(12) UK Patent Application (19) GB (11) 2 123 016 A

(21) Application No **8316701**
(22) Date of filing **20 Jun 1983**
(30) Priority data
(31) **393640**
(32) **30 Jun 1982**
(33) **United States of America (US)**
(43) Application published **25 Jan 1984**
(51) **INT CL**[3]
C08G 12/40 D06M 15/10
(52) Domestic classification
C3R 38B1B 38B2B 38D4A 38N1H 38N1MX 38N2Q3A 38N4 H
D1P 1273 DL
U1S 1372 C3R
(56) Documents cited
None
(58) Field of search
C3R
(71) Applicant
Sun Chemical Corporation, (USA—New York), 200, Park Avenue, New York, New York, United States of America
(72) Inventor
Bernard F. North
(74) Agent and/or address for service
Gill, Jennings and Every, 53 to 64 Chancery Lane, London, WC2A 1HN

(54) **Products and processes for treating textile fabrics**

(57) The products of the reaction of dimethyloldihydroxyethylene urea (DMDHEU) or an alkylated DMDHEU with a polyol impart permanent press properties to a textile fabric and contain only a small amount of free formaldehyde.

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SPECIFICATION

Products and processes for treating textile fabrics

This invention relates to textile finishing agents. More particularly it relates to finishing resins that impart permanent press characteristics to textile fabrics.

The use of thermosetting resins or reactants 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, ethylene urea, dihydroxyethylene urea, melamines, or the like. A serious drawback to the use of such material 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 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 percent of free formaldehyde, based on the total weight of the product, is undesirable, not only because of its unpleasant odour, 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 fabricated from the treated fabrics.

These problems associated with the presence of free formaldehyde or treated fabrics are well-known, and considerable efforts have been made to produce formaldehyde-free textile fabrics. One solution to the problem 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 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 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.

Other non-formaldehyde or low-formaldehyde materials such as alkylated condensates or glyoxal and cyclic urea (U.S. Patent No. 4,284,758) and blends of a condensate of glyoxal and a cyclic urea with dimethyloldihydroxyethylene urea (U.S. patent No. 4,300,898) are used to impart permanent press properties to a textile fabric.

In accordance with the present invention, novel products are prepared by reacting DMDHEU or alkylated DMDHEU with a polyol. DMDHEU is dimethyloldihydroxyethylene urea.

It has been found that these products are excellent crosslinking resins for textile fabrics and have a low potential for formaldehyde release.

Textile treatment compositions of the invention comprise the novel products, generally together with a solvent and a catalyst.

Suitable polyols include ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,2-butylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, polyethylene glycols having the formula $HO(CH_2CH_2O)_nH$ where n is 1 to about 50, glycerine, and the like, and their mixtures.

The dimethyloldihydroxyethylene urea (DMDHEU) may be used *per se* or it may be wholly or partially alkylated, such as methylated DMDHEU.

The DMDHEU and the polyol are generally reacted in a ratio of about 1—0.2:1—6 DMDHEU:polyol, and preferably the range is about 1—0.5:1—3.0 DMDHEU:polyol. The reaction may be carried out within the temperature range of about 10 to 100°C, and preferably within the range of about 50 to 80°C. for about 1 to 18 hours, and preferably for about 2 to 6 hours. The pH may range from about 1.0 to 6.0, and preferably it is within the range of about 2.0 to 4.0.

The pH may be adjusted with any suitable and convenient acid, such as for example sulfuric acid, nitric acid, phosphoric acid, hydrochloric acid; an organic acid such as citric acid; or the like; or their mixtures.

The product is a clear white to straw coloured liquid. Generally it is used as an aqueous or alcohol solution.

The products of this invention are suitable for use with cellulosic textile fabrics, woven or non-woven, including 100% cellulose fabrics, e.g. cotton, rayon, and linen, as well as blends, e.g. polyester/cotton or polyester/rayon. Such blends preferably but not necessarily contain at least 20% of cellulose. Both white and coloured (printed, dyed, yarn-dyed, cross-dyed, etc.) fabrics can be effectively treated with the resins of this invention. They are applicable also to fabrics containing fibers with free hydroxyl groups.

When applying the compositions 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; zirconium oxychloride; sodium or potassium bisulfate; ammonium chloride; amine hydrochlorides (such as the hydrochloride of 2-amino-2-methyl-1-propanol); and the like, and mixtures thereof. The amount of

catalyst generally is about 0.01 to 10 per cent, and preferably about 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 an 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, mildrew inhibitors, anti-wet soiling agents, fluorescent brighteners, and the like may be used in the treating bath in conventional amounts. Such auxiliaries must not, however, interfere with the proper functioning of the finishing compositions, must not themselves have a deleterious effect on the fabric, and desirably are free of formaldehyde.

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

In the process of treating fabrics with the products of this invention, the fabric is impregnated with an aqueous or alcoholic solution of the finishing resins, and the impregnated fabric is then dried and cured; the drying and curing steps may be 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 of the finishing resins 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 will be described with the use of a product of the reaction of DMDHEU or alkylated DMDHEU with a polyol as a textile finishing agent, it is not intended to be limited thereto. It is also suitable for use as an insolubilizer for binders in paper coatings; a dry-strength or a wet-strength resin in paper; a hand-builder in textiles, a binder in particle board, medium-density fiber board, plywood, foundry and shell mouldings, insulation materials including glass fiber mats, friction materials, coated and bonded abrasives, etc.; a component in moulding 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; an impregnant for filters, e.g. automotive filters; and the like.

In order that the present invention may be more fully understood, the following examples are given by way of illustration. Unless otherwise specified, all parts and percentages are by weight.

Example 1

(a) 600 Parts of a 54% DMDHEU solution (1.82 moles), 200 parts of diethylene glycol (1.89 moles), and 200 parts of water were acidified with sulfuric acid to a pH of 3.0 and heated for four hours at 70°C. The product was a clear pale straw coloured liquid with a very slight odour of formaldehyde. The degree of reaction was determined by HPLC (high performance liquid chromatography).

(b) The product of part (a) was used to treat 100% cotton fabric, as follows:

A solution of 15 parts of the product, 3.75 parts of Catalyst 531 (Sun Chemical Corporation's activated magnesium chloride catalyst), and 0.25 part of Sulfanole RWD (Sun Chemical Corporation's non-ionic wetting agent) was applied to the fabric by padding at a wet pick-up of 58%, based on the weight of the fabric. The treated fabric was dried for three minutes at 106°C. and cured, one sample (1) for 90 seconds at 149°C and a second sample (11) for 90 seconds at 171°C., except for determining chlorine scorch where the fabric was dried for five minutes at 106°C and cured for 60 seconds at 171°C.

The fabric was tested for wrinkle recovery angle, tensile strength, chlorine scorch, whiteness display, and formaldehyde on fabric. The results are fabric (a) in Table I below.

(c) The procedure of part (b) was repeated except that the fabric was 65/35 cotton/polyester. The treated fabric was tested for fabric smoothness and formaldehyde on product. The results are fabric (a) in Table II below.

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

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

Fabric smoothness was determined by AATCC Test Method 124—1978 "Appearance of Durable Press Fabrics after Repeated Home Launderings".

Chlorine scorch was determined by AATCC Test Method 114—1977 "Chlorine Retained, Tensile Loss: Multiple Sample Method".

Example 2

The procedure of Example 1(a and b) was repeated except that the 200 parts of water was replaced by an additional 200 parts of diethylene glycol, that is, a total of 3.78 moles of diethylene glycol. The product was a clear pale straw coloured liquid with a very slight odour of formaldehyde. It was determined by HPLC to have a greater degree of reaction than the product of Example 1. The product was tested in Example 1. The results are fabric b in Tables I and II.

Example 3

The procedures of Example 1 and a (part a) were repeated except that the DMDHEU was replaced by MeDMDHEU. The product was similar.

Example 4

The procedure of Examples 1 and 2 (part a) were repeated except that the diethylene glycol was replaced by each of the following polyols: ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, and glycerine. The results were comparable.

Example 5 (Comparative)

To illustrate the need to pre-react the DMDHEU and the polyol under acidic conditions so that etherification can occur, the following runs were made:

(a) 600 Parts of DMDHEU, 200 parts of diethylene glycol, and 200 parts of water were mixed, applied to a fabric, and tested as in Example 1 (parts b and c). The results are fabric (c) in Tables I and II below.

(b) 600 Parts of DMDHEU and 400 parts of diethylene glycol were mixed, applied to a fabric, and tested as in Example 1 (parts b and c). The results are fabric (d) in Tables I and II below.

Example 6 (Comparative)

The procedure of Example 1 (part b) was repeated except that the fabric was treated with diethylene glycol instead of a product of this invention. There was no change in the properties of the fabric, that is, the diethylene glycol imparted no resistance to wrinkling and did not improve fabric smoothness.

Example 7 (Comparative)

The procedure of Example 1 (part b) was repeated except that the fabric was treated with MeDMDHEU instead of a product of this invention. The results are fabric (e) in Tables I and II. The procedure of Sample 1(b) was also repeated using DMDHEU. The result is fabric (f) in Table 1.

In addition, the whiteness of fabrics treated with the products of Example 1 (part a) was comparable to that of fabrics treated with DMDHEU.

In each of Tables I and II:

(a) is a fabric treated with the product of Example 1(a)

(b) is a fabric treated with the product of Example 2

(c) is a fabric treated with the product of Example 5(a)

(d) is a fabric treated with the product of Example 5 (b)

(e) is a fabric treated with methylated dimethyloldihydroxyethylene urea MeDMDHEU

(f) is a fabric treated with DMDHEU

(g) is untreated fabric

Cure I is 90 seconds at 149°C. and Cure II is 90 seconds at 171°C.

AHL is automatic home launderings.

In Table I the fabric is cotton and in Table II the fabric is 65/35 polyester cotton.

Table I

Fabric	*(a)*	*(b)*	*(c)*	*(d)*	*(e)*	*(f)*	*(g)*
Wrinkle Recovery							
initial							
Cure I	262	269	266	266	253		180
Cure II	269	270	279	275	267		183
Wrinkle Recovery							
after 5 AHL							
Cure I	263	272	266	261	252		174
Cure II	263	270	275	270	266		182
Tensile							
Cure IW	50	46	42	60	60		82
F	12	10	18	16	25		27
Cure IIW	36	29	40	48	57		74
F	9	8	13	13	17		22
Free Formaldehyde, ppm							
Cure I	170	80	240	140	300		
Cure II	110	90	160	110	320		
Retained Chlorine							
Tensile Loss, %							
initial	2.0					31.9	
after 5 AHL	2.5					33.3	
after 5 hydrolysis washes	8.5					75.0	

Table II

Fabric	*(a)*	*(b)*	*(c)*	*(d)*	*(e)*	*(g)*
Fabric Smoothness						
after 1 AHL						
Cure I	3.3	3.3	3.6	3.3	3.3	2.8
Cure II	3.5	3.1	3.6	3.3	3.4	2.5
after 5 AHL						
Cure I	3.4	3.2	3.4	3.5	3.4	2.9
Cure II	3.4	3.3	3.4	3.4	3.3	2.9
Free formaldehyde, ppm						
Cure I	90	20	140	100	260	
Cure II	60	20	90	50	190	

From the data in Tables I and II it will be seen that the fabrics treated with the products of this invention (a) and (b) are comparable in wrinkle recovery, tensile strength, and fabric smoothness to fabrics treated with the commercial formaldehyde-containing agent (e) and have the advantage of having less formaldehyde than the commercial agent and the corresponding mixtures of DMDHEU and diethylene glycol (compare (a) with (c) and (b) with (d)). The chlorine resistance of a fabric treated with a product of this invention (a) is better than that of a fabric treated with DMDHEU (f).

Claims

1. A reaction product of (a) dimethyloldihydroxyethylene urea or an alkylated dimethyloldihydroxyethylene urea with (b) a polyol.

2. A product according to claim 1 wherein the ratio of amounts of a:b is 1—0.2:1—6.

3. A product according to claim 1 wherein the ratio of amounts of a:b is 1—0.5:1—3.0.

4. A product according to any preceding claim wherein the polyol is diethylene glycol.

5. A product according to any of claims 1 to 3 wherein the polyol is ethylene glycol.

6. A product according to claim 1 substantially as herein described with reference to any of Examples 1 to 4.

7. A process for preparing a product according to any preceding claim which comprises reacting (a) dimethyloldihydroxyethylene urea or an alkylated dimethyloldihydroxyethylene urea with (b) a polyol at about 10° to 100°C for about 1 to 18 hours at a pH of about 1.0 to 6.0.

8. A process according to claim 7 wherein (a) and (b) are reacted at a temperature within the range of about 50° to 80°C for about 2 to 6 hours at a pH of about 1.0 to 6.0.

9. A textile treatment composition comprising a product according to any of claims 1 to 6.

10. A composition for treating a textile fabric substantially as herein described with reference to any of Examples 1 to 4.

11. A process for producing a crease-resistant textile fabric which comprises impregnating a textile with a solution of a product according to any of claims 1 to 6 and a catalyst and heating the impregnated textile to cure the composition thereon.

12. A process for producing a crease-resistant textile fabric substantially as herein described with reference to any of Examples 1 to 4.

13. A crease-resistant textile fabric produced by a process according to claim 11 or claim 12.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1984. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.