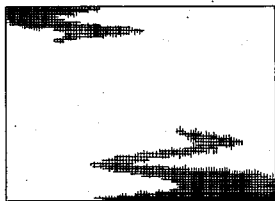


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M. D. HURWITZ
COMPOSITIONS FOR THE TREATMENT OF TEXTILES, THE
TEXTILES OBTAINED AND PROCESS FOR THE
TREATMENT THEREOF
Filed June 21, 1955

2,833,674



Textile material rendered crush-proof and shrink-proof by impregnation with a mixture of (1) polymethylol derivative of an N,N-disubstituted melamine and (2) a condensate of formaldehyde with melamine, urea, N,N'-ethyleneurea, or N,N'-trimethyleneurea.

INVENTOR

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COMPOSITIONS FOR THE TREATMENT OF TEXTILES, THE TEXTILES OBTAINED AND PROCESSES FOR THE TREATMENT THEREOF

Application June 21, 1955, Serial No. 517,061

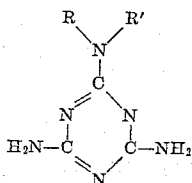
20 Claims. (Cl. 117—139.4)

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, especially when a white fabric is 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 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.

The single figure of the drawing is a diagrammatic face view of a textile product obtained in accordance with the present invention.

In accordance with the present invention, it has been discovered that certain N,N-disubstituted melamines of the Formula I:



where R and R' are each selected individually from the group consisting of allyl, hydroxyethyl, and alkyl groups having 1 to 3 carbon atoms, when applied to cellulosic fabrics, such as cotton and the like, have an extraordinarily slight yellowing tendency on chlorination and a very low loss of strength on ironing after chlorination. However, the polymethylol condensates of the compounds of Formula I have the disadvantages of high cost and limited solubility in water. Because of the latter characteristics, it is difficult to get sufficient concentration into an aqueous solution of the condensate to get an adequate amount of the condensate applied to the fabric for certain purposes, especially for such purposes as crease-proofing, crush-proofing, and stabilization against shrinkage on laundering.

However, it has been found in accordance with the invention that the incorporation of as little as five mole percent of a formaldehyde condensate of a compound of Formula I in a mixture comprising such condensate and a condensate of formaldehyde with melamine, urea, N,N'-ethyleneurea and N,N'-trimethyleneurea overcomes the disadvantages of discoloration and loss in strength of fabrics treated therewith that are normally encountered on heating after chlorination when a formaldehyde condensate of the last-mentioned type is applied alone in accordance with the prior art. For convenience of reference hereinafter, the formaldehyde condensate of melamine, urea or one of the cyclic ureas mentioned will be referred to as component A, and the formaldehyde condensate of a compound of Formula I hereinabove will be referred to as component B. If desired, component B may be used in greater than five mole percent proportion, but for practical efficiency in crease-proofing, the maximum proportion thereof is about 85 mole percent. 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 20 to 50 mole percent of component B and from 80 to 50 mole percent respectively of component A.

Examples of the N,N-disubstituted melamines that may be employed include N,N-dimethylmelamine, N,N-diethylmelamine, N,N-di-n-propylmelamine, N,N-diisopropylmelamine, N,N-dihydroxyethylmelamine, N,N-diallylmelamine. The methylol derivatives of any of these compounds of Formula I may be termed a polymethylol N,N-disubstituted melamine and the condensate used may include specific clear-cut compounds, such as trimethylol-N,N-dimethylmelamine, or it may include a mixture of compounds containing from 1 to 4 methylol groups. In any event, the formaldehyde condensates of this type may be obtained by the condensation of a mixture of from 2 to 5 moles and preferably at least 4 moles of formaldehyde per mole of the N,N-disubstituted melamine 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 condensate 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 di-

methoxymethylurea, 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 alkoxymethyl 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-amino-butanol, triethanolamine, 2-amino-2-ethyl-1-butanol, also ammonium chloride, pyridine hydrochloride, benzylidimethylamine 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 7% 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 also may 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 squeeze-rolling. 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. $\pm 2^\circ$ 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 6.3% of trimethylol-N,N-dimethylmelamine and 1.25% of dimethylol-N,N'-ethyleneurea and 1% of ammonium chloride. A bleached cotton fabric is passed 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 400° F. for 30 seconds. 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 trimethylol-N,N-dimethylmelamine is reduced to 4.2% 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 trimethylol-N,N-dimethylmelamine is reduced to 2.1% and the concentration of dimethylol-N,N'-ethyleneurea is increased to 3.75%.

(d) The procedure of part (a) hereof is repeated except that the concentration of the trimethylol-N,N-dimethylmelamine 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 trimethylol-N,N-dimethylmelamine is increased to 8.4% and the concentration of dimethylol-N,N'-ethyleneurea is reduced to zero.

In each of parts (a) to (e) 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.

Table 1

Example 1	Shrinkage (area) per- cent	Crease- Recovery W + F/2	After Chlorination and Ironing	
			Percent Ten. Loss	Discolora- tion
(a)-----	2.7	111	12	Slight.
(b)-----	3.0	104	16	Do.
(c)-----	2.8	113	16	Do.
(d)-----	2.5	110	90	Brown.
(e)-----	5.7	94	30	Slight.

EXAMPLE 2

The procedure of Example 1(a) is followed except that the trimethylol-N,N-dimethylmelamine is replaced with 2.6% of trimethylol-N,N-dipropylmelamine 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 3

The procedure of Example 1(a) is repeated except that the concentration of the trimethylol-N,N-dimethylmelamine is 4.2% and the ethyleneurea condensate is replaced with 2.5% of dimethoxymethylurea. After chlorination and ironing, the fabric exhibits only a slight discoloration, and the tensile loss is comparable to that of Example 1(a).

EXAMPLE 4

The procedure of Example 1(a) is repeated substituting for the trimethylol-N,N-dimethylmelamine 4.6% of trimethylol-N,N-diethylmelamine and 2.75% 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 5

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.

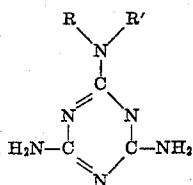
EXAMPLE 6

The procedure of Example 1(a) is repeated using 2.1% of trimethylol-N,N-dimethylmelamine 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 5 to 85 mole percent of a polymethylol derivative of a compound of Formula I:



where R and R' are each selected individually from the group consisting of allyl, hydroxyethyl, and alkyl having 1 to 3 carbon atoms, and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

2. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-diethylmelamine and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

3. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dihydroxyethylmelamine and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

4. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dipropylmelamine and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

5. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dimethylmelamine and 95 to 15 mole percent of dimethylol-N,N'-ethyleneurea.

6. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dimethylmelamine and 95 to 15 mole percent of a formaldehyde condensate of melamine.

7. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dimethylmelamine and 95 to 15 mole percent of dimethoxymethylurea.

8. A composition comprising an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol-N,N-dimethylmelamine and 95 to 15 mole percent of dimethylol-N,N'-trimethyleneurea.

9. A composition comprising an aqueous solution of a mixture of 20 to 50 mole percent of a polymethylol derivative of a compound of Formula I as defined in claim 1 and 80 to 50 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

10. A composition comprising an aqueous solution of a mixture of 20 to 50 mole percent of a trimethylol-N,N-dimethylmelamine and 70 to 50 mole percent of dimethylol-N,N'-ethyleneurea.

11. An article of manufacture comprising a cellulosic fabric modified by a reaction product of a mixture of 5 to 85 mole percent of a polymethylol derivative of a compound of Formula I as defined in claim 1 and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea.

12. An article of manufacture comprising a cellulosic fabric modified by a reaction product of a mixture of 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of dimethylol-N,N'-ethyleneurea.

13. An article of manufacture comprising a cellulosic fabric modified by a reaction product of a mixture of 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of a formaldehyde condensate of melamine.

14. An article of manufacture comprising a cellulosic fabric modified by a reaction product of a mixture of 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of dimethoxymethylurea.

15. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol derivative of a compound of Formula I as defined in claim 1 and 95 to 15 mole percent respectively of at least one condensate of

formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea, and drying and curing the condensates on the treated fabric.

16. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of 5 to 85 mole percent of a polymethylol derivative of a compound of Formula I as defined in claim 1 and 95 to 15 mole percent respectively of at least one condensate of formaldehyde with a member selected from the group consisting of melamine, urea, N,N'-ethyleneurea, and N,N'-trimethyleneurea, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

17. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of condensates comprising 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of dimethylol-N,N'-ethyleneurea, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

18. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of condensates comprising 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole

percent respectively of a formaldehyde condensate of melamine, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

19. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of condensates comprising 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of dimethoxymethylurea, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

20. A process for treating a fabric comprising applying to a cellulosic fabric an aqueous solution of a mixture of condensates comprising 5 to 85 mole percent of trimethylol-N,N-dimethylmelamine and 95 to 15 mole percent respectively of dimethylol-N,N'-trimethyleneurea, and drying and curing the condensates on the treated fabric at a temperature of 220° F. to 450° F.

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