United States Patent Office

3,219,632

Patented Nov. 23, 1965

3,219,632

WATER SOLUBLE CARBAMATE-FORMALDEHYDE CONDENSATE

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No Drawing. Original application June 6, 1961, Ser. No. 115,268, now Patent No. 3,144,299, dated Aug. 11, 1964. Divided and this application Oct. 17, 1962, Ser. No. 274,364

5 Claims. (Cl. 260—72)

(Granted under Title 35, U.S. Code (1952), sec. 266)

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This application is a division of Serial No. 115,268, filed June 6, 1961, now U.S. Patent No. 3,144,299.

This invention relates to the finishing of cellulosic textile fabrics whereby the fabric is given improved resistance to wrinkling or mussing, improved shape-holding properties, and the ability to dry smooth after laundering. Moreover, the cellulosic fabric so finished may be laundered by procedures usually used with textiles of the same type, which procedure can include the use of hypochlorite bleaching agents and acid sours, without suffering additional damage because of the finish or extensive loss of the improved properties imparted by the finish.

Because of their poor resiliency, cellulosic textile fabrics, such as cotton and rayon, tend to become wrinkled in use and acquire a mussed or unpleasant appearance. To overcome this objectionable property, it has been the practice to treat or finish cellulosic textiles with the methylol derivatives of organic nitrogen compounds, such as urea, ethyleneurea, guanidine, or melamine. These agents do produce a finished cellulosic textile that has improved resistance to wrinkling or mussing while in use, and in addition, give the textile, to a greater or lesser extent, the ability to dry smooth after laundering. Textiles finished with many of these agents, however, cannot be bleached with the usual hypochlorite bleaching agents during laundering without the danger of suffering severe strength loss or discoloration. In addition, the souring step common in many laundry procedures will often partially remove the finish produced by these agents, and cause extensive loss of the imparted properties. These disadvantages of presently used finishes are most pronounced with cotton textiles because of the more rigorous laundry procedures to which cotton textiles are submitted as compared with those which are employed with other cellulosic textiles.

The mechanism by which the agents mentioned produce the wrinkle resistance and smooth-drying properties in cellulosic textile is believed to be a crosslinking of the linear cellulose molecules in the fibrous material. The effect can be accomplished by etherification of cellulose with the methylol compound using an acidic or alkaline catalyst. To obtain the necessary crosslinking, the finishing agent must be polyfunctional, that is, contain two or more reactive methylol groups. The agents used, therefore, are di-, tri-, or tetra-methylol compounds formed by the reaction of an organic nitrogen compound, containing two or more nitrogen containing groups with formaldehyde in a ratio to give at least one molar equivalent of formaldehyde for each nitrogenous group. For example, the finishing agent dimethylol ethyleneurea is formed from the reaction of ethyleneurea with two molar equivalents of formaldehyde. Similarly, the agent trimethylol melamine is formed from the reaction of melamine with three molar equivalents of formaldehyde. Numerous investigators in this field have reported that similar agents derived from nitrogenous compounds containing a single nitrogenous group are ineffective in producing the desired wrinkle resistance and smooth-drying properties. The single known exception to this is the reaction product of formamide and formaldehyde. Accordingly, this agent has been described by some investigators as actually belonging to another class of agents and producing a nitrogen free finish on the fabric. On the other hand, other investigators have reported that this agent gives a finished fabric very susceptible to damage by hypochlorite bleaching agents, a property normally associated with the presence of nitrogen.

The use of dimethylol dicarbamates as wrinkle resistance finishing agents has been described. This type of agent, derived from compounds with two carbamate groups, has the disadvantages previously noted for the agents in present use. We have found, however, that agents can be prepared from organic monocarbamates, containing a single nitrogenous group, and formaldehyde, and that these agents are effective in producing wrinkle resistance and smooth drying properties in cellulosic textiles. Furthermore, textiles finished with the agents prepared from monocarbamates are less susceptible to damage from hypochlorite bleaching agents and have properties more durable to acidic souring than those finished with agents prepared from organic compounds with two or more nitrogenous groups.

It is the object of this invention, therefore, to provide a method of finishing or treating cellulosic textiles whereby the textile is rendered resistant to wrinkling or mussing during use and will have improved smooth drying properties after laundering. Furthermore, the cellulosic textiles so treated may be laundered by procedures normally used with untreated textiles of similar type, which procedure may include the use of hypochlorite bleaching agents and the use of acid sours in the rinse, without suffering any deleterious effects because of the treatment or drastic loss of the properties imparted by the treatment.

The object of this invention may be accomplished by applying to the textile a product formed from the reaction of a monocarbamate, such as methyl carbamate, ethyl carbamate, propyl carbamate, or butyl carbamate, and two moles of formaldehyde. The product is formed by allowing the carbamate and formaldehyde to react in a slightly alkaline aqueous solution. After the reaction is completed, the solution is diluted to the desired concentration for application to the textile and an acidic catalyst is added to the solution. The concentration of the product to be used will vary, usually between 5 and 20% of the solution, depending on the type of textile to be finished. The acidic catalyst can be an inorganic or amine salt of a strong mineral acid. Particularly suitable as catalysts are zinc nitrate and magnesium chloride used as the readily obtainable hydrates in a quantity 0.5 to 6.0% of the weight of the carbamate-formaldehyde solution containing the desired concentration of the carbamate-formaldehyde condensate.

The solution can be applied to textiles by usual finishing procedures, such as soaking the textile in the solution and padding or centrifuging so that the textile retains a weight of solution equal to 50 to 100% of its dry weight. The wet textile is dried at relatively low temperature, as 60 to 110° C., and then heated briefly at a higher temperature, such as 130–160° C. for 3 to 5 minutes. The textile is then preferably washed to remove unreacted materials.

In addition to the carbamate-formaldehyde product and catalyst, the treating bath for this finishing operation may contain other auxiliary agents commonly used in textile finishing. For instance, wetting agents may be included in the bath to provide more rapid impregnation of the applied solution. Softening agents may also be included to modify the hand and feel of the finished textile.

The properties of textiles finished by the method of this invention are illustrated in the following examples. All parts and percentages described are by weight. The degree of wrinkle resistance obtained in the finished textile is shown by the crease recovery angle determined by the American Society for Testing Materials Test D1424–56T. The resistance of the textiles to hypochlorite bleach is shown by the strength retained in the American Association of Textile Chemists and Colorists Test 69–1952. The tearing strength of the textiles is shown by the tearing strengths obtained by the Elmendorf method, American Society for Testing Materials Test D1424–56T.

Example 1

A 30% water solution of an ethyl carbamate-formaldehyde product was prepared in the following manner: ethyl carbamate was dissolved in 4 times its weight of water and sufficient 36% formaldehyde solution which was previously adjusted to pH 8 with sodium hydroxide was added to afford a ratio of formaldehyde to ethyl carbamate of 2:1. This solution was allowed to stand overnight at room temperature. After this time the solution was diluted to 13.5% solids concentration and made to contain 4% of hydrated magnesium chloride $MgCl_2 \cdot 6H_2O$). The solution was padded onto a sample of 80 x 80 cotton print cloth to give a 70–80% wet pickup. The wet fabric was dried at original dimensions for seven minutes at 60° C., and then cured at original dimensions for 3 minutes at 160° C. The curing step was followed by an afterwash in warm water with a nonionic detergent and then tumble dried. The finished fabric possessed a crease recovery angle of 262° (warp + filling) while an untreated, afterwashed sample had a crease recovery angle of only 187° (warp + filling).

Example 2

A sample was treated as described in Example 1, except that the solution contained 0.75% hydrated zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) instead of magnesium chloride as catalyst. The finished fabric had a crease recovery angle of 262° (warp + filling).

Example 3

A sample was treated as described in Example 1, except that 1.5% of 2-amino, 2-methyl, 1-propanol hydrochloride was used as catalyst instead of magnesium chloride. The finished fabric had a crease recovery angle of 268° (warp + filling).

Example 4

A sample was treated as described in Example 1 except that 1.5% of emulsified polyethylene was added to the treating bath. The finished fabric had a crease recovery angle of 294° (warp + filling) and a warp tearing strength of 627 g. by the Elmendorf method. A similar sample prepared as in Example 1 had a crease recovery angle of 262° (warp + filling) and a warp tearing strength of 480 g.

Example 5

Samples treated as described in Examples 1, 2, and 3 were subjected to 20 launderings in an automatic home type washer using detergent and hypochlorite bleach to give 0.02% available chlorine and to 5 launderings as described in AATCC Test 14–53. The properties of the fabrics are tabulated as follows:

Treatment	Original			After 20 Home Launderings			After 5 AATCC Washes		
	Crease Recovery Angle, W+F	Elmendorf Tear Strength, g. Warp	Scorch Test, Percent Strength, Retained	Crease Recovery Angle, W+F	Elmendorf Tear Strength, Warp	Scorch Test, Percent Strength, Retained	Crease Recovery Angle, W+F	Elmendorf Tear Strength, Warp	Scorch Test, Percent Strength Retained
Example 1	262	480	106	256	367	98	272	487	102
Example 2	262	480	102	247	413	87	254	580	98
Example 3	268	533	91	256	433	89	252	567	92

Example 6

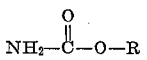
For comparison purposes to demonstrate the durability of the finish to an acid sour, a sample treated as described in Example 2 and a sample treated with water solution of 8% by weight of dimethylol ethyleneurea and 0.75% by weight of hydrated zinc nitrate were immersed in a solution buffered to pH 2.2 for 30 minutes at 40° C. The dimethylol ethyl carbamate treated sample retained 94% of its original nitrogen content and 94% of its original crease recovery angle after its treatment. The dimethylol ethyleneurea treated sample retained only 22% of its original nitrogen content and only 62% of its original crease recovery angle.

Example 7

A 15% water solution of a butyl carbamate-formaldehyde product was prepared in the following manner: butyl carbamate was dissolved in 7.7 times its weight of water and sufficient 36% formaldehyde solution, which was previously adjusted to pH 8 with sodium hydroxide, was added to afford a ratio of formaldehyde to butyl carbamate of 2:1. This solution was allowed to stand overnight at room temperature. After this time hydrated magnesium chloride was added to make 4% of the solution and the solution used to treat fabric as in Example 1. The finished fabric had a crease recovery angle of 254° (warp + filling) and retained 91% of its original strength in the scorch test.

We claim:

1. The water soluble carbamate-formaldehyde condensate formed by reacting at room temperature in aqueous alkaline solution and in a mole ratio of 2 to 1, formaldehyde and a compound represented by the formula



$$NH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-R$$

wherein R is a lower alkyl group containing from 1 to 4 carbon atoms.

2. The condensate of claim 1 wherein R is methyl.
3. The condensate of claim 1 wherein R is ethyl.
4. The condensate of claim 1 wherein R is propyl.
5. The condensate of claim 1 wherein R is butyl.

References Cited by the Examiner

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