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AQUEOUS DISPERSION OF AN AMINOPLAST AND AN EPOXY COMPOUND

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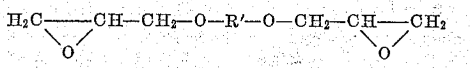
This invention relates to compositions for the treatment of textile materials, and it is particularly concerned with the treatment of textile materials of wool and cellulosic type to improve their characteristics, especially to render the fabrics resistant to crushing and to shrinkage on laundering. 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 their derivatives including cyclic urea derivatives, such as N,N'-ethyleneurea and methylol melamines and ureas and their alkylated derivatives and also N,N'-trimethyleneurea, have been applied to wool and 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.

The Suen patent, No. 2,730,427, discloses the treatment of textile materials for imparting resistance to shrinkage and creasing with certain diglycidyl ethers having the formula:



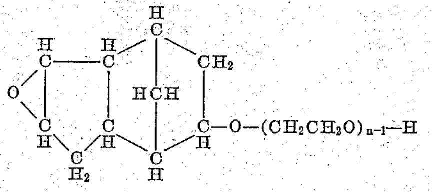
$$\underbrace{H_2C\text{——}CH}_{O}-CH_2-O-R'-O-CH_2-\underbrace{CH\text{——}CH_2}_{O}$$

wherein R' is an alkylene group of from 2 to 6 carbon atoms. United States Patent 2,752,269 discloses the use of other types of glycidyl ploymers and condensates such as those obtained by condensation of glycerol and epichlorohydrin and polymers of allyl glycidyl ether. The use of the glycidyl compounds of these patents, however, is quite expensive and comparatively inefficient with respect to certain nitrogen-containing condensates, and especially those of formaldehyde with N,N'-ethyleneurea and melamine. It is generally required that about three times as much of one of these glycidyl compounds must be applied to a cotton fabric to obtain crush proofing action comparable to that obtained with a given amount of the nitrogen-containing aminoplasts just mentioned. Generally, also the diethers are two or three times as expensive as these aminoplasts and as much as fifteen times the cost of the simpler urea-formaldehyde condensate.

U.S. Patent 2,794,754 discloses the use of a mixture of an aminoplast condensate with a resin-forming compound containing a plurality of vic-epoxy groups.

It has been found in accordance with the invention that the incorporation of a minor proportion of certain water-soluble or easily water-dispersible mono-(vic-epoxy) alcohols in aqueous solutions of water-soluble aminoplast condensates selected from the group consisting of condensates of formaldehyde with aminotriazines, certain triazones, N,N'-trimethyleneurea, and N,N'-ethyleneurea, and their alkylated derivatives serves to eliminate, or reduce to within practical limits, the chlorine damage that would otherwise occur as a result of the treatment with such aminoplasts. Surprisingly, the improvement is accomplished without the necessity to apply excessive quantities of the shrink-proofing or crease-proofing composition in spite of the fact that the mono-epoxy alcohol is incapable of crease-proofing cellulosic fabrics when applied without an aminoplast under conditions similar to those under which the mixture is applied.

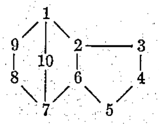
The monoepoxy alcohols of the present invention contain an epoxy group which is non-reactive toward cellulose whereas the vic-epoxy groups of the polyepoxides of the previously mentioned U.S. Patents 2,730,427, 2,752,269, and 2,794,754 do in fact react with cellulose. The mono-epoxy alcohols of the present invention are of the formula



(I)

wherein n is an integer having a value of 1 to 5. The preparation of these compounds is described in copending application for U.S. patent Ser. No. 13,986, filed March 10, 1960, now U.S. Patent 3,042,686, and the entire disclosure of the preparation in such application is incorporated herein by reference.

These compounds may be considered to be substituted tricyclodecanes and their nomenclature is herein based on the following system in which each carbon atom of the compound is represented by its corresponding number.



The unsubstituted hydrocarbon from which the compounds may be considered to be derived then should be designated tricyclo [5,2,1,$0^{2,6}$] decane.

The simplest of the compounds of Formula I in which n is 1 is accordingly designated 3,4-epoxy-8-hydroxy tricyclo [5,2,1,$0^{2,6}$] decane. It may also be simply called epoxy dicyclopentyl alcohol.

When n is 2, the compound may be designated as 3,4-epoxy-8-(β-hydroxyethoxy)-tricyclo [5,2,1,$0^{2,6}$] decane or more simply as the ethylene glycol monoether of 3,4-epoxy-8-hydroxy-tricyclo [5,2,1,$0^{2,6}$] decane.

The following table lists the compounds of the invention as compounds A, B, C, D, and E respectively depending on the value of n.

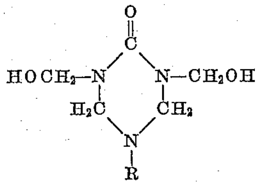
TABLE A

Compound A ($n=1$)	3,4-epoxy-8-hydroxy - tricyclo [5,2,1,$0^{2,6}$] decane.
Compound B ($n=2$)	The ethylene glycol monoether of compound A.
Compound C ($n=3$)	The diethylene glycol monoether of compound A.
Compound D ($n=4$)	The triethylene glycol monoether of compound A.
Compound E ($n=5$)	The tetraethylene glycol monoether of compound A.

A mixture of two or more of the compounds may be used so that the monoepoxy alcohol may be represented by Formula I in which *n* may either be an integral number or a mixed number having a value from 1 to 5.

The aminoplast constitutes the major or predominant part of, and is apparently the effective component of, the shrink-proofing, crease-proofing or crush-proofing compositions of the invention. The monoepoxy alcohol component constitutes from about 5% to about 40%, and preferably 10 to 20%, by weight of the total weight of aminoplast and monoepoxy alcohol. For most purposes, from the standpoint of cost, efficiency, optimum freedom from discoloration, and minimum tensile loss on ironing or heating after chlorination, it is preferred to use from 5% to 20% by weight of monoepoxy alcohol and 95% to 80% by weight respectively of aminoplast.

In accordance with the present invention, the aminoplast compositions with which the invention is concerned are water-soluble in character and include the simple condensates of N,N'-ethyleneurea, certain triazones described hereinafter and aminotriazines, such as melamine or its derivatives N-(C_1–C_4)alkylmelamine, N,N-di(C_1–C_4)alkylmelamines, and N,N'di(C_1–C_4)alkylmelamines, with formaldehyde as well as the alkylated methylol derivatives thereof, in which the alkylation is effected with lower alcohols from 1 to 3 carbons or with small proportions of higher alcohols, such as the butyl alcohols or with mixtures of such higher alcohols with the lower alcohols, so that in any event the akylated methylol derivatives are water-soluble or self-dispersible readily in water. Any water-soluble condensate of formaldehyde with melamine, N,N'-ethyleneurea, or N,N'-trimethyleneurea may be employed. Examples of specific compounds that may be used include trimethylolmelamine, dimethylol-N,N'-ethyleneurea, and dimethylol-N,N'-trimethyleneurea. The triazones that may be used include the polymethylol tetrahydro-s-triazones substituted in the 5-position by an alkyl or hydroxyalkyl group. These triazones have the Formula II:



(II)

where R is selected from the group consisting of 2-hydroxyethyl, 2-hydroxypropyl, and alkyl groups having 1 to 4 carbon atoms. In addition, the alkylated derivatives of these polymethylol condensates obtained from the lower alcohols from methyl through butyl may be employed. Examples include dimethoxymethyl-N,N'-dimethylmelamine, dimethoxymethyl-N,N'-ethyleneurea, dimethoxymethyl - 5 - (β - hydroxymethyl)tetrahydro - s-triazone-2, 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. For the most efficient action, the aminoplasts derived from N,N'-ethyleneurea and from melamine are preferred.

The aqueous solution of the water-dispersible components, including the aminoplast and the monoepoxy alcohol, may contain each of such components in a concentration in about 2% to 25% or more by weight. The particular concentration applied in any given instance may depend on the purpose for which the 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. In the case of wool, the concentration is preferably from 5% to 15%. While it is generally unnecessary, the aminoplast condensate and the monoepoxy alcohol 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 the aminoplast and the monoepoxy alcohol components or the co-reacted components is stable when subjected to ordinary conditions of storage and can be sold, shipped and stored as such. Shortly before use, an acidic catalyst may be added, if desired, as pointed out hereinafter.

An acidic catalyst for catalyzing the condensation of the aminoplast and the reaction of the cellulose with the hydroxyl group of the monoepoxy alcohol is applied to the fabric either simultaneously with the aminoplast condensate and monoepoxy alcohol or before or after the mixture thereof is applied. Preferably the acidic catalyst is dissolved in the aqueous solution of the mixture of aminoplast condensate and monoepoxy alcohol. Suitable catalysts include ammonium phosphate, ammonium fluoborate, 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 - propandiol, tris-(hydroxymethyl)aminomethane, 2-phenyl-2-amino-1-propanol, 2-methyl-2-amino-1-pentanol, 2-aminobutanol, triethanolamine, 2-amino-2-ethyl-1-butanol, and also ammonium chloride, pyridine hydrochloride, aluminum chloride, benzyldimethylammonium oxalate, magnesium perchlorate, zinc silicofluoride, zinc perchlorate, magnesium thiocyanate, zinc thiocyanate, zinc fluoborate, zinc nitrate, boron fluoride, and especially the boron fluoride ether complex of the boron fluoride water complex, hydrogen fluoride, hydrochloric acid, ammonium chloride, ammonium acid fluoride, phosphoric acid, oxalic acid, tartaric acid, citric acid, sulfuric acid and sodium bisulfate. The preferred catalysts which seem to be outstanding in their efficiency of action and freedom from detrimental effect on fabrics, especially with cellulosic types of fabrics, are the zinc salts such as zinc fluoborate and zinc nitrate. The catalyst is generally introduced into the aqueous solution of the condensates at a concentration of about 0.1 to 2% and preferably approximately 1%. The catalyst may be present in an amount from about ½ to about 25% on the total weight of aminoplast condensate and monoepoxy alcohol.

The compositions of the present invention may be applied to fibers, filaments, yarns, or fabrics of wool or 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 composition of the present invention may be used to make the fabrics wrinkle-resistant, crush-resistant and crease-resistant. The application of increasing amounts of the compositions serves to provide proportionately increased reduction in shrinkage of the treated fabric on laundering, and when about 3% to 7% by weight of the composition, based on the weight of the fabric, is applied, the wool or cellulosic fabric is generally substantially stabilized against shrinkage on laundering. The application of the composition of the present invention may be employed for the purpose of aiding embossing operations. It also may be applied to fabrics as part of a process for their conversion to plissé fabrics and embossed fabrics.

The aqueous solution of the aminoplast condensate and monoepoxy alcohol 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 under conventional conditions.

After the fabric has been dried, the composition 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 and percentages given are by weight unless otherwise noted. The chlorination test method referred to in the examples follows the A.A.T.C.C. (69–1952) procedure in general except the temperature of chlorination and that of ironing indicated hereinafter. The actual procedure used involves the treatment with a hypochlorite solution containing 0.25% available chlorine at a temperature of 140°±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 sample is ironed at 400° F. (iron temperature) for 30 seconds. The chlorine damage referred to hereinbelow is the percentage loss in tensile strength referred to hereinbelow and 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*) An aqueous solution is prepared containing 1% of 3,4-epoxy-8-hydroxy-tricyclo[5,2,1,$0^{2,6}$]decane, 5% of dimethylol-N,N′-ethyleneurea, and 0.4% of zinc nitrate as a catalyst. A white cotton fabric is padded through this solution, dried at 220° F. for 5 minutes and then heated at 340° F. for 5 minutes to cure the resin.

(*b*) Another piece of the same cotton fabric is treated in the same way except that the monoepoxy alcohol was reduced to 0.5%.

(*c*) Another piece of the same cotton fabric is treated in the same way except that the amount of monoepoxy alcohol was reduced to zero.

After five full sanforized washes, the fabrics are subjected to the chlorination test above. In all cases, yellowing after ironing is either non-existent or negligible.

The results of testing for crease-proofing and chlorine damage are shown in the following table (wherein the values given for crease-recovery, are the average of the values for warp and filling):

TABLE I

Example	Crease-Recovery Angle, degrees	Tensile Strength before chlorination test (Warp), lbs./sq. in.	Chlorine Damage	
			Percent loss in Tensile	Discoloration on Chlorination and Ironing
1(*a*)	114	46	13	None.
1(*b*)	118	46	28	None.
1(*c*)	120	46	70	Severe (brown).

Similar results are also obtained when the urea derivative is replaced with dimethoxymethyl-N,N′-ethyleneurea.

Similar results are also obtained when compound A is replaced with compound E of Table A.

EXAMPLE 2

(*a*) An aqueous solution is prepared containing 1.0% of compound B of Table A, 5% of dimethylol-N,N′-trimethyleneurea, and 0.5% of zinc fluoborate as a catalyst. A white cotton fabric is padded through this solution, dried at 240° F. for 5 minutes and then heated at 340° F. for 5 minutes to cure the resin.

After 5 full sanforized washes the fabric is subjected to the chlorination test with negligible discoloration.

EXAMPLE 3

(*a*) An aqeuous solution is prepared containing 0.5% of 3,4-epoxy-8-hydroxy-tricyclo[5,2,1,$0^{2,6}$]decane, 6% of dimethylol trimethoxymethyl melamine, and 1.25% of zinc nitrate as a catalyst. Application to white cotton fabric is made by the procedure of Example 1.

(*b*) Another piece of the same cotton fabric is treated in the same way except the monoepoxy alcohol is omitted. After five full sanforized washes and subjection to the chlorination test above, the results obtained are those listed in Table II.

TABLE II

Before Chlorination Test

Example	Crease-Recovery Angle ave. of warp and filling, degrees	Tensile Strength (Warp), lbs./sq. in.	Chlorine Damage, Percent Loss in Tensile
3(*a*)	112	47	9
3(*b*)	111	45	13

EXAMPLE 4

(*a*) An aqueous solution is prepared containing 1% of 3,4-epoxy-8-hydroxy-tricyclo[5,2,1,$0^{2,6}$]decane, 5% of 1,3-dimethylol-5-(β-hydroxy ethyl)-tetrahydro-s-triazone-2, 1% of dimethylolurea, and 1% of zinc nitrate as a catalyst. Application to white cotton fabric is made by the procedure of Example 1. After five full sanforized washes and subjection to the chlorination test, the loss in tensile strength was zero.

(*b*) Similar results are obtained when the triazone is replaced with dimethylol-5-ethyl-tetrahydro-s-triazone-2.

(*c*) Similar results are obtained when the monoepoxy alcohol is replaced with each of compounds B, C, and D of Table A hereinabove.

I claim:

1. A composition comprising an aqueous dispersion of a mixture of 60 to 95% by weight of a water-dispersible aminoplast condensate selected from the group consisting of condensates of formaldehyde with a compound selected from the group consisting of N,N′-ethyleneurea, N,N′-trimethyleneurea, a tetrahydro-s-triazone-2 substituted in the 5-position with a group selected from the group consisting of β-hydroxyethyl, β-hydroxypropyl, and $(C_1–C_4)$-alkyl groups, and a melamine and 5 to 40% by weight of a compound selected from the group consisting of those listed in Table A of the specification.

2. A composition comprising an aqueous dispersion of a mixture of 60 to 95% by weight of a water-dispersible aminoplast condensate of formaldehyde with N,N′-ethyleneurea and 5 to 40% by weight of 3,4-epoxy-8-hydroxy-tricyclo[5,2,1,$0^{2,6}$]decane.

3. A composition as defined in claim 2 in which the aminoplast is a water-dispersible dimethylol-N,N′-ethyleneurea.

4. A composition as defined in claim 2 in which the aminoplast is a dimethoxymethyl-N,N′-ethyleneurea.

5. A composition comprising an aqueous dispersion of a mixture of 60 to 95% by weight of a water-dispersible aminoplast condensate of formaldehyde with melamine and 5 to 40% by weight of 3,4-epoxy-8-hydroxy-tricyclo[5,2,1,$0^{2,6}$]decane.

6. A composition as defined in claim 5 in which the aminoplast is a water-dispersible methylated polymethylolmelamine.

7. A composition as defined in claim 5 in which the aminoplast is a dimethylol trimethoxymethylmelamine.

8. A composition comprising an aqueous dispersion of a mixture of 60 to 95% by weight of 1,3-dimethylol-5-(β-hydroxyethyl)-tetrahydro-s-triazone-2 and 5 to 40% by weight of a compound of Table A.

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