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Product suitable for use as a textile finishing agent

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1.

**"PRODUCT SUITABLE FOR USE AS A TEXTILE FINISHING  
AGENT"**

This invention relates to a product suitable for use as a textile finishing agent, and more particularly to a finishing resin that imparts crease-resistance to textile fabrics.

5 The use of thermosetting resins to impart crease resistance and dimensional stability to textile materials is well-known in the art. These materials, known as aminoplast resins, include the products of the reaction of formaldehyde with such compounds as urea, thiourea, 10 ethylene urea, dihydroxyethylene urea, and melamines. A serious drawback to the use of such materials is that they contain free formaldehyde. This is present during the preparation and storage of the finishing agent and its use in treating textiles, on the treated fabric, and 15 on the finished garments. Also, when the fabrics or garments made therefrom are stored under humid conditions, additional free formaldehyde is produced.

The presence of even less than one per cent of free formaldehyde, based on the total weight of the 20 product, is undesirable, not only because of its unpleasant odor, but because it is an allergen and an irritant, causing severe reactions in the operators who manufacture the agent and who treat and handle the treated fabrics and to persons who handle and wear garments 25 fabricated from the treated fabrics.

These problems associated with the presence of free formaldehyde on treated fabrics are well-known and considerable efforts have been made to produce formaldehyde free textile fabrics. One solution to the problem 5 has been to employ scavengers for the free formaldehyde. In U.S. patent No. 3,590,100 cyclic ethylene urea and propylene urea are disclosed as scavengers. Removal of the formaldehyde by reaction with phthalimide is disclosed in U.S. patent No. 3,723,058. U.S. patent No. 4,127,382 10 teaches certain nitrogen-containing heterocyclic compounds as scavengers.

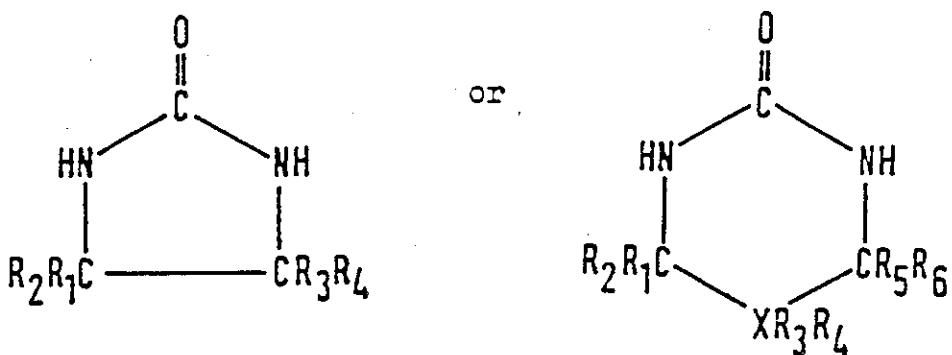
Treating textiles with resin compositions that do not contain or evolve formaldehyde is also known, as in U.S. patent No. 3,260,565 which teaches finishing agents 15 formed by the reaction of alkyl or aryl ureas or thioureas with glyoxal. These agents, however, have the disadvantage of having marginal permanent press properties. Finishing agents formed by the reaction of ethylene urea with glyoxal are disclosed in Japanese patent publication No. 53-044567, 20 but they too do not have satisfactory properties.

It has now been found that the alkylated products of the reaction of glyoxal and cyclic ureas are excellent cross-linking resins for textile fabrics and do not contain formaldehyde. Thus, in accordance with the present 25 invention, novel alkylated glyoxal/cyclic urea condensates are prepared that are useful for crosslinking textile fabrics.

Accordingly, the present invention in one aspect provides an alkylated product of the reaction of glyoxal and at least one cyclic urea, wherein the ratio of the amounts of glyoxal:cyclic urea is 0.8:1 to 1.2:1.

5 The invention in another aspect provides a finishing agent for imparting crease-resistance to a textile, comprising an alkylated product according to the first aspect of the invention.

10 The cyclic ureas which may be used have the following general formulas :



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  may be the same or different and each may be H, OH, COOH, R, OR or COOR wherein R is an alkyl or a substituted alkyl group having 1 to 4 carbon atoms, and X may be C, O, or N; wherein when X is O,  $R_3$  and  $R_4$  are each zero; and wherein when X is N,  $R_3$  or  $R_4$  is zero.

15 Typical examples of such compounds include ethylene urea, propylene urea, uron, tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, and mixtures of these.

The invention in a further aspect provides a process for imparting crease-resistance to a textile, which comprises impregnating a textile with a solution of a finishing agent according to the invention and a catalyst, and heating the impregnated textile to cure the finishing agent thereon.

The alkylated condensates can be prepared by any suitable and convenient procedure. The cyclic urea and the glyoxal are preferably reacted in stoichiometric amounts, although a slight excess of either of the reactants may be employed. The range of glyoxal: cyclic urea is 0.8:1 to 1.2:1. The reaction may be carried out within the temperature range of room temperature up to reflux, but preferably is run at 50 to 60°C. for about two hours. The pH may suitably range from 2 to 7.0, and preferably it is within the range of 5.0 to 7.0. The product is a water-soluble oligomer. These glyoxal/cyclic urea condensates are then partially or wholly alkylated, e.g. by reacting them with an alcohol such as methanol, ethanol, n-propanol, a butanol, and their mixtures.

Another method involves reacting glyoxal with an alkylated cyclic urea.

The finishing agent of this invention is suitable for use with cellulosic textile fabrics, woven or non-woven, including 100% cellulosic fabrics, e.g. cotton,

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rayon, and linen, as well as blends, e.g. polyester/cotton or polyester/rayon. Such blends preferably contain at least 20% of cellulose. Both white and coloured (printed, dyed, yarn-dyed, cross-dyed, etc.) fabrics can be effectively treated with the finishing agent of this invention, as can also fabrics containing fibers with free hydroxyl groups.

When applying the finishing agent of this invention to a fabric, there generally will be present an appropriate catalyst. Typical catalysts include acids (such as hydrochloric, sulfuric, fluoboric, acetic, glycolic, maleic, lactic, citric, tartaric, and oxalic acids), metal salts (such as magnesium chloride, nitrate, fluoborate or fluosilicate, zinc chloride, nitrate, fluoborate or fluosilicate, ammonium chloride, zirconium oxychloride, sodium or potassium bisulfate), amine hydrochlorides (such as the hydrochloride of 2-amino-2-methyl-1-propanol), and mixtures thereof. The amount of catalyst generally is 0.01 to 10 per cent, more preferably 0.05 to 5 per cent, based on the weight of the padding bath.

The finishing agents may be applied to the textile fabric in any known and convenient manner, e.g. by dipping or padding, and will generally be applied from aqueous or alcoholic solution. The solvent may be water, an aliphatic alcohol, e.g. methanol, ethanol, or isopropanol, or a mixture of water and an aliphatic alcohol. Other

conventional additives such as lubricants, softeners, bodying agents, water repellents, flame retardants, soil shedding agents, mildew inhibitors, anti-wet soiling agents, and fluorescent brighteners may be used 5 in the treating bath in conventional amounts. Such auxiliaries must not, however, interfere with the proper functioning of the finishing agent, must not themselves have a deleterious effect on the fabric, and preferably be free of formaldehyde.

10 The amount of finishing agent which is applied to the fabric will depend upon the type of fabric and its intended application. In general the amount applied is 0.5 to 10 per cent, more preferably 2 to 5 per cent, based on the weight of the fabric.

15 In the process of treating fabrics with the finishing agents of this invention, the fabric is impregnated with an aqueous or alcoholic solution of the finishing agent, and the impregnated fabric is then dried and cured; the drying and curing steps may be 20 consecutive or simultaneous.

If desired, the textile fabric may be finished by post-curing (also known as deferred or delayed curing). This consists of impregnating the fabric with a solution 25 of finishing agent and catalyst, drying the impregnated material carefully so that the finishing agent does not react, and then, after a prolonged interval, heating the

material to a temperature at which the agent reacts under the influence of the catalyst.

Although this invention is described with reference to the use of the alkylated product of the reaction of a cyclic urea and glyoxal as a textile finishing agent it is not intended to be limited thereto. The product of the invention is also suitable for use for example as a dry-strength or a wet-strength resin in paper; a hand-builder in textiles; a binder in particleboard, medium-density fiberboard, plywood, foundry and shell molding, insulation materials including glass fiber mats, friction materials, coated and bonded abrasives, etc.; a component in molding compounds; an adhesive for wood and laminates; a film-forming resin in coatings and printing inks; an additive in fibers, e.g. rayon; an additive in rubber processing; an agent in leather tanning; a textile size; a dry fixative for textiles; and an impregnant for filters, e.g. automotive filters.

The invention will be further described with reference to the following illustrative Examples.

Unless otherwise specified, all parts and percentages are by weight.

EXAMPLE 1

290 Parts (2 moles) of a 40% aqueous solution of glyoxal was adjusted to pH 6.5 with sodium bicarbonate. 176 Parts (2 moles) of ethylene urea was added and the temperature raised to  $55+5^{\circ}\text{C}$ . The mixture was stirred at this temperature for two hours, maintaining the pH between 6.0 and 7.0. After two hours 200 parts (6.25 moles) of methanol was added and the pH adjusted to about 3.0 with concentrated sulfuric acid. The reaction was held at reflux for three hours to effect methylation, the resin solution cooled to  $30^{\circ}\text{C}$ ., and the pH adjusted to about 7.0 with a 25% solution of caustic soda.

15 The product was a clear-viscous liquid, pale yellow, with negligible odor. The reaction was essentially complete, as determined by IR and NMR analyses. IR analysis indicated that methylation had occurred.

EXAMPLE 2

20 360 Parts (2.5 moles) of a 40% aqueous solution of glyoxal was added to 905 parts (2.5 moles) of a 44% methanol solution of dimethyl methoxy propylene urea. The mixture was heated to  $55+5^{\circ}\text{C}$ . for two hours, the pH being maintained between 6.0 and 7.0. After cooling at  $30^{\circ}\text{C}$ . there was obtained a 45%-solids, slightly viscous, water-white solution with no odor of formaldehyde. The reaction was essentially complete, as determined by IR and NMR analyses.

EXAMPLE 3

30 The procedure of Example 1 was repeated except that the glyoxal was reacted with each of the following instead of ethylene urea: propylene urea, uron, tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazin-2-one, and 4,5-dihydroxy-2-imidazolidinone. The results were comparable.

EXAMPLE 4

The procedure of Example 1 was repeated except that each of the following alcohols was used instead of methanol: ethanol, n-propanol, and isopropanol. The results were comparable.

EXAMPLE 5

The resin product of Example 1 was used to treat 100% cotton fabric. The test results are tabulated below and compared with those of a sample of the same fabric treated with a conventional formaldehyde-containing agent. In each case the solution of resin and catalyst was applied to samples of the fabric by padding with a wet pickup of about 60%, based on the weight of the fabric. The treated fabrics were dried by heating for 3 minutes at 107°C., and the resin cured on the fabrics by heating for 90 seconds at 171°C.

Wrinkle Recovery was measured by AATCC Test Method 66-1978 "Wrinkle Recovery of Fabrics: Recovery Angle Method".

Tensile was measured by ASTM Test Method D-1682-64 (Reapproved 1975) "Tensile-Grab-CRT Pendulum Type".

TABLE I

		(a)	(b)	(c)
25	Reactant, parts			
	A	15.0		
	B		15.0	
	Catalyst 531, parts	4.5	4.5	
	Sulfanole <sup>®</sup> RWD, part	0.25	0.25	
30	Tensile			
	warp	40	40	~89
	fill	16	15	~37
	Wrinkle Recovery			
	initial	245	286	168
35	after 5 AHL	245	280	173

A is the product of Example 1.

B is 1,3-bishydroxymethyl-4,5-dihydroxy-2-imidazolidinone (45% aqueous solution).

(c) is untreated 100% cotton fabric.

5 Catalyst 531 (Sun Chemical Corporation) is an activated magnesium chloride catalyst.

Sulfanole<sup>®</sup> RWD (Sun Chemical Corporation) is a non-ionic wetting agent.

AHL is average home launderings.

10 From these data it can be seen that the fabric treated with the product of this invention (a) is comparable in tensile strength and wrinkle recovery to the fabric treated with a commercial formaldehyde-containing agent (b) and has the advantage of being free of formaldehyde.

15 EXAMPLE 6

The procedure of Example 5 was repeated with the resin products of Examples 2, 3, and 4. The results were comparable.

EXAMPLE 7

20 An aqueous solution containing 15.0 parts of the resin product of Example 1 and 4.0 parts of Catalyst 531 was applied to samples of 65/35 polyester/cotton fabric by padding. The treated fabrics were dried; the resin cured on the fabrics by heating for 5 minutes at 150°C., 25 5 minutes at 177°C., and 1 minute at 193°C.; and the fabric smoothness determined by AATCC Test Method 124-1978 "Appearance of Durable Press Fabrics after Repeated Home Launderings". The results are tabulated below.

TABLE II

(a) (d)

Fabric Smoothness			
5	after 1 AHL		
	150°C.	3.7	3.2
	177°C.	3.6	3.1
	193°C.	3.4	3.0
10	after 5 AHL		
	150°C.	3.5	3.1
	177°C.	3.7	3.1
	193°C.	3.6	3.1
15	after 10 AHL		
	150°C.	3.4	3.2
	177°C.	3.8	3.2
	193°C.	3.8	3.2

(d) is untreated 65/35 polyester/cotton fabric.

The whiteness of the fabric (a) was good, and the fabric showed no chlorine scorch either initially or after 5 launderings.

20 EXAMPLE 8

The following solutions were prepared, applied to 100% cotton, and tensile and wrinkle recovery measured as in Example 5:

TABLE III

(a) (e) (c)

Reactant, parts			
25	A	15.0	
	C		15.0
	Catalyst 531, parts	4.5	4.5
30	Sulfanole <sup>®</sup> RWD, part	0.25	0.25
Tensile			
	warp	40	41
	fill	16	17
Wrinkle Recovery			
35	initial	245	199
	after 5 AHL	245	187
			173

A is the product of Example 1.

C is the product of the reaction of stoichiometric amounts of glyoxal and dimethyl urea (disclosed in U. S. patent No. 3,260,565).

5 (c) is untreated 100% cotton fabric.

From these data it can be seen that the fabric treated with the product of this invention (a) is comparable in tensile strength to the fabric treated with the reactant disclosed in U. S. patent No. 3,260,565 (e) and 10 considerably superior to it in wrinkle recovery.

EXAMPLE 9

The procedure of Example 5 was repeated with each of the following fabrics instead of 100% cotton: 50/50 polyester/cotton, 65/35 polyester/cotton, 50/50 15 polyester/rayon, and 65/35 polyester/rayon. The results were comparable.

EXAMPLE 10

A sample of 65/35 polyester/cotton fabric was impregnated with an aqueous solution containing 20 parts 20 of the product of Example 1, 5 parts of Catalyst KR (Sun Chemical Corporation's magnesium chloride catalyst), and 0.25 part of Sulfanole RWD. The fabric was then dried at 100°C. and stored at elevated temperature for several weeks. A crease was then pressed into the fabric, and it 25 was cured for 15 minutes at 150°C. The fabric was washed and evaluated by AATCC Test Method 88C-1975 "Appearance of Creases in Wash-and-Wear Items after Home Laundering". It had an appearance rating of 5 as compared with a blank having a rating of 3.

30 EXAMPLE 11

To illustrate the superiority of an alkylated glyoxal/cyclic urea condensate over a nonalkylated glyoxal/cyclic urea condensate, the following experiments were carried out:

35 (1) 176 Parts of ethylene urea (2 moles) was reacted with 320 parts of 40% glyoxal (2.2 moles) at a

pH of 6 and a temperature of 50-60°C. for two hours. The product was then reacted with 200 parts of methanol (6.25 moles) at pH 3.0, and then adjusted to pH 6.0 and 45% solids. The temperature was lowered to, and held at, 48°C., and viscosity measurements were taken at intervals with a Brookfield Viscometer.

(2) 176 Parts of ethylene urea (2 moles) was reacted with 320 parts of 40% glyoxal (2.2 moles) at a pH of 6 and a temperature of 50-60°C. for two hours. The product was adjusted with water to 45% solids. The temperature was lowered to, and held at, 48°C., and viscosity measurements were taken at intervals with a Brookfield Viscometer.

TABLE IV

	<u>Viscosity, cps</u>	(1)	(2)
15	initial	52	26.5
	after weeks - 1	65	gelled
	- 2	107.5	
	- 3	115	
20	- 4	127.5	
	- 8	210	
	- 9	232	
	- 10	240	

(1) is an alkylated glyoxal/cyclic urea condensate.

(2) is a nonalkylated glyoxal/cyclic urea condensate.

From these data it can be seen that the non-alkylated product (2) was unstable, gelling in one week, whereas the alkylated product (1) remained stable after 10 weeks at 48°C.

EXAMPLE 12

To illustrate the superiority of an alkylated glyoxal/cyclic urea condensate over a nonalkylated glyoxal/cyclic urea condensate as a textile treating agent, the following experiments were carried out:

(1) Japanese publication No. 53- 044567 Example 1

300 Grams of ethylene urea was charged into a 4-necked flask equipped with a reflux condenser, a thermometer, and a stirrer and dissolved in 450 grams of water. Then 1 kg. of 40% glyoxal (glyoxal:ethylene urea ratio of 2:1) and 2 grams of concentrated hydrochloric acid were added. The mixture was reacted for three hours at 40°C. After cooling, the pH was adjusted to 5.0 with sodium hydroxide solution. The slightly coloured transparent product had a solids content of 40%.

(2) Japanese publication No. 53- 044567 Example 2

300 Grams of ethylene urea was charged into a flask as in (1) and dissolved in 450 grams of water. 750 Grams of 40% glyoxal (glyoxal:ethylene urea ratio of 1.5:1) and 2 grams of concentrated hydrochloric acid were added. The mixture was reacted for three hours at 40°C. After cooling, the pH was adjusted to 5.0 with sodium hydroxide solution. The slightly coloured transparent product had a solids content of 40%.

15 Parts of each of these products and of the product of Example 1 was each mixed with 3.75 parts of an activated magnesium chloride catalyst and 0.25 part of Sulfanole RWD, and the solutions were applied by padding to samples of fabric. The treated fabrics were dried for 3 minutes at 107°C. and the resin cured on the fabrics by heating for 90 seconds at 177°C.

The blue and whiteness indexes of each were measured by AATCC Test Method 110-1975 and are tabulated as follows:

30

TABLE V

		(a)	(f)	(g)	(h)
<b>cotton</b>					
	blue index	81.85	74.83	76.16	85.46
	whiteness index	65.53	42.04	47.69	78.23
<b>35 65/35 polyester/cotton</b>					
	blue index	78.99	70.07	72.51	82.35
	whiteness index	57.63	29.51	37.74	67.62

(a) is the product of Example 1 of this application.

(f) is the product of Example 1 of Japanese publication No. 53-044567.

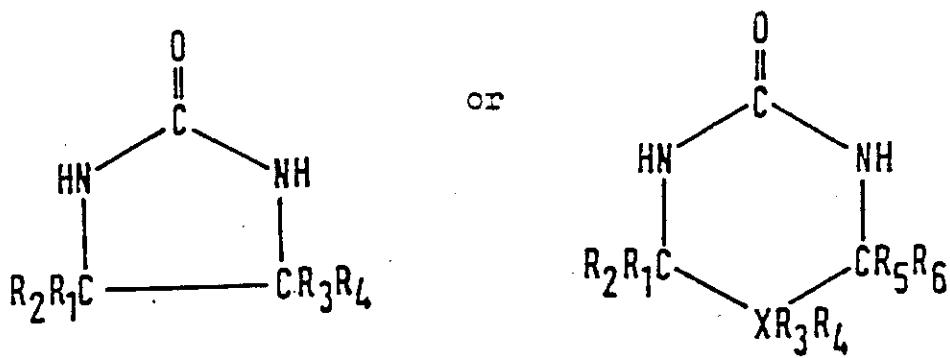
5 (g) is the product of Example 2 of Japanese publication No. 53-044567.

(h) is untreated fabric.

10 It is evident from these data that the product of this invention (a) is superior to the products of the Japanese publication (f) and (g) in both blue index and whiteness index. In addition, it was noted that the dry scorch on the fabrics treated with products (f) and (g) was extremely severe.

C L A I M S :

1. An alkylated product of the reaction of glyoxal and at least one cyclic urea, wherein the ratio of the amounts of glyoxal: cyclic urea is 0.8:1 to 1.2:1.
2. A product as claimed in Claim 1, wherein the 5 cyclic urea has the formula :



wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  may be the same or different and each may be H, OH, COOH, R, OR or COOR 10 wherein R is an alkyl or a substituted alkyl group having 1 to 4 carbon atoms, and X may be C, O, or N; wherein when X is O,  $R_3$  and  $R_4$  are each zero; and wherein when X is N,  $R_3$  or  $R_4$  is zero.

3. A product as claimed in Claim 2, wherein the cyclic urea is ethylene urea, propylene urea, uron, 15 tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazin-2-one, 4,5-dihydroxy-2-imidazolidinone, or a mixture thereof.

4. An alkylated product according to Claim 1, as described in any of the foregoing Examples 1 to 4.

5. A finishing agent for imparting crease-resistance to a textile, comprising an alkylated product as claimed in any of Claims 1 to 4.

6. A process for imparting crease-resistance to a  
5 textile, which comprises impregnating a textile with a solution of a finishing agent as claimed in Claim 5 and a catalyst, and heating the impregnated textile to cure the finishing agent thereon.

7. A process according to Claim 6, substantially  
10 as herein described in any of the foregoing Examples  
5 to 12.

8. A crease-resistant textile produced by the process as claimed in Claim 6 or 7.

9. A water-soluble resinous product prepared by  
15 alkylating the product of the condensation of glyoxal and at least one cyclic urea, the ratio of glyoxal:cyclic urea being 0.8:1 to 1.2:1.

10. A resinous product prepared by condensing glyoxal with at least one alkylated cyclic urea,  
20 the ratio of glyoxal:cyclic urea being 0.8:1 to 1.2:1.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office

2062661

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or withdrawn:

Patent granted:

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18th Year

19th Year

20th Year

Patent ceased or  
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RENEWAL DETAILS

PATENT No .... 2062661.....

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*first renewal fee due*  
RENEWAL FEE PAID FOR ..... YEAR ON 6 Nov 1984

.....  
FOR THE COMPTROLLER

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