dyed fabrics treated with these agents show little or no decrease in lightfastness of the color. Furthermore, the effects of the treatment show a durability that will allow retention of wrinkle-resistance and smooth-drying properties through a relatively large number of launderings, and susceptibility of the treated fabric to damage from chlorine bleaches is low. As used herein the term "cellulosic material" includes fibrous cellulosic material in which the major component is natural or synthetic.

It has been found that these qualities can be imparted to cellulosic fabrics by finishing agents that are prepared by the reaction of hydrolyalkyl carbamates and formaldehyde. Although they have not been isolated in a pure form, it is believed that the primary constituent of these reaction mixtures is the hydroxyalkyl N,N-dimethylol-carbamate. The preferred hydroxyalkyl carbamates for preparing the condensates used in this invention are the 2-hydroxyalkyl carbamates such as 2-hydroxyethyl carbamate and 2-hydroxypropyl carbamate. These carbamatesbamates can be prepared by known methods such as are disclosed in U.S. Patent No. 2,627,524.

The hydroxyethyl carbamate-formaldehyde condensates used in this invention are prepared by treating a hydroxyethyl carbamate containing two to six carbon atoms with at least two molar equivalents of formaldehyde in an aqueous alkaline solution. An excess o formaldehyde over the two molar equivalents theoretically require is ordinarily preferred to help complete the reaction. Best results are obtained when the reaction is allowed to proceed under alkaline conditions, preferably at pH 9–11, at a temperature from about 20° to 80° C. for a period of time. The time required will depend upon the temperature selected with longer times required at the lower temperatures. The time required may vary from about 20 minutes at 80° C. to 20 hours at ambient room temperature.

The essential requirement is to continue the reaction until at least an average of about 1.5 moles formaldehyde has combined with the carbamate. This may be determined by titrating the uncombined formaldehyde and subtracting this quantity from the total formaldehyde added initially. After the reaction period, the solution is neutralized and is ready for the preparation of the treating bath.

To treat cellulosic fibrous material by the method of this invention, the reaction solution is diluted to contain about 5 to 20 weight percent of the condensate, after which an acidic salt catalyst is added to make 0.5 to about 6.0 weight percent of the solution. It is also within the scope of our invention to use organic acids such as maleic acid or maleic anhydride. Concentration of the condensate in the treating solution will be determined by the type fabric to be treated, the equipment to be used, and the degree of wrinkle-resistance or wash-wear property desired. Concentration of the acidic catalyst will depend on the type catalyst to be used and the concentration of condensate selected. Preferred catalysts are metallic, ammonium, or amine salts of strong mineral acids. In addition to condensate and catalyst, the treating solution or treating bath may contain auxiliary agents commonly used in textile finishing. These include wetting agents to assist impregnation of the fabric, softening agents to modify the hand and feel of the fabric, and fluorescent agents to give the fabric a bright appearance.

The carbamate-formaldehyde condensate is applied to the fabric by the usual finishing procedures. The fabric is soaked with the treating bath and padded (passed between padder rolls) or centrifuged so that it weighs one and a half to twice its dry weight. The fabric is then dried at relatively low temperatures and heated 1 to 5 minutes at 130 to 200° C. to effect reaction of the hydroxyalkyl carbamate-formaldehyde condensate. The fabric may then be washed, if desired.

The treatment of the cellulosic material by the process of our invention may be carried out as a continuous series of steps; or the treatment may be carried out as a series of intermittent steps. For those commercial finishers who have commercially available ranges at their disposal, the various steps in the finishing process may be carried out continuously, that is, wetting the cellulosic material with the treating bath, maintaining a period of dwell to enable the aqueous treating bath to penetrate into and through the cellulosic material, removing the excess treating bath, drying the wet cellulosic material preferably at relatively low temperatures and subsequently subjecting the dried material to a heat treatment to complete the treatment. The temperature for the heat treatment (cure) may range from about 130° C. to about 200° C. for 1 to 5 minutes, the longer time being required for the lower temperatures.

On the other hand, for those commercial finishers who do not have "continuous" equipment, or prefer to spread out their work, it is an advantage of our process that the different steps in the finishing operation may be carried out intermittently. The cellulosic material may be wet out and squeezed in a commercial padder to remove the excess treating bath after which the wet material may be transported to another part of the finishing plant to be dried. The dried material may then be held for a period of time prior to receiving the high-temperature heat treatment during which interval it may be passed through a button-breaker to soften the fabric, or passed through a friction calender or an embossing calender to impart physical properties to the fabric which will then be retained after the heat treatment. It is an advantage of the treating agents of our invention that cellulosic materials treated therewith may be held for substantial periods of time prior to heat-setting during which time the fabrics may be converted into garments prior to the heat-setting operation.

The process of this invention and properties imparted to cellulosic fabrics by this invention are illustrated in the following examples. All parts and percentages used in the examples are by weight. The degree of wrinkle resistance obtained in the finished fabric is shown by the crease recovery angle determined by Test D 1424–56T of the American Society for Testing Materials. Susceptibility of the fabrics to damaging effects of chlorine bleaches is shown by the strength lost as determined by Test 92–1962 of the American Association of Textile Chemists and Colorists.

It is to be understood that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

EXAMPLE 1

A condensate was prepared by mixing one mole of hydroxyethyl carbamate, 2.2 moles of formeldehyde, and sufficient water to make a 33% solution of the condensate on the basis of reaction with only 2.0 moles of formaldehyde. The solution was adjusted to pH 9.5–10 with sodium hydroxide and allowed to stand overnight, 16 hours, at 23° C. The solution was then adjusted to pH 6.5–7.0 with hydrochloric acid. The above solution was diluted with water and sufficient zinc nitrate hexahydrate added to give a treating bath containing 10% condensate and 0.6% zinc nitrate hexahydrate. Cotton printcloth was held in this treating bath until saturated, the excess removed by passing the wet fabric between squeeze-rolls and the process repeated. The wet fabric was then dried at 60° C. for seven minutes after which it was heated at 160° C. for three minutes. The heat-treated fabric was then washed in a detergent solution, thoroughly rinsed, and dried. It was then tested using an untreated sample of the same fabric as a control. The results follow:

	Untreated fabric	Treated fabric
Crease recovery angle (warp plus fill value)	186	252
Percent strength loss in test for chlorine resistance	21	22

Portions of dyed cotton fabrics were treated with the above condensate as described. Samples of the treated dyed fabrics and untreated dyed fabrics were exposed to light from a carbon arc for 20 hours. Exposed and unexposed fabrics were compared and rated using the International Geometric Gray Scale with the following results:

Gray scale rating of fabric dyed with—	Untreated fabric	Treated fabric
Direct Blue 78	5	5
Direct Red 26	2	3

Test results show that the fabric treated with the hydroxyethyl carbamate-formaldehyde condensate had noticeably greater wrinkle resistance, essentially no greater susceptibility to damage by chlorine, and the treatment did not promote degradation by actinic light.

EXAMPLE 2

A condensate was prepared by mixing one mole of hydroxyethyl carbamate, 2.5 moles of formaldehyde, and sufficient water to make a 50% solution of the condensate on the basis of reaction with only 2.0 moles of formaldehyde. The solution was adjusted to and maintained at pH 10 with sodium hydroxide and allowed to stand overnight, 16 hours at 23° C. The solution was then adjusted to pH 6.5–7.0 with hydrochloric acid. The above solution was diluted with water and zinc nitrate hexahydrate added to give a treating bath containing 10% hydroxyethyl carbamate-formaldehyde condensate and 0.6% zinc nitrate hexahydrate. Cotton printcloth was then passed into and through the treating bath, squeezed, and the process repeated. The wet fabric was dried at 60° C. for seven minutes, and then heat treated at 160° C. for three minutes. The treated fabric was washed in a detergent solution, preferably nonionic, thoroughly rinsed, and dried. It was then tested with an untreated sample of the fabric with the following results:

	Untreated fabric	Treated fabric
Crease Recovery Angle (Warp plus fill value)	186	252
Percent strength loss in test for chlorine resistance	22	1

A portion of each of five samples of dyed cotton fabric was treated with the condensate just described. Portions of the treated and untreated dyed cotton fabrics were exposed to light from a carbon arc for 20 hours. Exposed and unexposed fabrics were compared and rated by the procedure of the International Geometric Gray Scale with the following results:

Fabrics dyed with—	Untreated fabric	Treated fabric
Direct Red 153	3—	4
Reactive Red 9	2	3
Reactive Red 15	4	4—
Direct Red 26	1	2
Diphenyl Fast Green GL (Geigy)	5	5

These results show that the fabric treated with the hydroxyethyl carbamate-formaldehyde condensate had noticeably greater wrinkle resistance, practically no susceptibility to damage by chlorine, and showed little, if any, increase in tendency toward fading when exposed for twenty hours to actinic light.

When the cotton printcloth is replaced by viscose rayon fabric, a noticeable increase in wrinkle-resistance results.

EXAMPLE 3

A condensate of hydroxyethyl carbamate and formaldehyde was prepared as described in Example 1. This condensate and condensates of urea and ethyl carbamate with formaldehyde were applied to samples of cotton printcloth. The treated fabrics were tested for crease recovery angle (CRA) and analyzed for nitrogen content before and after exposure to hydrolytic solutions of pH 1.4 and pH 14 at 43° C. for 30 minutes to demonstrate durability of the treatments. Results of the testing follow:

Fabric treated with condensate of—	Original		After hydrolysis at—			
			pH 1.4		pH 14	
	CRA warp plus fill	Percent N	CRA	Percent N	CRA	Percent N
Hydroxyethyl carbamate	255	0.70	226	0.52	244	0.66
Ethyl carbamate	255	0.60	221	0.46	242	0.63
Urea	248	1.39	159	0.07	180	0.68

These results show that both carbamate formaldehyde condensates are superior to the urea-formaldehyde condensate in the durability of properties imparted by the treatment.

The same treatments were applied to cotton fabric dyed with various dyes. Samples of these treated dyed and untreated dyed fabrics were exposed 20 hours to the light from a carbon arc and resistance to change in color due to the exposure rated by the International Geometric Gray Scale. The results follow:

Fabric treated with condensate of—	Gray scale rating on fabric dyed with—		
	Reactive Red 15	Direct Red 153	Vat Red 30
Hydroxyethyl carbamate	4	3	5
Ethyl carbamate	2	4	4
Urea	4	2	5

The results show that fabric treated with the hydroxyethyl carbamate condensate is superior to that treated with the ethyl carbamate condensate minimizing light fading of dyes.

EXAMPLE 4

A condensate was prepared by mixing 0.1 mole of dihydroxypropyl carbamate, 0.25 mole of formaldehyde, and sufficient water to make a 50% solution of the condensate, on the basis of reaction with only 0.2 mole of formaldehyde. Another condensate was prepared by mixing 0.11 mole of hydroxypropyl carbamate, 0.275 mole of formaldehyde, and sufficient water to make a 50% solution of the condensate, on the basis of reaction with only 0.22 mole of formaldehyde. These solutions were adjusted to and maintained at pH 9.5–10 with sodium hydroxide for 4–6 hours then allowed to stand overnight, 16 hours, at 23° C. The solutions were then adjusted to pH 6.5–7.0 with hydrochloric acid.

The solutions were diluted with water and magnesium chloride-hexahydrate added to give treating baths containing 10% of the condensates and 2.5% magnesium chloride-hexahydrate, the condensates were applied to cotton print cloth and tested to demonstrate improvement in crease recovery. Results are as follows:

Fabric treated with condensate of—	Crease recovery angle, warp plus fill value	
	Untreated	Treated
Dihydroxypropyl carbamate	186	225
Hydroxypropyl carbamate	186	% 244

This shows that treatment with the dihydroxypropyl carbamate-formaldehyde and the hydroxypropyl carbamate-formaldehyde condensates impart noticeable wrinkle resistance to the fabric.

Dyed cotton fabrics with various dyes were treated with the two condensates and with condensates of hydroxyethyl carbamate and ethyleneurea with formaldehyde. Samples of these treated fabrics were exposed for 20 hours to the light of a carbon arc and resistance to change in color due to the exposure rated by the International Geometric Gray Scale.

Fabric treated with condensate of—	Gray scale rating on fabric dyed with—		
	Reactive Red 15	Direct Red 153	Cibacron Scarlet 2G
Dihydroxypropyl carbamate	3	3	3
Hydroxypropyl carbamate	3	3	3
Hydroxyethyl carbamate	4—	2	3
Ethyleneurea	1	2	2
Untreated	4—	3—	3

These results show that dyed fabrics treated with dihydroxypropyl carbamate-formaldehyde and hydroxypropyl carbamate-formaldehyde condensates are superior to dyed fabric treated with the ethyleneurea-formaldehyde condensate. They are also comparable to the hydroxyethyl carbamate-formaldehyde condensate finish and to the untreated dyed control in fading of dyes due to actinic light.

We claim:

1. A process for imparting a wrinkle-resistance and wash-wear finish to a cellulosic fibrous material, comprising:

(a) passing the cellulosic fibrous material into and through a treating bath containing about 5 to about 20 weight percent of the monomeric condensation product produced by the reaction at a pH of from about 8.5 to 11 and at temperatures of less than about 80° C. of a hydroxyalkyl carbamate and formaldehyde and from about 0.5 to 6.0 weight percent of an acidic salt catalyst,

(b) maintaining a period of dwell to enable the aque-

ous treating bath to penetrate into and through the cellulosic material,

(c) removing the excess treating bath,

(d) drying the wet cellulosic material, and

(e) thereafter exposing the dried cellulosic material to a temperature of from about 130° C. to about 200° C. for from about 1 to 5 minutes to impart the wrinkle-resistance and wash-wear finish to the cellulosic fibrous material.

2. A process according to claim 1 wherein the ratio of formaldehyde to carbamate in the condensation product of hydroxyalkyl carbamate and formaldehyde is at least 2.0 equivalents formaldehyde per mole carbamate.

3. A process according to claim 2 wherein the hydroxyalkyl carbamate is 2-hydroxyethyl carbamate and the acidic salt catalyst is zinc nitrate hexahydrate.

4. A process according to claim 2 wherein the hydroxyalkyl carbamate is dihydroxypropyl carbamate and the acidic salt catalyst is magnesium chloride hexahydrate.

5. A process according to claim 2 wherein the hydroxyalkyl carbamate is hydroxypropyl carbamate and the acidic salt catalyst is magnesium chloride hexahydrate.

6. Cellulosic fibrous material treated by the process of claim 2.

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