United States Patent Office

3,369,931

Patented Feb. 20, 1968

3,369,931

N,N'-BIS(ACYLOXYMETHYL)URONS AS FINISHES FOR CELLULOSIC TEXTILE MATERIALS, A TEXTILE TREATED THEREWITH, AND A PROCESS FOR MANUFACTURING SAID URONS

Michael Thomas Beachem, Somerset, and John Christian Oppelt, Manville, N.J., assignors to American Cyanamid Company, Stamford, Conn., a corporation of Maine

No. Drawing. Filed Aug. 14, 1964, Ser. No. 389,775

13 Claims. (Cl. 117—139.4)

ABSTRACT OF THE DISCLOSURE

N,N'-bis(acyloxymethyl)urons, which are novel compounds and which when used in the treatment of cellulosic textile materials, impart an unexpectedly high degree of wrinkle recovery, with a concurrent low degree of loss in tensile strength, the treated textile and a process for producing said urons.

The present invention relates to a novel water-soluble textile finishing composition, to the process of applying the composition to textile materials, and to textile materials treated with the composition. In particular, the present invention relates to the N,N'-bis(acyloxymethyl) urons, which are novel compounds and which when used in the treatment of cellulosic textile materials, impart an unexpectedly high degree of wrinkle recovery, with a concurrent low degree of loss in tensile strength.

In the finishing of cellulose containing textile materials to impart shrinkage control or to impart wrinkle resistance, or both, numerous textile resins have been employed. Among those employed are the methylated methylolurea resins, the alkylated methylol melamine resins, and dimethylolethyleneurea, for example. Because of the characteristic of the melamine resins to retain chlorine and, to some extent, discolor therefrom, these resins have been blended with materials such as dimethylolethyleneurea in order to minimize discoloration resulting from chlorine, and to minimize the adverse effect of chlorine retention. The search by industry has been extensive to obtain textile finishing materials which impart a high degree of wrinkle recovery with a minimum of tensile strength loss initially as well as a minimum loss after laundering in the presence of chlorine.

In the use of the uron resins to impart wrinkle recovery, it has long been recognized the dimethylolated uron could be expected to give a high degree of wrinkle recovery. However, the use of this compound in such a form can be said to be substantially inoperative, because of the high degree of instability of the dimethyloluron. Thus, it was found to be necessary to further modify the compound in order to impart the necessary degree of stability, in order to produce a compound suitable for use commercially as a finish. It was found that if the dimethyloluron compounds were alkylated, the compounds became sufficiently stable to be commercially acceptable. Thus, the alkylated methylol urons were substituted for the unalkylated compounds in order to provide the necessary stability. In so doing, however, the urons became less effective in producing a degree of wrinkle recovery, and the alkoxymethyl urons produce an undesirably high loss

in tensile strength in the treated fabric, both initially and after washing in the presence of chlorine.

It is an object of this invention to provide a novel class of compounds suitable for use as a textile finish for the treatment of cellulosic material, to impart a high degree of wrinkle recovery.

It is a further object of the present invention to provide a composition suitable for use as a finish for the treatment of cellulosic textile material, to impart a commercially acceptable degree of wrinkle recovery and concurrently impart a minimal degree of loss in tensile strength.

It is a further object of this invention to provide a method of treating cellulosic textile material with the composition of this invention, to impart a high degree of wrinkle recovery with a concurrent minimal degree of loss in tensile strength.

These and other objects and advantages of the present invention will become apparent from the detailed description thereof set forth hereinbelow.

In accordance with the present invention, a water-soluble composition of matter is provided which comprises a compound selected from the group consisting of N,N'-bis(acyloxymethyl)urons alone, or in admixture with an etherified methylol melamine resin, so long as the N,N'-bis(acyloxymethyl)uron resin is present in an amount sufficient to impart the higher degree of wrinkle recovery with the lower degree of tensile strength loss. Determination of the optimum concentration of such mixtures is a matter which is within ordinary skill, and would be adjusted to the particular purpose and to the particular fabric.

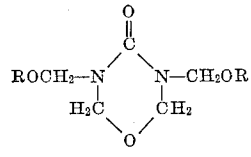
Further in accordance with the present invention, processes are provided for producing the novel compounds of this invention. There are two such methods. By the first method, N,N'-bis(alkoxymethyl)uron may be reacted with a carboxylic acid of the fatty acid series. By the second and preferred method, N,N'-bis(alkoxymethyl)uron is reacted with the corresponding acid anhydride, advantageously in the presence of hydrogen ions.

Further in accordance with the present invention, a process of treatment and a treated product are provided which are unexpectedly superior to the conventional N,N'-bis(alkoxymethyl)uron finish. The N,N'-bis(acyloxymethyl)urons of this invention give a wrinkle recovery unexpectedly higher than the N,N'-bis(alkoxymethyl) urons. Furthermore, the N,N'-bis(acyloxymethyl)urons can be cured at lower temperatures than the N,N'-bis-(alkoxymethyl)urons. Finally, at the given curing temperatures, the N,N'-bis(acyloxymethyl)urons cure more rapidly than the N,N'-bis(alkoxymethyl)urons. Thus, N,N'-bis(acyloxymethyl)uron and the process of making it has definite and unexpected commercial advantages.

By the term "cellulose containing textile materials," as that term is employed herein, it is meant fibers, yarns, filaments, formed fabrics, whether knitted, woven or non-woven, felted or otherwise formed, containing at least a substantial amount of cellulosic fiber, preferably at least 50%, such as for example, cotton, viscose rayon, linen, flax, jute, or other cellulosic material. These cellulosic textile materials may be employed in combination with other known textile materials, as for example, they may be blended with other natural or synthetic fibers, as for example, silk, wool, nylon, acrylic and polyester fibers and the like.

By the term "uron resin," as that term is employed herein, is meant the products obtained by the process described by Kadowaki [Bull. Chem. Soc. Japan 11,248 (1936)], or by modifications of said process whereby urea (1.0 mole) and formaldehyde (4.25 moles) are reacted under alkaline conditions and the reaction product then alkylated under strongly acid conditions, followed by extraction of the product with chloroform or chloroform and ether. According to the Kadowaki procedure, the product is then distilled and N,N'-bis(alkoxymethyl) uron (I) is obtained. This product has the following structural formula:

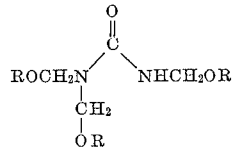
(I)



Formula I set forth above is identified as a uron resin, so long as approximately 30% of the reaction product is present.

By the term "distilled uron resins" as that term is employed herein, it is intended to include a uron resin containing at least 60% of the compound of Formula I above and the balance of N,N,N'-tris(alkoxymethyl)urea of Formula II hereinbelow and other reaction products, some of which are identified more fully hereinafter.

(II)



In the Formulae I and II above, R is a saturated aliphatic group containing from 1 to 4 carbon atoms such as methyl, ethyl, propyl, including normal and iso, and butyl, including normal, iso, and tertiary. Of these, methyl is greatly preferred.

The term "uron resin," discussed above, includes the product of Teruo Oshima U.S.P. No. 3,089,859, which product is predominantly Formula I, as the term is used herein.

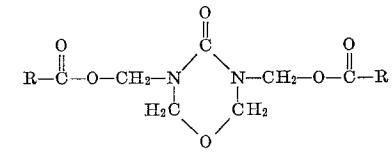
The term "distilled," however, should not be construed as limiting on the present invention since distillation is but one means of obtaining a uron resin characterized by the quality and purity identified hereinabove and any means whereby a uron resin of comparable characteristics is obtained is contemplated.

By the term "crude uron resin," as that term is employed herein, refers to uron resin compositions containing at least 30% of the compound of Formula I, and in additon significant amounts of the compound of Formula II, as well as other methylol ureas and alkylated methylol ureas. While the crude uron resins are acceptable and highly useful in the present invention, they normally do not produce the outstanding results obtained by employing the distilled uron resins. However, the cost of the distilled uron resins is markedly more than those of the crude products because of comparatively low yields and expensive manipulative operations. Therefore, while the distilled uron resins are superior in the combination of the present invention, their economics render them less attractive than the crude uron resins.

Of the N,N'-bis(acyloxymethyl)urons of this invention, the two preferred embodiments are (1) N,N'-bis (acetoxymethyl)uron, and (2) N,N'-bis(propionyloxymethyl)uron.

The formula characteristic of the N,N'-bis(acyloxymethyl)uron is:

(III)

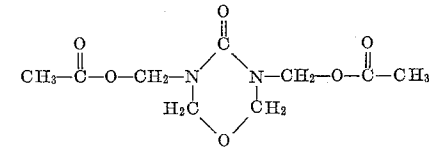


where R is lower alkyl of about 1 to 4 carbon atoms.

Two preferred compounds of the above Formula III are represented by the Formulae IV and V.

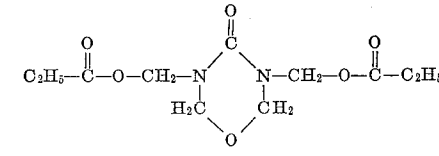
The formula of N,N'-bis(acetoxymethyl)uron is:

(IV)



The formula of N,N'-bis(propionyloxymethyl)uron is:

(V)



The application of the finish of this invention may be made by conventional means such as padding, spraying, and the like.

The intended commercial use of treated fabric governs the form of the particular treating method utilized for applying the finish of this invention. For example, good wrinkle recoveries are obtained by merely drying the fabric at conventional drying temperatures, which for purposes of this invention are temperatures of about 225° F., but may range from about 70° F. to about 250° F. However, unless the fabric is cured at a higher temperature, the fabric has a high affinity for chlorine when laundering in the presence of chlorine. The curing temperature employed, if the fabric is cured subsequent to the drying, is a temperature normally ranging from about 250° F. up to about 350° F., for a period from about 3 to about 1 minutes. Preferably, the curing temperature ranges from about 300° F. up to about 350° F., for a period from about 2.0 to about 1.5 minutes. However, curing temperatures in excess of 350° F. may be employed for fabrics of heavier weights. Cure-time decreases as cure-temperature increases.

In acquiring the textile finish of this invention, between about 2% and 10% solids o.w.f. (based on the weight of the fabric), preferably between 5% and 7%, of the novel urons is applied to the fabric. The wet pickup normally be varied within conventional ranges, for example, from about 50% to about 200%. During the curing operation, any conventional curing catalysts and method may be used. Typical of the curing catalysts is magnesium chloride. However, other conventional curing catalysts include, for example, zinc chloride, zinc nitrate, aluminum chloride, and diammonium hydrogen phosphate.

As referred to above, one method of preparation of the N,N'-bis(acyloxymethyl)urons of this invention comprises reacting N,N'-bis(alkoxymethyl)urons with a reactant selected from the group consisting of carboxylic acids of the fatty acid series. Typical of the N,N'-bis (alkoxymethyl)urons are those discussed above, formed according to the Kadowaki procedure. The carboxylic acids suitable for use in this invention include all saturated or unsaturated fatty acids. In the preferred embodiments, the acids of low molecular weight are employed. However, fatty acids containing 10 or more carbon atoms, such as stearic, palmitic, oleic, linoleic, and ricinoleic acids, as well as all substituted fatty acids such

as naphthenic acids, etc., or polybasic acids, such as succinic acids, sebacic acids, and the like, are within the scope of this invention. The preferred higher degree of wrinkle recovery may be obtained by use of short carbon chains. Instead of the free acid, derivatives may be used, if desired, which react in the same manner, for example, the anhydrides.

Any excess acid used can be readily removed by normal methods; in such cases the products obtained are neutral, or almost neutral, oils, viscous liquids or solids and can be characterized, like fats or oils, by their acid numbers, saponification numbers and ester numbers.

As noted above, the preferred method of preparation of the composition of this invention, comprises reacting N,N' - bis(methoxymethyl)uron with the corresponding acid anhydride in the presence of catalytic hydrogen ions. The presence of a catalyst is not essential to carry out the reaction. Normally, however, a catalyst is present for practical purposes. The hydrogen ions are conveniently provided by a catalytic amount of a sulfonated polymer, such as the polymers and copolymers of sulfonated styrene. The sulfonated polymers and copolymers are preferred catalysts for applicants' process, because they are insoluble in the reaction mixture and may be easily removed by filtration. It is possible, however, to employ other acidic catalysts such as sulfuric acid or paratoluenesulfonic acid, which are soluble in the reaction mixture and therefore require a removal step such as by neutralization, or by employing a basic ion exchange resin. Neutralization is not completely practical because the neutralizing agent normally would be present in a water solvent which when added to the above reaction mixture, would hydrolyze the reaction product.

The solubility of the pure products is particularly influenced by the nature of the organic acids which have taken part in the reaction. Usually the products obtained are readily soluble in various solvents such as benzene, toluene, solvent naphtha, turpentine, butyl acetate, butanol, as well as linseed oil and many resins.

The following examples are for illustration of the present invention, and are not restrictive of the scope of the invention.

Example 1

This example illustrates a method of preparation of N,N' - bis(acetoxymethyl)uron, of the formula shown above and referred to as IV.

A mixture of 36.6 parts (0.19 mole) of N,N'-bis(methoxymethyl)uron and 119.0 parts (1.07 moles) of acetic anhydride without a catalyst is heated at 125° C. for about 240 minutes while distilling off methyl acetate. The product, N,N'-bis(acetoxymethyl)uron, is obtained in yield of about 71% of theory by distilling the reaction mixture in vacuo. The product boils at 172–175° C. at about 0.4 mm. pressure.

Example 2

Example 2 illustrates a method of preparation of N,N'-bis(propionyloxymethyl)uron, as shown above and referred to as V.

A mixture of 100 parts (0.53 mole) of N,N'-bis(methoxymethyl)uron, 394 parts (3.03 moles) of propionic anhydride and 1.0 part of a sulfonated copolymer of styrene and vinylstyrene (dowex 50) is heated at 175° C. for about 90 minutes while distilling off the methyl propionate. The product N,N'-bis(propionyloxymethyl)uron is obtained in yield of about 84% of theory by distilling the reaction mixture in vacuo. The product boils at about 160° C. at 0.5 mm. pressure.

Example 3

A padding application of N,N'-bis(acetoxymethyl)uron (product of Example 1) is made on 80 x 80 percale from an aqueous bath at a 5% solids o.w.f. level. Magnesium chloride (12% on the weight of the resin) is also applied. The treated fabric is dried at 225° F. for 2 minutes, and then portions of the fabric are heated at 350° F. for varying lengths of time.

The wrinkle recovery of the treated fabrics is measured on a Monsanto wrinkle recovery tester following Test Method 66–1959T described on p. B–128 of the 1962 edition of the Technical Manual of the American Association of Textile Chemists and Colorists.

The tensile strength is measured on a Scott tester by the A.S.T.M. Standard Method D–39.

The washes are carried out at 212° F. in an automatic washing machine by the procedure described under Test Method 96–1960T on p. B–95 of the above reference.

(A) Untreated fabric
(B) No cure
(C) 0.5-min. cure
(D) 1.0-min. cure
(E) 1.5-min. cure

The results of the tests are shown in Table I.

TABLE I

Method of Treatment (Below)	Wrinkle Recovery				Tensile Strength			
	(1) Initial		(2) After 5 Washes		(3) Initial		(4) After 5 Washes	
	Total degrees	Percent increase	Total degrees	Percent increase	Lbs.	Percent decrease	Lbs.	Percent decrease
A (Control)	180	----------	175	----------	94	----------	102	----------
B (Dried only)	251	+39	210	+20	75	−25	78	−24
C (Dried and Cured)	296	+64	198	+13	38	−60	37	−64
D (Dried and Cured)	294	+63	208	+19	34	−63	32	−67
E (Dried and Cured)	288	+60	205	+17	30	−68	35	−66

From Table I, columns 1 and 2 disclose, that the wrinkle recovery of the treated fabric which was dried only i.e. B., gave a substantial increase in wrinkle recovery. Subsequent to drying, C, D, and E each were cured for varying periods of time, and as seen from Table I, there was further substantial increase in the wrinkle recovery as compared to A and B.

Example 4

The product of Example 1 (which shall now be designated as A), i.e. N,N'-bis(acetoxymethyl)uron, and N,N'-bis(methoxymethyl)uron (designated as B) are applied to 80 x 80 cotton percale from aqueous baths by padding procedures. The applications are made at the 5% o.w.f. resin solids level. The pad baths contain 6% magnesium chloride based on the resin solids in the bath. The treated fabrics are dried for one minute at 225° F. Portions of the dried fabrics are then cured for 1.5 min. at temperatures of 250°, 300°, or 350° F.

The wrinkle recovery measurements are carried out on both dry and wet fabrics by the procedure used in Example 3.

The results of the measurement are shown in Table II.

TABLE II

Compound employed in treatment	Dry Wrinkle Recovery							
			250° F.		300° F.		350° F.	
	(Degrees) Dried only	Percent increase	(Degrees) Dried and cured	Percent increase	(Degrees) Dried and cured	Percent increase	(Degrees) Dried and cured	Percent increase
A	188	+39	223	+64	224	+65	252	+85
B	137	+1	147	+9	162	+19	219	+61
Untreated	136 degrees							
A–B	+38%		+55%		+46%		+24%	

Compound employed in treatment	Wet Wrinkle Recovery							
			250° F.		300° F.		350° F.	
	(Degrees) Dried only	Percent increase	(Degrees) Dried and cured	Percent increase	(Degrees) Dried and cured	Percent increase	(Degrees) Dried and cured	Percent increase
A	164	+15	212	+48	232	+62	221	+56
B	165	+15	176	+23	158	+11	205	+43
Untreated	143 degrees							
A–B	+0.0%		+25%		+51%		+13%	

From the above Table II, it is clear that the degree of wrinkle recovery using N,N'-bis(acetoxymethyl)uron (A) was far superior to that obtained using N,N'-bis(methoxymethyl)uron (B), both (1) when dried only, and (2) when dried and cured.

Example 5

A=N,N'-bis(acetoxymethyl)uron
B=N,N'-bis(methoxymethyl)uron

Pad baths contain 6.25% of the above compounds and 6% magnesium chloride based on the compounds. The wet pickup is 80%. Therefore, the fabrics (80 x 80 cotton percale) contain 5% of the compounds. The fabrics are dried at 225° F. for 1 minute and samples are cured for 1.5 minutes at 250° F., 300° F., and 350° F. The results are illustrated in Table III and Table IV. Table III illustrates wrinkle recovery.

Table III illustrates the results obtained by the experiments conducted in Example 5. This example and table represent a repetition of the experiment of Example 4, further illustrating the superiority of N,N'-bis(acyloxymethyl)urons as compared to N,N'-bis(alkoxymethyl)urons. Both Table II and Table III illustrate the higher degree of wrinkle recovery obtained with the N,N'-bis(acyloxymethyl)urons, both when dried only and also when cured at varying curing temperatures.

The resinous composition of the present invention may be employed with other textile finishing resins, such as is disclosed in U.S. Patent 3,063,869, either thermosetting or thermoplastic, to improve the durability of such finishes or to modify the hand or other characteristics of the finished fabric. Thus, for example, the resinous product of this invention may be employed with other aminoplast textile finishing resins such as urea-formaldehyde resins,

TABLE III

Treatment	Dry When Measured							
			250° F.		300° F.		350° F.	
	Dried only, degrees	Percent increase	Dried and cured, degrees	Percent increase	Dried and cured, degrees	Percent increase	Dried and cured, degrees	Percent increase
A	254	+25	277	+37	283	+40	289	+43
B	187	−8	246	+21	270	+33	279	+37
Untreated	203							
A–B	+33%		+16%		+7%		+6%	

Treatment	Wet When Measured							
			250° F.		300° F.		350° F.	
	Dried only, degrees	Percent increase	Dried and cured, degrees	Percent increase	Dried and cured, degrees	Percent increase	Dried and cured, dgerees	Percent increase
A	204	+67	230	+90	251	+106	259	+112
B	135	+11	223	+83	225	+85	243	+100
Untreated	122							
A–B	+56%		+7%		+21%		+12%	

thiourea-formaldehyde resins, various cyclic urea-formaldehyde resins, as for example, 1,2-propyleneurea-formaldehyde resins, 1,3-propyleneurea-formaldehyde resins and their corresponding thiourea-formaldehyde resins, guanamine-formaldehyde resins and the alkylated derivatives of these materials. In addition to these, acetone-formaldehyde resins, epoxy resins such as diglycidyl ether, the diglycidyl ether of ethylene glycol, and other polyglycol, and other polyglycidyl ethers of polyhydric alcohols having an epoxy equivalency greater than 1, such as are disclosed in U.S. Patent Nos. 2,730,437 and 2,752,269, may be employed. Among the thermoplastic resins which may be mentioned are homopolymers and copolymers of lower alkyl acrylates, such as methyl acrylates, ethyl acrylates, methyl methacrylates, butyl methacrylates or copolymers of these or their equivalents with styrenes, including ring and chain substituted styrenes, acrylonitrile, polyvinyl chloride, and the like. In addition, the resinous mixture of this invention may be employed with softeners, stiffeners, lubricants, water-repellants and other conventional finishing agents.

Other suitable changes and variations may be made in the carrying out of the invention disclosed herein without departing from the spirit and scope thereof, as described in the foregoing disclosure and as defined in the appended claims.

What is claimed is:

1. N,N'-bis(acyloxymethyl)uron.
2. N,N'-bis(acetoxymethyl)uron.
3. N,N'-bis(propionyloxymethyl)uron.
4. A process of treating a substrate comprising cellulosic textile material, said process comprising applying an aqueous solution of N,N'-bis(acyloxymethyl)uron to said substrate, and drying said uron-treated substrate.
5. A process according to claim 4, including the additional step of curing said treated substrate.
6. A process according to claim 5, in which said uron is N,N'-bis(acetoxymethyl)uron.
7. A process of treating a substrate comprising a cellulosic textile material, said process comprising applying to said substrate from an aqueous solution, N,N'-bis(acetoxymethyl)uron, drying the treated fabric at a temperature ranging from about 70° F. up to about 250° F., and subsequently curing said treated substrate at a temperature ranging from about 250° F. up to about 350° F. for a relative period ranging between about 2.0 minutes to about 1.5 minutes.
8. A process of treating a substrate comprising a cellulosic textile material, said process comprising applying to said substrate from an aqueous solution, N,N'-bis(propionyloxymethyl)uron, drying the treated fabric at a temperature ranging about 70° F. up to about 250° F., and subsequently curing said treated substrate at a temperature ranging from about 250° F. up to about 350° F. for a relative period ranging between about 2.0 minutes to about 1.5 minutes.
9. A substrate comprising cellulosic textile material treated with a textile finish comprising, N,N'-bis(acyloxymethyl)uron.
10. A substrate comprising cellulosic textile material treated with a textile finish comprising, N,N'-bis(acetoxymethyl)uron.
11. A substrate comprising cellulosic textile material treated with a textile finish comprising, N,N'-bis(propionyloxymethyl)uron.
12. A process of making N,N'-bis(acyloxymethyl)uron comprising heating at an elevated temperature a reaction mixture comprising N,N'-bis(alkoxymethyl)uron with a fatty acid anhydride.
13. A process for producing N,N'-bis(acyloxymethyl)uron comprising heating at an elevated temperature a reaction mixture comprising N,N'-bis(alkoxymethyl)uron with a reactant selected from the group consisting of fatty carboxylic acids.

References Cited

UNITED STATES PATENTS

2,373,135	4/1945	Maxwell	117—139.4 X
2,485,203	10/1949	Kvalnes et al.	260—69
3,048,500	8/1962	Musser et al.	117—139.4
3,063,869	11/1962	Roth	117—139.4
3,089,859	5/1963	Oshima	260—67.6
3,264,241	8/1966	Abrahams	117—139.4 X

WILLIAM D. MARTIN, *Primary Examiner.*

T. G. DAVIS, *Assistant Examiner.*