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2,901,463

COMPOSITIONS, TEXTILES TREATED THEREWITH AND PROCESSES FOR THE TREATMENT THEREOF

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This invention relates to compositions for the treatment of textile materials, and it is particularly concerned with the treatment of textile materials of cellulosic type to improve their characteristics, especially to render the fabrics resistant to crushing and to shrinkage on laundering. It is also concerned with the treated fabrics thereby obtained and with methods for treating fabrics with the novel compositions.

Heretofore, condensates of formaldehyde with melamine, urea, and cyclic urea derivatives, such as N,N'-ethyleneurea and N,N'-trimethyleneurea have been applied to cellulosic fabrics, such as cotton, for the purpose of imparting crush-resistance and reduced shrinkage on laundering. However, fabrics treated with these condensates pick up chlorine during bleaching operations using chlorine, such as those using it in the form of a hypochlorite. On ironing the fabrics that have been bleached in this manner, severe discoloration and/or loss in tensile and/or tear strengths have generally resulted. In those cases where severe discoloration is encountered, the treatment with these condensates is unsuitable when a white fabric is ultimately desired. In some cases, as much as 90% loss in strength is encountered as a result of the action of heat as in ironing, on fabrics treated with these condensates and bleached with chlorine. The presence on a fabric of a thermoset condensate of formaldehyde with melamine frequently gives rise to some discoloration of the fabric on the mere treatment with a hypochlorite bleach, unless care is taken to avoid excess chlorine and elevated temperatures. Ironing in such cases serves to aggravate the discoloration.

It has also been suggested, for crease-proofing cellulosic fabrics, to apply polymethylol-tetrahydro-s-triazones substituted in the 5-position, such as dimethylol-5-methyl-tetrahydro-s-triazone-2. However, fabrics treated therewith develop an unpleasant odor unless extreme care is taken to wash out by-products after the curing thereof on the fabric. In addition, the fabrics treated therewith frequently show discoloration on heating or ironing whether or not the fabrics have been treated with chlorine before the heating or ironing is effected. The fabric leaves the curing stage in distinctly yellow condition. Heating after chlorination aggravates this yellowing severely.

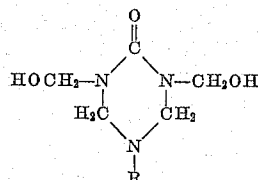
It has been suggested in U.S. Patent 2,690,404 to combine a melamine-formaldehyde condensate with a dimethylol ethyleneurea in an effort to reduce the discoloration and loss of strength of cellulosic fabrics treated with such condensates on bleaching and ironing. However, the improvement obtained by this combination of condensates is generally relatively insignificant and the proportions in which the two condensates may be employed are quite narrow in range.

In accordance with the present invention, it has been discovered that cellulosic fabrics, such as cotton and the like, can be treated, to effect crease-proofing and so on without encountering serious odors, discoloration, and loss of strength, with an aqueous solution containing in

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certain proportions (1) a condensate of formaldehyde with melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea (which will be termed hereinafter Component A), with (2) a compound of Formula I following (which will be termed Component B):

I



where R is selected from the group consisting of 2-hydroxyethyl, 2-methyl-2-hydroxyethyl, and alkyl groups having 1 to 4 carbon atoms.

It has been found in accordance with the invention that the incorporation of at least 25 mole percent and not over 75 mole percent of a compound of Formula I (Component B) in a mixture comprising such compound and a condensate of formaldehyde with melamine, urea, N,N'-ethyleneurea and N,N'-trimethyleneurea (Component A) overcomes the disadvantages of discoloration and loss in strength of fabrics treated therewith that are normally encountered on heating after chlorination when any of these formaldehyde condensates are applied alone in accordance with the prior art. In addition, the odor normally associated with fabrics on which a triazone condensate has been cured is minimized. When less than 25 mole percent of the triazone condensate is employed, the improvements in respect to discoloration and loss of tensile strength are inappreciable, and when more than 75 mole percent is employed, the benefits in these factors are substantially reduced. For most purposes, from the standpoint of cost, efficiency, freedom from discoloration, and low tensile loss on ironing or heating after chlorination, it is preferred to use from 30 to 50 mole percent of Component B and from 70 to 50 mole percent respectively of Component A.

Examples of the tetrahydro-s-triazones that may be employed include dimethylol-5-methyl-tetrahydro-s-triazone-2, dimethylol-5-hydroxymethyl-tetrahydro-s-triazone-2, dimethylol-5-ethyl-tetrahydro-s-triazone-2, dimethylol-5-n-propyl-tetrahydro-s-triazone-2, dimethylol-5-isopropyl-tetrahydro-s-triazone-2, dimethylol-5-t-butyl-tetrahydro-s-triazone-2, dimethylol-5-n-butyl-tetrahydro-s-triazone-2, dimethylol-5-sec-butyl-tetrahydro-s-triazone-2. These methylol derivatives may be termed a dimethylol-tetrahydro-s-triazone-2, and the condensate used may include the specific clear-cut compounds named or it may include a mixture of compounds containing the dimethylol compound. In any event, the formaldehyde condensates of this type may be obtained in known manner, such as by the condensation of a mixture of from 2 to 5 moles and preferably at least 2.5 moles of formaldehyde per mole of the tetrahydro-triazone in an aqueous solution thereof. The condensation may be effected at a pH of 6 to 8 at a temperature of 30 to 120° C. and preferably between about 80° to 210° C. The extent of condensation and the completion of the desired reaction may be controlled by varying the time and temperature.

As Component A, any water-soluble condensates of formaldehyde with melamine, urea, N,N'-ethyleneurea or N,N'-trimethyleneurea may be employed. Examples of specific compounds that may be used include dimethylol-urea, trimethylolmelamine, dimethylol-N,N'-ethyleneurea, and dimethylol-N,N'-trimethyleneurea. In addition, the alkylated derivatives of these polymethylol condensates obtained from the lower alcohols from methyl through

butyl may be employed. Examples include dimethoxymethylurea, diethoxymethylurea, dimethoxymethyl-N,N'-ethyleneurea, and so on. Again, it should be noted that the condensates employed as Component A may be fairly sharply defined compounds including those just named as well as others, or it may comprise mixtures of compounds of varying degrees of substitution wherein the number of methylol groups or alkoxyethyl groups may be different in the several compounds within the mixture.

The aqueous solution of the water-soluble condensates, including Component A and Component B, may contain such condensates in a concentration in about 2% to 25% or more, based on total condensate solids. The particular concentration applied in any given instance may depend on the purpose for which the condensate mixture is applied and on the particular substrate or fabric to which it is applied. In the case of cotton, the concentration is preferably from 2% to 12%, whereas in application to rayon the concentration is preferably 5% to 20%, when the purpose of the application is to impart crease-resistance, crush-resistance, or shrinkage stabilization.

While it is generally unnecessary, Component A and Component B may be reacted together provided any such reaction leaves the final condensate in a water-soluble condition. However, for most purposes, it is preferred not to co-react these components.

The solution containing the mixture of condensates (Component A and Component B) or the co-reacted condensates is stable when subjected to ordinary conditions of storage and can be sold, shipped, and stored as such. Shortly before use, the acidic catalyst may be added, if desired, as pointed out hereinafter.

An acidic catalyst is applied to the fabric either simultaneously with the condensates or before or after the mixture of condensates is applied. Preferably the acidic catalyst is dissolved in the aqueous solution of the mixture of condensates. Suitable catalysts include ammonium phosphate, ammonium thiocyanate, hydrochloric or other acid salts of a hydroxy aliphatic amine including 2-methyl-2-amino-1-propanol, 2-methyl-2-amino-1,3-propanediol, tris(hydroxymethyl)aminomethane, 2-phenyl-2-amino-1-propanol, 2-methyl-2-amino-1-pentanol, 2-aminobutanol, triethanolamine, 2-amino-2-ethyl-1-butanol, also ammonium chloride, pyridine hydrochloride, benzyltrimethylammonium oxalate. The catalyst is generally introduced into the aqueous solution of the condensates at a concentration of about 1/2% to 2% and preferably approximately 1%.

The compositions of the present invention may be applied to fibers, filaments, yarns, or fabrics of cellulosic type and especially those of cotton or rayon for various purposes. For example, they may be applied simply to modify the feel or texture of the surface of the fabrics. When applied in greater quantities, the condensates of the present invention may be used to stiffen the fabrics and to make them wrinkle-resistant, crush-resistant and crease-resistant. The application of increasing amounts of the condensates serves to provide proportionately increased reduction in shrinkage of the treated fabric on laundering, and when about 3% to 8% by weight of the condensate, based on the weight of the fabric, is applied, the cellulosic fabric is generally substantially stabilized against shrinkage on laundering. The application of the condensates of the present invention may be employed for the purpose of aiding embossing operations. They may also be applied to fabrics as part of a process for their conversion to plissé fabrics.

The aqueous solution of the condensates may be applied by spraying, brushing, dipping, as in padding, or by roller-coating. After the application, excess may be removed, as by squeezing or squeegeeing. The treated fabric is then dried, such as by air-drying at room temperature or by the treatment with heated air up to temperatures of about 212° F.

After the fabric has been dried, the condensate mixture

is baked or cured on the fabric at a temperature of about 220° to 450° F. or higher, depending on the particular substrate. The time may be varied generally in inverse proportions to the temperature. For example, the time may vary from about five seconds to half an hour. A time of 30 seconds at 400° F. is quite practical and a time of 15 to 30 minutes at 220° F. is generally satisfactory. The baking operation may simply be a continuation of the drying operation so that drying and curing may be effected in essentially a one-stage procedure.

The drying and/or the baking may be effected by any suitable means for applying the heat, such as by the application of heated air currents, by infra-red radiation or by high frequency electric induction.

In the following examples which are illustrative of the invention, the parts given are by weight unless otherwise noted: The A.A.T.C.C. chlorination test referred to in the examples involves the treatment with a hypochlorite solution containing 0.25% available chlorine at a temperature of 77° F.±2° F. for 15 minutes with intermittent stirring. This treatment is followed by rinses in six fresh water baths at 70° to 80° F. with a squeeze between rinses and drying in air at room temperature. The drying is followed by conditioning for at least four hours at 70° F. and 65% relative humidity. The percentage loss in tensile strength referred to hereinbelow is calculated by the formula

$$100 \left(\frac{t_c - t_{cs}}{t_c} \right)$$

where t_c is the tensile strength after chlorination only and t_{cs} is the tensile strength after both chlorination and ironing (or scorch test).

EXAMPLE 1

(a) A solution is made up in water containing 4.5% of dimethylol-5-methyl-tetrahydro-s-triazone-2 and 1.25% of dimethylol-N,N'-ethyleneurea and 0.5% of ammonium chloride. A bleached cotton fabric is padded through this solution. After draining excess and drying at 240° F. for five minutes, the fabric is cured at 300° F. for ten minutes. Chlorination is carried out under A.A.T.C.C. conditions above and the fabric is ironed at 365° F.±2° F. for 30 seconds (the standard A.A.T.C.C. scorch test). The ironed fabric is conditioned at 70° F. and 65% relative humidity for at least four hours before testing for strength.

(b) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is reduced to 3% and the concentration of dimethylol-N,N'-ethyleneurea is increased to 2.5%.

(c) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is reduced to 1.5% and the concentration of dimethylol-N,N'-ethyleneurea is increased to 3.75%.

(d) The procedure of part (a) here is repeated except that the concentration of the triazone derivative is reduced to zero and the concentration of dimethylol-N,N'-ethyleneurea is increased to 5.0%.

(e) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is increased to 6% and the concentration of dimethylol-N,N'-ethyleneurea is reduced to zero.

In each of parts (a) to (d) inclusive of Example 1, the total concentration of formaldehyde condensate is equivalent in molarity to that in each other part. The mole ratio of the Component A to Component B in part (a) is 1:3, in part (b) is 1:1, and in part (c) is 3:1.

Table I shows the comparative results of the procedures described in parts (a) to (e) inclusive of Example 1. In the crease-recovery test, W is the angle of return in the warp, and F is the angle of return in the fill as measured by the Shirley crease-recovery test.

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Table I

Example 1	Shrinkage (area) Percent	Crease- Recovery, W+F/2	Percent Tensile Loss After Chlorination and Ironing
(a)-----	3.7	106	29
(b)-----	3.5	119	35
(c)-----	2.5	105	21
(d)-----	2.5	110	90
(e)-----	2.5	114	29

EXAMPLE 2

(a) A solution is made up in water containing 4.5% of dimethylol-5-methyl-tetrahydro-s-triazone-2 and 1.5% of a low molecular weight condensate of methanol, formaldehyde, and urea comprising largely dimethoxymethylurea and 0.5% of ammonium chloride. A bleached cotton fabric is padded through this solution. After draining excess and drying at 240° F. for five minutes, the fabric is cured at 300° F. for ten minutes. Chlorination is carried out under A.A.T.C.C. conditions above and the fabric is ironed at 365° F.±2° F. for 30 seconds (the standard A.A.T.C.C. scorch test). The ironed fabric is conditioned at 70° F. and 65% relative humidity for at least four hours before testing for strength.

(b) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is reduced to 3.0% and the concentration of the urea condensate is increased to 3.0%.

(c) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is reduced to 1.5% and the concentration of the urea condensate is increased to 4.5%.

(d) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is reduced to zero and the concentration of the urea condensate is increased to 6.0%.

(e) The procedure of part (a) hereof is repeated except that the concentration of the triazone derivative is increased to 6.0% and the concentration of the urea condensate is reduced to zero.

In each of parts (a) to (e) inclusive of Example 2, the total concentration of formaldehyde condensate is equivalent in molarity to that in each other example. The mole ratio of the Component A to Component B in part (a) is 1:3, in part (b) is 1:1, and in part (c) is 3:1.

Table II shows the comparative results of the procedures described in parts (a) to (e) inclusive of Example 2.

Table II

Example 2	Shrinkage (area) Percent	Crease- Recovery, W+F/2	After Chlorination and Ironing	
			Percent Ten. Loss	Discolora- tion
(a)-----	2.8	108	12	None.
(b)-----	3.3	104	25	None.
(c)-----	3.4	118	53	Slight.
(d)-----	2.5	115	84	Yellow.
(e)-----	2.8	120	25	None.

EXAMPLE 3

The procedure of Example 1 (a) is followed except that the triazone is replaced with 2.0% of dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2 and the concentration of the dimethylol-N,N'-ethyleneurea is increased to 3.75%. The discoloration and loss in tensile strength after chlorination and ironing is comparable to those of Example 1(a).

EXAMPLE 4

The procedure of Example 2(a) is repeated except that the concentration of the triazone derivative is 3.0% and the condensate is replaced with 3.0% of diethoxy-

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methylurea. After chlorination and ironing, the fabric exhibits only a slight discoloration, and the tensile loss is comparable to that of Example 1(a).

EXAMPLE 5

The procedure of Example 1(a) is repeated substituting for the triazone derivative 3.4% of dimethylol-5-ethyl-tetrahydro-s-triazone-2 and for the ethyleneurea derivative 3.0% of dimethylol - N,N' - trimethyleneurea. After chlorination and ironing, only a slight discoloration is evident and the tensile loss is comparable to that obtained in Example 1(a).

EXAMPLE 6

The procedures of Examples 1(a) and 1(c) are repeated on a bleached rayon fabric. In each case, even less evidence of discoloration is obtained and less tensile loss is caused by the chlorination and ironing procedures than is obtained in Examples 1(a) and (c) on the cotton.

EXAMPLE 7

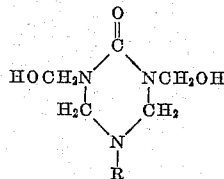
The procedure of Example 1(a) is repeated using 2.5% of dimethylol-5-(β-methyl-β-hydroxyethyl)-tetrahydro-s-triazone-2 and replacing the ethyleneurea with 3.5% of trimethylolmelamine. The crease-proofed fabric, after chlorination and ironing exhibits a slight discoloration and a loss of tensile strength comparable to that obtained in Example 1(a).

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. A composition comprising an aqueous solution of a mixture of 25 to 75 mole percent of a compound of Formula I:

I



where R is selected from the group consisting of 2-hydroxyethyl, 2-methyl-2-hydroxyethyl, and alkyl groups having 1 to 4 carbon atoms, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

2. A composition comprising an aqueous solution containing a mixture of 25 to 75 mole percent of dimethylol-5-methyl-tetrahydro-s-triazone-2, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

3. A composition comprising an aqueous solution containing a mixture of 25 to 75 mole percent of dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

4. A composition comprising an aqueous solution containing a mixture of 25 to 75 mole percent of dimethylol-5-ethyltetrahydro-s-triazone-2, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

5. A composition comprising an aqueous solution containing a mixture of 25 to 75 mole percent of dimethylol-5-(β-methyl-β-hydroxyethyl)-tetrahydro-s-triazone-2, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

6. A composition comprising an aqueous solution of a mixture of 25 to 75 mole percent of dimethylol-5-methyl-tetrahydro-s-triazone-2 and 75 to 25 mole percent of dimethylol-N,N'-ethyleneurea.

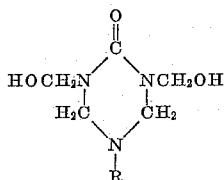
7. A composition comprising an aqueous solution of a mixture of 30 to 50 mole percent of dimethylol-5-meth-

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yl-tetrahydro-s-triazone-2 and 70 to 50 mole percent of dimethylol-N,N'-ethyleneurea.

8. An article of manufacture comprising a cellulosic textile fabric modified by a reaction product of a mixture of 25 to 75 mole percent of a compound of Formula I:

I

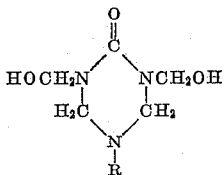


where R is selected from the group consisting of 2-hydroxyethyl, 2-methyl-2-hydroxyethyl, and alkyl groups having 1 to 4 carbon atoms, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea.

9. An article of manufacture comprising a cellulosic textile fabric modified by a reaction product of a mixture of 25 to 75 mole percent of dimethylol-5-methyl-tetrahydro-s-triazone-2 and 75 to 25 mole percent respectively of dimethylol-N,N'-ethyleneurea.

10. A process for treating a fabric comprising applying to a cellulosic textile fabric an aqueous solution of a mixture of 25 to 75 mole percent of a compound of Formula I:

I



where R is selected from the group consisting of 2-hydroxyethyl, 2-methyl-2-hydroxyethyl, and alkyl groups having 1 to 4 carbon atoms, and 75 to 25 mole percent respectively of a water-soluble condensate of formaldehyde with N,N'-ethyleneurea, applying an acidic catalyst to the fabric, and drying and curing the condensates at

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a temperature of 220° F. to 450° F. on the treated fabric.

11. A process for treating a fabric comprising applying to a cellulosic textile fabric an aqueous solution containing 2% to 25% of a mixture of condensates comprising 25 to 75 moles percent of dimethylol-5-methyl-tetrahydro-s-triazone-2 and 75 to 25 mole percent respectively of dimethylol-N,N'-ethyleneurea, applying an acidic catalyst to the fabric, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

12. A composition comprising an aqueous solution containing a mixture of 25 to 75 mole percent of dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2, and 75 to 25 mole percent of dimethylol-N,N'-ethyleneurea.

13. An article of manufacture comprising a cellulosic textile fabric modified by a reaction product of a mixture of 25 to 75 mole percent of dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2, and 75 to 25 mole percent of dimethylol-N,N'-ethyleneurea.

14. A process for treating a fabric comprising applying to a cellulosic textile fabric an aqueous solution containing 2% to 25% of a mixture of condensates comprising 25 to 75 mole percent of dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2 and 75 to 25 mole percent respectively of dimethylol-N,N'-ethyleneurea, applying an acidic catalyst to the fabric, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

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