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WRINKLE RESISTANT CELLULOSIC TEXTILES AND METHOD OF PRODUCTION

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This invention relates to the treatment of cellulosic textile materials to produce textiles having improved properties. More specifically, the present invention relates to new textile treating agents and a method of treating cellulosic textile fabrics with these agents whereby the fabrics are rendered resistant to wrinkling, have improved resiliency, and possess wash-and-wear properties. Moreover, the fabrics so treated may be laundered by procedures usually employed with untreated textiles of the same type, which procedure can include the use of hypochlorite bleaching agents, without suffering discoloration or severe loss in strength either in the bleaching operation or on subsequent ironing.

Fabrics composed of cellulosic fibers, such as cotton, rayon and the like, have poor resiliency and consequently, when in use tend to become wrinkled and acquire a mussed or unpleasant appearance. In order to overcome this objectionable property, it has been the practice to treat cellulosic fabrics with various agents designed to produce wrinkle resistant and wash-and-wear fabrics. One of the types of agents used for this purpose is the methylolmelamines produced by the reaction of melamine and formaldehyde. However, the fabrics treated with the conventional methylolmelamines have a tendency to discolor when exposed to hypochlorite bleaching agents. As a result these agents are not acceptable for use on white fabrics or others that would show the discoloration after contact with hypochlorite bleach.

In general, this objectionable discoloration of the methylolmelamines has been combatted in several ways in prior art processes. These include treatment of the melamine with sufficient formaldehyde to theoretically react with all or nearly all of the amino hydrogens present in the melamine molecule; alkylation of the methylol groups present in the methylolmelamine molecule; and the use of N,N-dialkylmelamines containing four unsubstituted amino hydrogen atoms. The alkylation of the methylol groups is also necessary to impart water solubility to some of the methylolmelamines for their practical use as textile treating agents. The aforementioned conventional processes reduce to some extent the amount of yellowing produced by hypochlorite bleaching of the treated textiles, but do not entirely eliminate this discoloration. Consequently, these treating agents and processes can not be used to produce acceptable white wash-and-wear cellulosic fabrics.

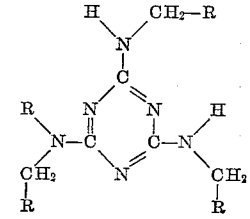
A primary object of the present invention is to provide new N-alkylmelamines, which upon reaction with formaldehyde produce water-soluble methylolmelamines having outstanding characteristics as treating agents for cellulosic textiles.

Another object of the invention is to provide a process for the treatment of textile fabrics, composed mainly of cellulose, with a new type of methylolmelamine treating agent whereby the fabric acquires the properties of increased resiliency and wrinkle resistance, and which properties are retained after repeated laundering. It is further-

more an object of this invention to provide such a treatment whereby the treated fabrics, with the properties described, may be laundered repeatedly by ordinary procedures, which procedures may include the use of hypochlorite bleaching agents, without suffering discoloration or loss in strength in the laundering procedure or subsequent treatment greater than occurring on untreated fabric.

A further object of the present invention is to provide a new type of methylolmelamine agent which is suitable for imparting the above described desirable properties to cellulosic textiles without resort to an additional alkylation step of the treating agent.

In general, these and other objects of the invention are accomplished by treating the cellulosic textile with an aqueous solution containing a N-methylol-N-alkylmelamine produced by the reaction of formaldehyde and a substituted melamine having the following structure:



wherein R is a member of the group consisting of H, an alkyl group of 1 to 3 carbon atoms, and a substituted-alkyl group of 1 to 3 carbon atoms. As is evident from the above structural formula, the substituted melamines suitable for use in the present invention must have at least one alkyl or substituted alkyl group of the aforementioned type attached to each of the amino nitrogen atoms of the melamine molecule, with at least two unsubstituted amino hydrogen atoms being present for reaction with the formaldehyde to form N-methylol groups. It is frequently advantageous, though not essential, to use as substituents on the amino nitrogens of the melamine molecule substituted-alkyl groups containing hydrophilic groups, such as free hydroxyl groups, to increase the water-solubility of the N-methylol-N-alkylmelamine employed in the textile treating solution. The hydroxyl or other group substituted on the alkyl group attached to the amino nitrogen atom can be substituted at any available position on the carbon chain of the alkyl group except the alpha position. Substituents in the alpha position are undesirable, since they render the alkyl group labile and susceptible to removal, with the result that the treated textile's resistance to discoloration is destroyed.

The N-methylol-N-alkylmelamines used for the treatment of the cellulosic textile in the process of this invention can be conveniently obtained by the reaction of formaldehyde and a substituted melamine of the above-described structure in aqueous media under slightly alkaline conditions. It is preferred to employ about stoichiometric quantities of formaldehyde and substituted melamine in said reaction, based upon the number of hydrogens available in the particular substituted melamine for reaction with the formaldehyde to produce N-methylol groups. A smaller than stoichiometric quantity of formaldehyde can be used, but in this case it is preferable that the amount present be sufficient to react with available hydrogens of the substituted melamine to form at least two N-methylol groups. An amount of formaldehyde slightly in excess of the stoichiometric quantity can also be employed, but it is inefficient and uneconomical to use a large excess of formaldehyde. The temperature of the reaction between the substituted melamine and formaldehyde can be varied depending on the rapidity of reaction desired. It is generally preferred to conduct the reaction at a temperature ranging from about

room temperature to about 80° C., using a longer reaction time with the lower temperature. For example, a reaction time of about one-half hour at 60° C. is usually adequate, whereas overnight reaction at room temperature is generally employed.

Following completion of the reaction between the substituted melamine and formaldehyde, the aqueous solution containing the reaction product is diluted to the desired strength for treatment of the cellulosic material, and 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 N-methylol-N-alkylmelamine reaction product present in the diluted solution 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. It is generally preferred to use from about 5% to about 15% by weight of the N-methylol-N-alkylmelamine reaction product in the diluted treating solution. A metal salt of a strong mineral acid is a particularly suitable acidic catalyst to add to the diluted treating solution of the process of the present invention. Magnesium chloride and zinc nitrate are examples of particularly suitable catalysts. From about 0.5% to about 5% by weight of the acidic catalyst is generally preferred.

Treatment of the cellulosic textile material according to the process of this invention comprises uniformly impregnating (thoroughly wetting) the textile with the above-described diluted treating solution, mechanically removing excess liquid, then drying and curing the goods. All of these steps can be conveniently carried out with conventional textile finishing equipment. The wet pickup (increase in weight of the textile upon wetting), after mechanically removing excess liquid, should preferably be from about 70 to 80% when using the preferred treating solution. Adjustment to the desired wet pickup can be conveniently achieved by passing the impregnated textile through squeeze rolls or the like. The drying time and temperature are not critical, but it is preferable to dry the wet textile, adjusted to the desired pickup, at relatively low temperatures, from about 60° to 100° C., until the textile is dry to the touch. After drying, the textile is cured by subjecting it to a higher temperature, from about 130° to 160° C., for a brief time, usually from about ½ to 5 minutes, to cause reaction of the applied materials. In the curing operation, the longer time is used with the lower curing temperature. Curing temperatures above 160° C. are not generally desirable, since there is danger of degradation of the cellulose at the high temperatures.

Following the curing operation, it is preferable to water-wash the treated textile to remove any unreacted materials. The washing operation can be carried out using the procedures and equipment conventionally employed for the washing of textiles. After it is washed and dried, the treated textile has the same appearance as the original untreated textile and its feel is also essentially unchanged; but the treated fabric possesses resiliency, wrinkle resistance, and the other desirable properties previously described.

In addition to being employed as the sole methylol agent in the treating solution of the present invention, the N-methylol-N-alkylmelamines may also be used in blends with various conventional treating agents to produce economical and improved cellulosic textile products. For example, it is well known in the art that cellulosic textiles treated with the methylolureas suffer strength losses when subjected to elevated temperatures (as in ironing) following hypochlorite bleaching. However, when these inexpensive methylolureas are blended with the N-methylol-N-alkylmelamines according to this invention and applied to the textiles, these strength losses of the resultant textiles are reduced or essentially eliminated.

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 unless noted otherwise. The fabrics were tested by the following methods: Wrinkle recovery angle, Monsanto method, American Society for Testing Materials (ASTM) test D1295–53T; breaking strength, ASTM test D39–49; damage caused by retained chlorine, American Association of Textile Chemists and Colorists tentative test method 69–1952 ("scorch test"). Also, the fabrics were subjected to ten home washes using hypochlorite bleach unless after two washes a yellow color was clearly visible. The home washes were performed in an agitator-type, home automatic washer with a household detergent, 0.02% available chlorine in hot water, and followed by drying in a tumble dryer. A Hunter multi-purpose reflectometer with the blue filter was used to measure the yellowing of the hypochlorite bleached fabrics.

EXAMPLE 1

N,N' - dimethyl-N'',N''-bis(2-hydroxyethyl) melamine was prepared in the following manner: 2,4-bis(methylamino)-6-chloro-s-triazine was prepared from 0.2 mole of cyanuric chloride and excess aqueous methylamine essentially according to the procedure of J. T. Thurston et al., Journal of the American Chemical Society 73, 2981–83 (1951). The intermediate was separated by filtration and added to a suitable reaction vessel, equipped with a reflux condenser and heating mantle, containing about 300 ml. of Cellosolve and 0.4 mole of diethanolamine. The solution was refluxed for 4 to 5 hours. After about 2–3 hours of refluxing the solution became clear indicating conversion of the intermediate into the desired product. Isolation of the product was achieved by concentration and cooling of the solution to permit crystallization. Further purification if desired was obtained by recrystallization from water. The N,N'-dimethyl-N'',N''-bis(2-hydroxyethyl) melamine had a melting point of 133°–136° C., and contained 34.1% nitrogen (theory=34.7% nitrogen for $C_9H_{18}N_6O_2$).

EXAMPLE 2

N,N'-dimethyl-N'',N''-bis(2 - hydroxyethyl) melamine prepared as described in Example 1 was dissolved in about 9 times its weight of warm water and sufficient 36.3% formaldehyde solution was added such that the melamine to formaldehyde molar ratio was 1:2. The pH of the resulting solution was adjusted to about 8 with sodium hydroxide, and the solution was heated to 45° C. The solution, containing 11.7% solid, was then allowed to return to room tempertaure. After one hour a magnesium chloride catalyst, about 4% of solution weight, was added. A sample of 80 x 80 cotton print fabric was dipped in the treating solution and padded to give about 70–80% increase in weight of the fabric (i.e., wet pick-up of 70–80%). The wet fabric was then dried eight minutes at 70° C. and cured for 3–5 minutes at 160° C. This treatment was followed by a process wash in warm water, with a nonionic detergent added, and then tumble drying. The finished fabric was pleasant to the touch and was wrinkle-resistant, possessing a crease recovery angle of 251 degrees (sum of the determinations in warp and fill direction). The original, untreated fabric had a crease recovery angle of only 181° (warp+fill).

EXAMPLE 3

For comparison purposes, the following conventional

types of solutions of methylolaminotriazines and methylolureas were applied to cotton print fabric with an acidic catalyst and processed in the same manner as described in Example 2. The wet pickups were 70 to 80% in each case.

Solution A.—A 12% methylolmelamine solution, prepared with a formaldehyde-melamine molar ratio of 3:1.

Solution B.—An 11% methylated methylolmelamine solution prepared with a formaldehyde-melamine molar ratio of 3:1.

Solution C.—A 12% methylol - N,N - bis(2 - hydroxyethyl) melamine solution prepared with a formaldehyde-melamine molar ratio of 2:1.

Solution D.—Solution C prepared with a 4:1 molar ratio of formaldehyde to the melamine. The concentration of the solution was such that the melamine concentration was the same as that in solution C.

Solution E.—Solution D methylated with methanol using an acid catalyst with the melamine concentration remaining the same as that in solution C.

Solution F.—A 10% methylolacetoguanamine solution prepared with a formaldehyde-acetoguanamine molar ratio of 2:1.

Solution G.—Solution F prepared with a 4:1 molar ratio of formaldehyde to acetoguanamine. The concentration of the solution was such that the acetoguanamine concentration was the same as that in solution F.

Solution H.—A 10% dimethylolurea solution, that is, one prepared using a methylolurea having a formaldehyde-urea molar ratio of 2:1. It is well known in the industry that this finishing agent is non-yellowing on bleaching in hypochlorite.

The various conventionally treated fabrics, as well as the treated fabric of Example 2, were subjected to a series of home washes using hyprochloride bleach, and the extent of yellowing was determined by reflectance readings on the washed fabrics. The results are given in Table I.

Table I

REFLECTANCE READINGS ON TREATED FABRICS AFTER TWO OR TEN[1] HOME WASHINGS WITH BLEACH

Treatment	Two Washings	Ten Washings
As in Example 2		81
Example 3, Solution A	68	
Example 3, Solution B		75
Example 3, Solution C	73	
Example 3, Solution D		78
Example 3, Solution E		78
Example 3, Solution F	75	
Example 3, Solution G	75	
Example 3, Solution H		81
Untreated Fabric (Control)		81

[1] Readings were taken after two washes on only those samples which appeared yellow after the second wash.

The data in Table I reveal that the new type of methylolmelamine of this invention (produced as in Example 2) will not yellow after ten washes in hyprochlorite bleach.

EXAMPLE 4

The treating agent of Example 2 was blended with solution H, Example 3, in the following proportions, and the blends were used to treat cotton print cloth according to the procedure described in Example 2:

A. Blend of 50% treating solution of Example 2 and 50% of solution H, Example 3.

B. Blend of 25% treating solution of Example 2 and 75% of solution H, Example 3.

These two blends cover a range of from about 3 to 6% by weight of the reaction product of formaldehyde and the melamine derivative and from about 5 to 8% by weight of dimethylol urea.

Properties of the treated fabrics, as well as of fabrics treated with the unblended treating agents, are given in Table II.

Table II

Treatment	Wrinkle Recovery Angle (Warp +Fill), degrees	Breaking Strength Retained After Scorch Test, percent
As in Example 2	251	100+
As in Example 3, Solution H	293	46
As in Example 4, Blend A	267	98
As in Example 4, Blend B	268	56
As in Untreated Fabric (Control)	181	

As is evident from the data in Table II, the new type of methylolmelamine product of this invention, prepared as illustrated in Example 2, gives cotton fabric a satisfactory wrinkle recovery angle and the treated fabric shows no damage in the Scorch Test. Further, when it is blended with the conventional, inexpensive urea-formaldehyde agent, as illustrated in blends A and B of the present example, a fabric of improved wrinkle recovery is obtained; and excessive damage from hypochlorite bleaching and scorching normally obtained with the urea-formaldehyde agent is reduced or essentially eliminated.

EXAMPLE 5

N,N',N''-trimethylmelamine was prepared essentially according to the procedure of D. W. Kaiser et al., Journal of the American Chemical Society 73, 2984–6 (1951), except that an excess of the amine was present in the reaction mixture until substantially all of the solids went into solution. At this point, anhydrous potassium carbonate was added until an oil layer appeared. The oil layer was separated, and the product crystallized from benzene-petroleum ether. The product had a melting point of 129°–130° C. and contained 49.1% nitrogen (theory= 49.97% nitrogen for $C_6H_{12}N_6$). Methylol derivatives of this substituted melamine compound were prepared by the following two methods:

A. The substituted melamine compound was added to an aqueous solution of formaldehyde such that the combined formaldehyde-substituted melamine content was 11% and the molar ratio of formaldehyde to the substituted melamine was 3 to 1. A drop or two of dilute caustic was added to adjust the pH to about 9. The solution was allowed to stand at room temperature overnight. The precipitate which formed was filtered off, thereby reducing the "solids" content from 11 to 9.5%. Magnesium chloride was added to the filtered solution such that the catalyst strength was 4% $MgCl_2 \cdot 6H_2O$. Cotton fabric was dipped in this solution and processed as described in Example 2.

B. This preparation was similar to that in A except after mixing the solution and adjusting the pH to about 9, the solution was heated for 30 minutes at 50°–60° C. As soon as the solution had cooled to 30° C., the catalyst was added as in A and any loss of weight through evaporation was made up by the addition of water. Treating solutions containing 7 and 11% "solids," respectively, were prepared in this manner and used to treat cotton fabric as described in Example 2.

Properties of the treated fabrics are given in Table III.

Table III

Treatment	"Solids" Content, percent	Wrinkle Recovery Angle (Warp +Fill), degrees	Breaking Strength Retained After Scorch Test, percent	Reflectance Readings After 10 Home Washes With Bleach
As in A	9.5	284	98	82
As in B	11	263	89	81
As in B	7	238		80
Untreated fabric (control)		181		81

We claim:

1. A process for treating a cellulosic textile material whereby said material is rendered wrinkle-resistant and resistant to damaging effects from hypochlorite bleaching agents comprising impregnating said cellulosic textile material to a wet pickup of about from 70% to 80% with an aqueous solution containing from about 7% to about 12% by weight of the reaction product of formaldehyde and a substituted melamine selected from the group consisting of N,N'-dimethyl-N'',N''-bis(2-hydroxyethyl)-melamine and N,N',N''-trimethylmelamine, and from about 0.5% to about 5% by weight of an acidic catalyst, drying the impregnated material, and then curing it at a temperature of about 160° C.

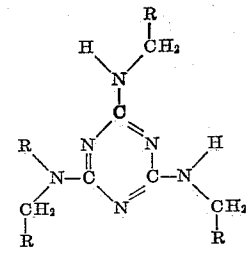
2. The process of claim 1 in which the substituted melamine is N,N'-dimethyl-N'',N''-bis(2-hydroxyethyl) melamine.

3. The process of claim 1 in which the substituted melamine is N,N',N''-trimethylamine.

4. A process for treating a cellulosic textile material whereby said material is rendered wrinkle-resistant and resistant to damaging effects from hypochlorite bleaching agents comprising impregnating said cellulosic textile material to a wet pickup of about from 70% to 80% with an aqueous solution comprising from about 3% to about 6% by weight of the reaction product of formaldehyde and N,N'-dimethyl-N'',N''-bis(2-hydroxyethyl) melamine, from about 5% to about 8% by weight of dimethylolurea, and from about 0.5% to about 5% by weight of an acidic catalyst, said reaction product and dimethylolurea being present in amounts totalling about 11% by weight of said aqueous solution, drying the impregnated material, and then curing it at a temperature of about 160° C.

5. A process comprising impregnating a cellulosic textile material to a wet pickup of about from 70% to 80% with an aqueous solution containing about from 5% to

15% by weight of the reaction product of formaldehyde and a substituted melamine of the formula



wherein R is a member of the group consisting of H, an alkyl group of from 1 to 3 carbon atoms, and a substituted alkyl group of from 1 to 3 carbon atoms in which the substituent is positioned in any position on the carbon chain other than the alpha position, and from 0.5% to 5% by weight of an acidic catalyst, drying the thus impregnated material, and curing the dried, impregnated material at a temperature of about from 130° C. to 160° C. to produce a cured cellulosic material which is wrinkle-resistant and resistant to damaging effects of hypochlorite bleaching agents.

6. The process of claim 5 wherein the acidic catalyst is magnesium chloride.

7. The process of claim 5 wherein the acidic catalyst is zinc nitrate.

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