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Powanda et al.

[11] **3,903,050**

[45] **Sept. 2, 1975**

[54] **PERMANENT PRESS FABRIC RESIN FROM CROTONYLIDENEDIUREA-GLYOXAL-FORMALDEHYDE AMINOPLAST MATERIAL**

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[21] Appl. No.: **381,116**

Related U.S. Application Data

[62] Division of Ser. No. 135,781, April 20, 1971, Pat. No. 3,764,263.

[52] **U.S. Cl.**..... **260/67.7**; 260/67.6 R; 260/256.4 C; 260/256.4 F

[51] **Int. Cl.**..... **C08g 9/26**

[58] **Field of Search**..... 260/67.5, 67.6 R, 67.7, 260/256.4 F, 256.4 C

[56] **References Cited**

UNITED STATES PATENTS

2,197,357	4/1940	Widmer et al.	260/67.6
2,264,400	12/1941	Ott et al.	260/69 UX
3,190,742	6/1965	Brandeis et al.	71/11 X
3,329,519	7/1967	Mills	106/165
3,470,134	9/1969	Ungar	260/67.6
3,487,048	12/1969	Deuzeman	260/67.7
3,557,031	1/1971	Standish et al.	260/67.7 X

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[57] **ABSTRACT**

Crotonylidenediurea is reacted with glyoxal and the resulting adduct methylolated with formaldehyde to produce the corresponding trimethylolated derivative which exhibits very desirable properties as a permanent press resin for fabrics.

2 Claims, No Drawings

PERMANENT PRESS FABRIC RESIN FROM CROTONYLIDENEDIUREA-GLYOXAL-FORMALDEHYDE AMINOPLAST MATERIAL

This is a division of application Ser. No. 153,781, filed Apr. 20, 1971, now U.S. Pat. No. 3,764,263.

BACKGROUND OF THE INVENTION

In the last decade "permanent press" fabrics have been a real boon to the textile industry. The future looks even brighter as consumers look for permanent press properties in other than casual wear, shirts and like apparel. It is anticipated, for instance, that use of permanent press resins in household white goods, e.g., sheets, pillowcases and tablecloths, will account for a substantial amount of the increased demand in this decade. To meet this demand the resins must be able to impart "permanent press" properties without degrading the fiber from which the fabric is made. Typically, the fabric is made of cellulosic materials, e.g., cotton, cotton-polyester blends, "regenerated" cellulosic materials, such as rayon, etc. Degradation can occur, for example, when the resin finish is applied and cured; it may also occur as a result of repeated washings of the treated fabric using the various popular bleaches and detergents.

The concept of "permanent press" is twofold: "crease resistance" and "crease retention". "Crease resistance" is synonymous with "wrinkle resistance" and "wrinkle recovery", viz., the ability of a treated fabric to resist wrinkling and to retain smoothness of shape and hand upon repeated wear and laundering. "Crease retention" is synonymous with "durable press", viz., the ability of a treated fabric to drip-dry without loss of crease and to be worn without ironing.

Obviously, achievement of all of these desirable properties, and others such as resistance to soil redeposition, and the like, requires chemicals which are quite special. The objects of the present invention, therefore, are to produce and provide just such special chemical compositions which, when applied to fabrics as taught herein, impart these very desirable properties.

THE INVENTION

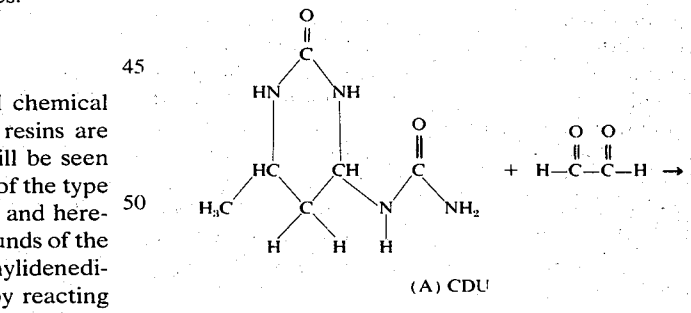
According to the instant discovery, novel chemical compositions have been found from which resins are readily prepared, the latter exhibiting, as will be seen hereinafter, permanent press characteristics of the type intensely sought after by the textile industry and hereinbefore briefly described. The novel compounds of the present invention are prepared from crotonylidenediurea (A), also referred to herein as CDU, by reacting

(A) with glyoxal to form a 1,2-hdyroxyethyl-substituted crotonylidenediurea adduct (B) which is methylolated with formaldehyde to produce the corresponding trimethylolated derivative (C), the latter being used to treat fabrics, pursuant to the present invention, to impart thereto significant permanent press characteristics.

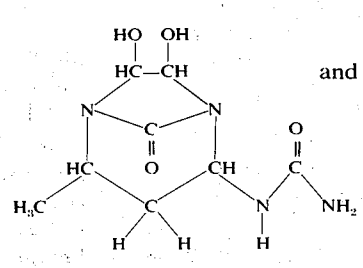
Reactant (A), above, viz., crotonylidenediurea, may be prepared by reacting urea with acetaldehyde in an acidic hydroxylic medium, e.g., as described in U.S. Pat. No. 3,190,741. While it has been found that crotonylidenediurea suitable for use in the present invention is conveniently and preferably prepared according to the following procedure, it should be understood that other methods of synthesis can be used: Thus, 270 parts of urea, parts and percentages used herein being by weight unless otherwise indicated, is added to a mixture of 99 parts of acetaldehyde and 600 parts of distilled water in a suitable conventional reaction vessel. The resultant solution is heated to a temperature of about 60°C. Thirty parts of phosphoric acid (catalyst) is then added and the temperature is thereafter maintained at between about 60°C and about 70°C for 1 hour during which time product crystallizes and settles out. The reaction mixture is subsequently cooled to ambient temperature whereupon further crystalline product crotonylidenediurea settles out. The product is separated from the supernatant liquid by filtration, washed with water, and dried in vacuo. The yield of white, solid crotonylidenediurea (135.3 grams) is 69.9 percent of the theoretical, based on the weight of acetaldehyde. Elemental analysis of the product corresponds to the formula $C_6H_{12}O_2N_4$ and the infrared spectrum thereof (Nujol mull) is identical to that reported in the literature (cf. Japanese Letters Patent No. 492,348) for crotonylidenediurea.

In accordance with the instant discovery, CDU readily reacts with glyoxal as follows:

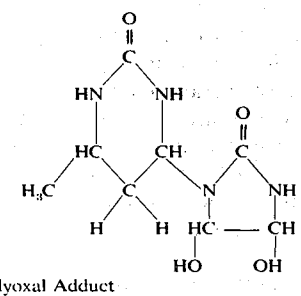
EQUATION I



(A) CDU



and

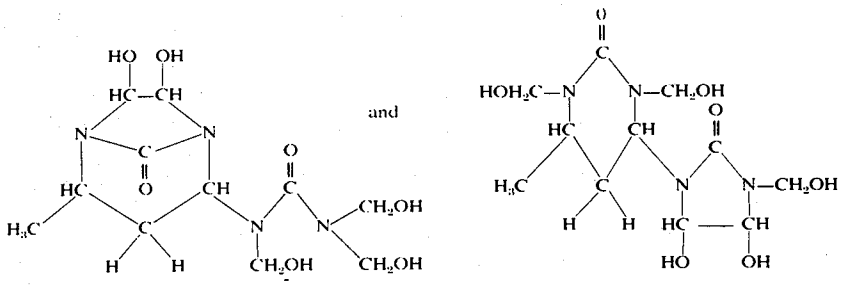


(B) CDU-Glyoxal Adduct

The CDU-glyoxal reaction product (adduct B) is reacted, according to the present invention, with between about 2.80 and about 5.0 molar proportions of formaldehyde as illustrated in the equation which follows:

EQUATION II

CDU-Glyoxal Adduct + 3HCHO →
(B)



(C) CDU-Glyoxal-HCHO

The exact nature of adduct (B) in Equation I, above, is not known but it is believed to be a mixture as shown in the equation; likewise, trimethylolation of the intermediate (B) of Equation I yields what is believed to be the CDU/Glyoxal/HCHO mixture (C) illustrated in Equation II.

Intermediate (B) is best prepared by reacting equimolar proportions of glyoxal and CDU in a hydroxylic medium, preferably water, at elevated temperatures and atmospheric pressure. Preferably, reaction is carried out for the most part at relatively low temperatures, e.g., in the range of about 40°C to about 75°C, and then the reaction is completed by increasing the temperature to atmospheric reflux for a relatively short period of time. Usually it is best to maintain the lower temperature for less than about an hour and then bring the reaction mixture to reflux for about 3 to about 15 minutes. Of course, these temperatures may be varied considerably, depending upon concentrations of reactants, medium used, and other like factors. It should be understood that, in view of the fact that the reaction proceeds rather readily, a wide variety of temperatures, concentrations and pressures is permissible, the reaction conditions just mentioned being those best suited for equimolar proportions of reactants. Obviously, pressures above or below atmospheric require higher or lower temperatures, respectively; obviously, also, lean or excess concentrations, below or above stoichiometric, affect the temperature requirements for optimum results. In short, the reaction conditions are quite flexible, the stringencies being imposed by desired efficiencies.

Conversion of intermediate (B) to the CDU-Glyoxal-HCHO composition (C) of Equation II, above, likewise admits of a wide variety of reaction conditions. Reaction is best carried out in a hydroxylic medium, usually water. Generally, between about 2.80 and about 5.0 molar proportions of formaldehyde, preferably between about 2.90 and about 3.05, is used based on adduct (B). Typical desirable formaldehyde sources are formalin, paraformaldehyde, and the like.

Admixture of adduct (B) with, say, an aqueous solution of formaldehyde gives rise to an exotherm. When the exotherm subsides (about 40°C), the mixture of reactants if preferably heated for up to several hours, cooled and pH adjusted to about neutral. Broadly, a temperature above about 40°C to about 105°C is contemplated herein, the upper temperature being, preferably, no greater than about atmospheric reflux temperature.

As in the case of the Equation I reaction described hereinbefore, reaction conditions for the Equation II reaction are very flexible, the stringencies also generally being dictated by desired efficiencies. If pressures above or below atmospheric are used, proportionately higher or lower temperatures, respectively, are usually indicated; likewise, lean or excess concentrations of formaldehyde with respect to adduct (B) could affect the temperature requirements for optimum results, as would, of course, the amount of water or other hydroxylic medium used relative to the reactants.

Fabric treatment is carried out in a conventional pad bath in an aqueous medium containing the resin-forming compound (C), viz., the CDU-Glyoxal-HCHO composition derived from adduct (B), and a curing catalyst as the principal ingredients. Generally, small amounts of surfactant and softener are present to enhance transfer of compound (C) to the fabric being treated.

The catalyst functions to catalyze the curing process which takes between about 5 seconds and about 30 minutes, preferably between about 3 minutes and about 15 minutes, at temperatures in the range of about 275°F to about 425°F, preferably between about 300°F and about 350°F. Substances suitable for catalysing the curing process include any conventional acidic catalysts or like catalysts heretofore known to be useful in catalysing the curing of conventional aminoplast materials. Such acid catalysts are employed in conventional amounts, e.g., at a concentration of between about 1 percent and about 50 percent by weight, based on the weight of aminoplast material. Typical catalysts contemplated herein are the water-soluble inorganic salts which behave as so-called latent acid catalysts, e.g., ammonium chloride, magnesium chloride, zinc nitrate, and the like.

According to a preferred mode of carrying out the fabric treatment process of the present invention, the aqueous reaction mixture containing novel compound (C) dissolved therein is cooled to ambient temperature, brought to a pH of about 7.0, and filtered to remove any insolubles which may be present. Then it is diluted with water to the desired concentration, mixed with a

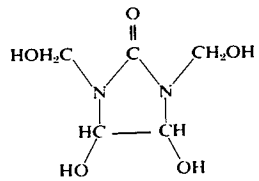
conventional amount of an acidic curing catalyst, and the fabric to be treated is immersed therein. The amount of resin "pickup" by the substrate fabric is determined in large measure by the concentration of the resin-forming material, viz., compound (C), in the aqueous pad bath solution. Generally, the concentration of compound (C) in the pad bath solution (which can be determined gravimetrically) ranges between about 2 percent or less and about 65 percent by weight or more, for cellulosic fabrics. Preferably, a pad bath concentration of between about 5 percent and about 45 percent is used, with a concentration of between 10 percent and about 25 percent being especially preferred. Percentages are based upon the total weight of the pad bath solution. The particular desired concentration of resin-forming substance in any given instance can be conveniently achieved by appropriate adjustment of the concentrations of reactants (i.e., CDU/glyoxal/HCHO) or by the judicious addition of water to an initially relatively highly concentrated solution of resin-forming compound (C).

After saturating the fabric with the pad bath solution, the treated fabric is withdrawn from the bath, wrung between rollers made of an inert material (e.g., metal, ceramic, rubber, and the like), preferably rubber rollers or adjacent, cooperatively-functioning stainless steel/rubber rollers, dried and simultaneously or subsequently heat cured at a temperature within the aforementioned range. The heat curing step can, if desired, be conducted by contacting the fabric with heated metal rollers, preferably heated stainless steel rollers.

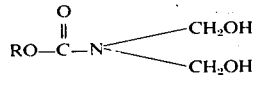
In the present invention, the percent pickup of the CDU/Glyoxal/HCHO composition is measured as: % Wet Pickup, after immersion in the pad bath solution; % Dry Pickup, after curing; % Dry Pickup, after 1 wash; and % Dry Pickup, after 21 washes.

As will be seen hereinafter, all tests are comparative tests using commercial resins as controls and comparing these resins with the novel composition (C) of the instant discovery. The tests recorded herein, other than resin pickup characteristics, are intended to illustrate the effectiveness of compound (C) with respect to wrinkle recovery, hand, deterioration of fabric, soil redeposition, and the like. Obviously, permanent press resins are not attractive if they deleteriously affect fiber strength, if wrinkle recovery is poor, etc.

Fabrics, particularly cellulosic fabrics, treated with compound (C) according to the present invention exhibit, as will be seen hereinafter, very desirable and valuable permanent press properties. The examples which follow teach the novel CDU-Glyoxal adduct (B) and the novel CDU/Glyoxal/HCHO composition (C) of the instant discovery and processes for preparing same. In addition, treatment of fabrics with resin-forming compound (C) is fully disclosed, as well as a number of tests comparing the latter's efficacy with that of the following commercially popular resin-forming compounds:



PERMAFRESH*113B
(dimethyloldihydroxyethyleneurea)
DMDHEU



[R = hydroxyalkyl or alkyl]

AEROTEX**82
(carbamate)

*Trademark for permanent press compound sold by Sun Chemical Co., Wood River Junction, R.I.

**Trademark for permanent press compound sold by American Cyanamid Co., Bound Brook, N.J.

The following examples are merely intended to be illustrative of certain of the preferred embodiments within the spirit and scope of the present invention and, therefore, are not to be interpreted too restrictively; parts and percentages given in the examples are by weight, unless otherwise indicated:

EXAMPLE I

To a reaction vessel is fed 468 grams of crotonylidenediurea, 395 grams of 40% glyoxal aqueous solution and water, thus providing a CDU/Glyoxal molar ratio of 1:1. Sufficient water is introduced to obtain good stirring (approximately 165 grams). The mixture of reactants is heated to 60°C, held at that temperature for 45 minutes, and then slowly heated to atmospheric reflux (103°C) and held at that temperature for 5 minutes before cooling the reaction mixture to ambient temperature and then filtering to remove unreacted CDU (128 grams). The filtrate (1055 grams) therefore contains 340 grams (approximately 2 moles) of reacted CDU, i.e., the CDU/Glyoxal adduct (B), described hereinabove in Equation I, in solution.

EXAMPLE II

To the filtrate, 1055 grams, of Example I containing intermediate adduct (B) is charged 487 grams of 37% aqueous uninhibited formaldehyde solution, the same reaction vessel being used. When the resulting exotherm subsides at about 40°C, the reaction mixture is heated to atmospheric reflux and held at reflux for three hours, at which time the mixture is cooled to ambient temperature and its pH adjusted to 7 using triethanolamine. The resulting product CDU/Glyoxal/HCHO compound (C) mixture of Equation II analyzes and compares with the aforementioned commercial aminoplast materials as follows:

TABLE I

Compound	% Solids	pH	% free HCHO
Aerotex 82	48±2*	6.5	3.2
Permafresh 113B	45±2*	5.9	0
CDU/Glyoxal/HCHO	39	7.0	1.5

*Published values

EXAMPLE III

The product CDU/Glyoxal/HCHO composition (C) of Example II, above, is used to treat plain weave white 50/50 cotton-polyester (PE) cloth, of the type used in shirts or household goods (e.g., sheets and pillowcases). The tests procedure is as follows:

Bath:	Compound tested	%
	(dry weight basis)	10.0
	Surfactant (Triton*X-100)	0.2
	Softener (Lubritron**KN)	3.0
	Catalyst - KR($MgCl_2$solution)***	5.0
	Water	81.8
		100.0

-Continued

Procedure: Standard Pad Bath
70-80% Wet Pickup
Dry at 220°F for 2 minutes
Cure at 325°F for 12 minutes
7-9% Dry Pickup
After wash
Half of the test swatches are laundered through 20 cycles.

Tests: Wrinkle Recovery
Stiffness
Tearing Strength
Abrasion Resistance (ASTM D-1175-64T)

*Triton X-100 is a trademark for an alkylaryl polyether alcohol surfactant sold by Rohm & Haas Co., Philadelphia, Pa.

**Lubriton KN is a trademark for a softener comprised of a nonionic emulsion of a high density olefin sold by Chas. S. Tanner Co., Warwick, R.I.

***Catalyst-KR is a magnesium chloride-based catalyst solution sold by Sun ChemicalCo., Wood River Junction, R.I.

The following table shows the pickup properties of each of the controls as compared with compound (C), the product of Example II, above:

TABLE II

	RESIN ADD-ON			
	% Wet Pickup	% Dry Pickup	% Dry Pickup (after 1 wash)	% Dry Pickup (after 21 washes)
Aerotex 82	78	7.0	5.4	
Permafresh 113B	78	8.7	6.5	
CDU/Glyoxal/HCHO	77.7	8.9	3.6	

Wrinkle recovery characteristics of the fabric of Example III, above, treated with the compounds of Table II is determined by a well-known method: ASTM D-1295-67-Warp direction only. The results of these tests follow:

TABLE III

	WRINKLE RECOVERY	
	Recovery in Degrees	
	Initial	After 20 Wash Cycles
Blank (Untreated 50/50 PE:Cotton)	107	120
CONTROLS Aerotex 82	142	142
CONTROLS Permafresh 113B	145	144
CDU/Glyoxal/HCHO	140	140

Cantilever stiffness of the fabric of Example III using the compounds of Table II is determined using the method: ASTM D-1388-64-Warp direction only. The results are as follows:

TABLE IV

	CANTILEVER STIFFNESS	
	Flexural Rigidity (mg-cm.)	
	Initial	After 20 Wash Cycles
Blank (Untreated 50/50 PE:Cotton	79.95	67.58
CONTROLS Aerotex 82	88.68	62.17
CONTROLS Permafresh 113B	89.43	55.94
CDU/Glyoxal/HCHO	65.25	60.73

Tearing strength of the fabric of Example III, above, using the compounds of Table II is determined by the method: ASTM D-2261-64T-Warp direction only. The results are as follows:

TABLE V

	TEARING STRENGTH BY THE TONGUE (SINGLE RIP) METHOD	
	Break Load (in pounds)	
	Initial	After 20 Wash Cycles
Blank (Untreated 50/50 PE:Cotton)	3.14	4.08
CONTROLS Aerotex 82	3.62	3.69
CONTROLS Permafresh 113B	3.75	4.13
CDU/Glyoxal/HCHO	3.02	2.97

Conventional soil redeposition tests showed the product of Example II, i.e., compound (C), to be superior to Permafresh 113B (DMDHEU). Using a small amount of anti-soil-redeposition agent for polyester/-cotton blends when subjecting the fabric of Example III, treated as taught in the same Example, to an otherwise conventional soil redeposition test showed the fabric treated with CDU/Glyoxal/HCHO compound (C) performed as well as the Aerotex 82 treated fabric and better than the Permafresh 113B-treated fabric under the same conditions. In other words, the Aerotex 82-treated fabric and the compound (C)-treated fabric both remained almost completely white. The anti-soil-redeposition agent used is a water-soluble methyl cellulose derivative (4000 cps) bearing the trademark METHOCEL-90-HG and sold by Dow Chemical Corp., Midland, Michigan. A concentration of 1%, by weight, of Methocel-HG is added to the conventional soil redeposition test soiling bath alluded to hereinabove; the concentration, viz., 1% by weight, is based on the total weight of the soil bath. The use of methyl cellulose derivatives (Methocel) is claimed in copending application Ser. No. 22,140 filed Apr. 2, 1970, by A. S. Forschirm et al. and entitled Anti-Soiling Polyester Textile Material, now U.S. Pat. No. 3,668,000.

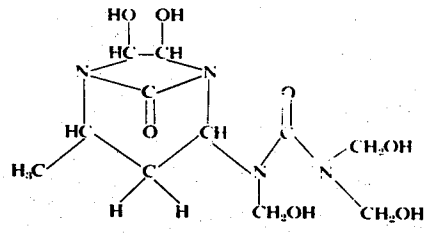
As is evident from Tables III and IV, above, the wrinkle recovery and stiffness performance of compound (C) compares very favorably with the performance of the commercial resins, even after multiple launderings. This indicates, in the case of wrinkle recovery, good

bonding of the compound (C) resin to the fabric. Tear strength data reported in Table V. above, showed compound (C), like the commercial controls, produced no significant deterioration in fiber strength. Abrasion resistance tests (ASTM D-1175-64T) not tabulated hereinabove, likewise indicated no significant deterioration in fiber strength.

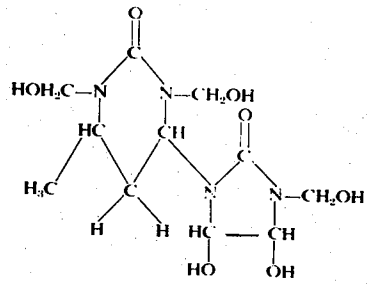
Pursuant to statutory requirements, there are described above the invention and what are now considered its best embodiments. It should be understood, however, that the invention can be practiced otherwise than as specifically described, within the scope of the appended claims.

What is claimed is:

1. A trimethylolated CDU/Glyoxal/HCHO derivative of the formulae (C):



and



2. A method for the preparation of an aminoplast material comprising

reacting crotonylidenediurea with an about equimolar proportion of glyoxal in a hydroxylic medium at an elevated temperature of from about about 40°C to about atmospheric reflux to form a 1,2-hydroxyethyl-substituted crotonylidenediurea adduct; and

reacting said adduct with between about 2.80 and about 5.0 molar proportions of formaldehyde in a hydroxylic medium at an elevated temperature of from about 40°C to about atmospheric reflux; and

recovering an aminoplast material.

* * * * *