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PROCESS OF TREATING NATIVE CELLULOSE WITH A LIQUID ALKYLENEPOLYAMINE AND A TEXTILE RESIN

Leon Segal, Metairie, and Leopold Loeb and Carl M. Conrad, New Orleans, La., assignors to the United States of America as represented by the Secretary of Agriculture

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This invention relates to treating native cellulose fibers; to reduce their crystallinity and/or to distend and enlarge their crystalline unit cells.

Native cellulose fibers have a crystal form of cellulose I and are composed of two phases or modifications. One of the phases is the relatively dense, brittle and inert crystalline phase, and the other is the less dense, more flexible and reactive, amorphous phase. It is known that treatments which reduce the relatively high crystallinity (about 85 to 90% in the case of cotton fibers) of the native cellulose fibers, without chemically degrading the fibers or changing their crystal form, improve the desirability and utility of the fibers.

It was found that while most amines exert little decrystallizing effect upon native cellulose fibers, treating the fibers with anhydrous methyl or ethylamine, or with a mixture of either of those amines with anhydrous primary alkylamines containing 6 or 7 carbon atoms, materially reduces the crystallinity of the fibers. A process of producing undegraded native cellulose fibers of reduced crystallinity by such a treatment is described in U.S. Patent No. 2,580,491.

We have now discovered that the properties of native cellulose fibers can similarly be improved by a treatment with a liquid alkylenepolyamine, which need not be conducted under anhydrous conditions. In addition, we have discovered that by a treatment with such an amine, the native cellulose fibers can be converted to a novel and particularly useful form of liquid-free permanently distended fibers.

One object of the present invention is to provide a process of producing undegraded native cellulose fibers of reduced crystallinity, comparable to those obtainable by the process of U.S. Patent No. 2,580,491, by means of a simple treatment in which anhydrous conditions need not be maintained. Another object of the invention is to provide liquid-free distended native cellulose fibers in which unit cells are distended by the presence of molecules of an alkylenepolyamine held between glucose units in an alkylenepolyamine-cellulose complex in which the polyamine is resistant toward extraction by non-polar organic liquids but is susceptible to extraction with hot water or polar organic liquids that are inert toward cellulose.

In general, the process in accordance with this invention comprises contacting native cellulose fibers with a liquid of the group consisting of liquid alkylenepolyamines and solutions consisting essentially of from about 55 to 95 weight percent of liquid alkylenepolyamines and from about 5 to 45 weight percent of liquids which are unreactive toward the alkylenepolyamines and cellulose, until an alkylenepolyamine-cellulose complex is formed, and then

freeing the so-treated fibers from unattached alkylenepolyamine.

The process of the present invention can be employed in the treatment of native cellulose fibers such as cotton, linen, ramie, and the like vegetable fibers. Such fibers can be treated in the form of free fibers, sliver, yarn, threads, fabrics and the like. The treatment of vegetable textile fibers in the form of yarns and threads is preferred.

Illustrative examples of liquid alkylenepolyamines which can be used in the present process include ethylenediamine, tetramethylenediamine, diethylenetriamine, hexamethylenediamine, and the like. Alkylenepolyamines containing from about 2 to 6 carbon atoms are preferred. These may also contain from about 0 to 5% by weight of water and/or other amines.

Treatment of the fibers with the polyamine can be conducted in any apparatus adapted for contacting solids with a liquid. It can be conducted under subatmospheric or superatmospheric pressure; but the use of normal atmospheric pressure is preferred.

The temperature at which the fibers are contacted with the alkylenepolyamine can be varied widely; but, in general, the use of temperatures of from about 20° to 50° C. is preferred.

The alkylenepolyamine with which the fibers are contacted can be diluted with up to about 50% of its weight of substantially any liquid which is an unreactive solvent for the polyamine and is unreactive toward cellulose. Illustrative examples of suitable liquid diluents include "polar liquids," which term is used to refer to liquids having a relatively high dielectric constant which yield hydrogen-bonded complexes of noticeable strength with alkylenepolyamines, such as: water; water-soluble ketones such as acetone, and the like. Also suitable are non-polar organic liquids including hydrocarbons such as the hexanes, the pentanes, and the like; and symmetrically halogenated hydrocarbons such as carbon tetrachloride, and the like.

The fibers which have been contacted with the alkylenepolyamine-containing liquid can be freed of the unattached polyamine by a mechanical removal employing the usual procedures and apparatus for removing a liquid from textile fibers. The use of squeeze rolls or centrifuges is preferred.

Where it is desired to produce substantially undegraded native cellulose fibers of reduced crystallinity, the fibers are preferably immersed in a polar liquid solution of an alkylenepolyamine, such as a water-diluted alkylenepolyamine containing at least about 60% by weight of the polyamine. The use of such solutions containing from about 70 to 96% polyamine, and the freeing of the contacted fibers of the polyamine by mechanically removing part of the polyamine and extracting the remainder with a low boiling polar liquid which is inert toward cellulose is preferred. The use of acetone as the polar extracting liquid is particularly preferred. The extent of the reduction of crystallinity depends upon the length of time for which the fibers are contacted with the polyamine.

The X-ray diffraction patterns of cellulose fibers which have been treated with polyamine solutions to produce polyamine-decrystallized fibers are those of cellulose I; but the heights of the characteristic diffraction peaks are much reduced, indicating reduced crystallinities. Crystallite size in a polyamine-treated decreases from about 220 glucose units (for the untreated cotton) to about 110 glucose units. The polyamine-treated cellulose exhibits an increased moisture regain as well as increased water retention or imbibition. Tensile tests made on polyamine-treated yarns and cords show that the breaking strength has not been significantly changed, but the percent elongation-at-break has been increased, resulting

in increased toughness. Determinations of twist show that the treatment causes no significant change in the twist of a yarn.

Where it is desired to produce liquid-free distended native cellulose fibers in which the unit cells remain distended due to an alkylenepolyamine-cellulose complex, the cellulose fibers are preferably immersed in a substantially pure polyamine. In general, the formation of polyamine-cellulose complex is completed in about 4 hours. The fibers are preferably freed of unattached polyamine by mechanically removing part of the polyamine and evaporating the remainder of the unattached polyamine. The evaporation of the polyamine is preferably conducted under a reduced pressure. A pressure of less than about 10 millimeters of mercury is preferred.

Liquid-free distended native cellulose fibers in which unit cells are distended by alkylenepolyamine-cellulose complexes, are characterized by a wooly handle i.e., springiness with a warm feel. The cross-sectional area of ethylenediamine distended cotton fibers is about 40% greater than that of the original fibers. X-ray diffraction analyses reveals that the liquid-free distended fibers exhibit the interferences characteristic of the ethylenediamine-cellulose complex which have heretofore been observed only in fibers that were wet with liquid ethylenediamine. An extremely rapid rate of hydrolysis in the presence of hot aqueous acid is one indication of the enhanced reactivity of the polyamine distended fibers. The crystallite length of the distended fibers is short; that of distended cotton fibers being about 100 glucose units, as compared to 225 for the native fibers. The greatly increased interplanar distances of the distended fibers make it easy for dyes and other fiber impregnants that are applied dissolved to penetrate into the crystallite region where they become securely held by a collapse of the distended structure that occurs when the dyestuff solvent is removed. This trapping of the dyestuffs within the crystalline region tends to produce dyed cottons which are fast toward laundering and tends to enable the fibers to take up more dyestuff, resulting in deeper shades.

The presence of the alkylenepolyamine molecules held within the cellulose fiber by hydrogen bond-type linkages renders the distended fibers susceptible to the production of alkylenepolyamine derivatives in situ within the fibers. Such reactions can be accomplished by contacting the distended fibers with a non-polar organic liquid solution, such as a hexane or carbon tetrachloride solution of a reactant capable of reacting with an alkylenepolyamine.

The following examples, which are not to be considered as limiting, illustrate details of the production of substantially undegraded cellulose fibers of reduced crystallinity which are free of non-cellulosic components and the production of liquid-free cellulose fibers in which the unit cells are distended by the presence of alkylenepolyamine-cellulose complexes.

EXAMPLE 1

Decrystallization of cotton cellulose with alkylenepolyamines

Air-dry kiered cotton singles yarn (20 g.) was immersed in 300 ml. of 96% ethylenediamine, under a nitrogen atmosphere. After a 4-hour immersion, the major portion of the liquid diamine was expelled from the reaction vessel by nitrogen pressure. The diamine-wet cotton was thoroughly washed with acetone and finally extracted with acetone to remove the remaining ethylenediamine.

Examination of the air-dry product by X-ray diffraction methods indicated that a considerable reduction in crystallinity has been obtained and that the crystalline modification of the remaining crystalline regions was still that of native cellulose (cellulose I). The size of the crystallites was found to have been largely reduced from an original value of 220 glucose units for the untreated cotton to 116 for the decrystallized product.

EXAMPLE 2

Twenty gram skeins of air-dry kiered cotton yarn were treated as in Example 1 with 300 ml. of aqueous solutions of ethylenediamine of the following concentrations: 60%, 70%, and 80%.

X-ray examination of the products indicated that the cotton treated with the 60% ethylenediamine had been little affected. Considerable decrystallization was effected by the two higher concentrations.

The effect of these solutions on the crystallinity was confirmed from crystallinity determinations by a chemical method based on the rate of hydrolysis of the treated cottons by hot, mineral acid. According to this method the sample treated with the 60% ethylenediamine solution was 66% crystalline while the other two treated cottons were 40–45% crystalline. The length of the crystallites in the cotton treated with the 60% solution was found to be 172 glucose units while the more concentrated solutions of the diamine both reduced the crystallite length to 114–116 glucose units.

EXAMPLE 3

Alkylenepolyamine-distended cotton fibers

Air-dry kiered cotton yarn (20 g.) was treated with 300 ml. of 98% ethylenediamine (containing about 2% of water) for 4 hours at 20° C. under a nitrogen atmosphere. The major portion of the liquid diamine was expelled after the 4-hour period and the remaining liquid was removed by vacuum evaporation at 8 mm. pressure. The vacuum distillation was continued for 8 hours with boiling water surrounding the reaction vessel. The product so obtained was dry to the touch and had only a slight odor of the diamine although it contained 17.3% of ethylenediamine.

Examination of this product by X-ray diffraction methods indicated the formation of a cellulose-ethylenediamine complex with greatly distended interplanar spacings in the crystalline regions. The 101 interplanar spacing in the complex is 11.37 A. as compared to 6.03 A. for this same spacing in untreated cotton.

EXAMPLE 4

Twenty grams of air-dry kiered cotton yarn was treated with 300 ml. of 97% ethylendiamine (containing about 3% of water) exactly as in Example 3. The diamine content of this yarn after vacuum distillation was 19.7%. The stability of the diamine complex towards solvents was determined by extracting 1 g. samples of the yarn for 4 hours with 200 ml. each of the following solvents (the extractions were made in Soxhlet extractors at the boiling point of the respective solvents):

Hexane	Methyl ethyl ketone
Carbon tetrachloride	Isopropyl alcohol
Chloroform	Methyl n-propyl ketone
Ethyl acetate	Methyl isobutyl ketone
Diethyl ketone	Methyl alcohol
Acetone	Water

The complex was found to be stable toward extraction with the non-polar solvents, hexane and carbon tetrachloride. Chloroform removed only about 30% of the initial diamine from the complex during extraction. All the oxygen-containing polar solvents removed at least 90% of the diamine from the complex during a 5-hour extraction.

Of those solvents which decompose the complex, the low boiling polar solvents give a decrystallized product mainly of the cellulose I crystalline modification. The high boiling polar solvents, including water, give a highly crystalline product of the cellulose I modification.

Microscopic examination of fibers from the treated yarns indicated that the cross section of the dry fibers

containing 19.7% ethylenediamine was 40% greater than for untreated fibers.

EXAMPLE 5

Six approximately 5 g. skeins of alcohol extracted, kiered cotton yarn were treated with 800 ml. of 95% ethylenediamine (containing about 5% water) exactly as in Example 3. These yarns were found to contain 23.7% ethylenediamine. They were tested for dye receptivity with the following three dyes: Chloratine Fast Blue 4GL (2%), Ponsol Jade Green D (2%), and Cloth Fast Red BR (2%). These represent a direct dye, a vat dye, and an acid type dye, respectively. In each case the receptivity of the dye was considerably greater for the complex as compared with the untreated cotton.

EXAMPLE 6

A batch of diamine-distended yarns containing 21.6% ethylenediamine, was prepared exactly as in Example 3 from kier-boiled, cotton singles yarns. The tensile data obtained on the treated yarns as compared with the untreated control yarn are summarized below:

	Treated Yarn		Control Yarn
	Conditioned 48 hours	Not conditioned	
Yarn Number (Grex)	427.95	395.28	369.7
Breaking Strength (Grams)	595±11	578±19	395±9
Tenacity at Break (Grams/Grex)	1.391	1.463	1.067
Elongation at Break (Percent)	12.7	11.2	7.45
Elastic Recovery (Percent)	14.1±0.3	----------	27.3±1.6

EXAMPLE 7

Air-dry kiered cotton yarn (16.5 g.) was immersed in 340 g. of anhydrous hexamethylenediamine (HMDA) at 50° C. under a nitrogen atmosphere. After 4 hours the liquid hexamethylenediamine was drained off. Portions of the remaining liquid diamine were removed by vacuum distillation at 8 mm. pressure. The vacuum distillation was continued until the yarn in the flask appeared to be free of excess diamine. On cooling and examination the yarn was found to be encrusted with a coating of solidified hexamethylenediamine. To remove the remaining excess diamine, the treated yarn was extracted for 4 hours at the boiling point with n-hexane. After air-drying the skeins of yarn were perfectly dry to the touch and had no odor of the hexamethylenediamine. The treated skeins were found to contain 29.2% HMDA.

X-ray examination of this material indicated that a new cellulose-complex had been obtained with greatly expanded interplanar spacings in the crystalline regions. The interplanar spacing for the HMDA-cellulose complex was found to be 15.5 A. as compared with 6.03 A. in untreated cotton.

Tensile data on the yarn containing the HMDA-cellulose complex together with that of the control yarn are summarized below:

	Yarn containing HMDA-cellulose complex		Control Yarn
	Conditioned 24 hours	Not conditioned	
Yarn Number (Grex)	466.5	469.7	369.7
Mean Break Strength (Grams)	573.5±15.6	567.5±12.8	394.7±8.9
Tenacity (Gram/Grex)	1.229	1.208	1.067
Mean Elongation at Break (Percent)	11.4±.5	12.2±.5	7.4±.2
Mean Elastic Recovery (Percent)	18.3±1.5	----------	27.3±1.6

A microscopic examination of fibers from the treated yarns indicated that the cross-sectional area is 62% greater than for the untreated fibers.

Dye receptivity tests were run on skeins of the HMDA-cellulose complex using the same three dyes listed in Example 5. The same effect was observed here as with the ethylenediamine-cellulose complex, except to a greater degree. In all cases the yarn containing the HMDA-cellulose complex dyed to a much deeper and brighter shade than did the control yarn.

EXAMPLE 8

Air-dry kiered cotton yarn (20.5 g.) was treated with 400 ml. of redistilled diethylenetriamine (DETA) (98.5% triamine containing 1.5% of water). The excess liquid triamine was drained off after a 4-hour period and most of the remaining excess triamine was removed by vacuum evaporation at 5 mm. pressure. The vacuum distillation was continued overnight. The treated cotton was completely dry to the touch and had only a slight odor of the amine. Electrometric titration of a water extract of the treated cotton indicated a triamine content of 36.7%.

X-ray examination of this product indicated that a new triamine-cellulose complex was formed. The X-ray diffraction data show that the DETA-cellulose complex possesses interplanar spacings similar to those of the ethylenediamine-cellulose complex described in Example 3.

Tensile tests of the DETA-cellulose complex showed that there was practically no change in tenacity of the treated yarn relative to the control, but elongation increased 56% and elastic recovery decreased 24%.

A decrystallization which produces substantially undegraded native cellulose fibers of reduced crystallinity changes the fiber properties in a way that cooperates advantageously with the changes brought about by impregnating fibers with a resin. Numerous processes of treating textile fibers with resins are known to impart desirable properties such as wrinkle resistance, shrink resistance, water repellency, flame resistance and the like. Typical textile treating resins include the aminoplast resins such as polymethylolmelamines, poly(dimethylolethylene urea), the melamine and/or urea-formaldehyde polymers; alkyd resins such as the polyesters of polyhydric alcohols with maleic acid and the like acids; polyethers such as the polyethers produced by reacting an epihalohydrin with a polyhydric alcohol; and the methylol phosphorus polymers such as those described in U.S. Patent No. 2,668,096 and copending patent application Serial No. 378,437 filed September 3, 1953. While treating textiles with such resins produced one or more of the indicated advantageous effects, a resin treatment is characteristically accompanied by an undesirable reduction in the strength of the textile fibers. However, a combination of a decrystallization treatment with the resin treatment imparts the desired effects of the resin treatment and results in a reduction in strength which is materially less than that caused by the resin treatment of the native fibers. A process of imparting the advantageous effects of a resin treatment to native cellulose fibers, without materially reducing the strength of the fibers, comprises, decrystallizing the fibers by a process which produces substantially undegraded native cellulose fibers of reduced crystallinity, and impregnating the decrystallized fibers with the resin.

EXAMPLE 9

Resin treatment of decrystallized cotton cellulose

Cotton singles yarn having the crystalline modification and the crystal size of the decrystallized cotton yarns of Examples 1 and 2 were produced by the decrystallization process of U.S. Patent No. 2,580,491.

Samples of both the decrystallized yarn and the undecrystallized native yarns were padded, to a dry pickup of about 8%, with a precondensate of a modified urea formaldehyde resin. The resin treatment imparted a loss of about 48% breaking strength to the native cotton

yarns; but it imparted a loss of only about 36% to the decrystallized yarns.

Precondensates of three ketone-formaldehyde resins, one a commercial product, were also applied to native and decrystallized yarns, to a dry pickup of about 10%. These resin treatments imparted strength losses of 35–48% to the native cotton yarns; but imparted losses of only 10–30% to the decrystallized yarns.

In each case the resin-treated decrystallized yarns exhibited an elongation which was greater than that of the native yarns.

We claim:

A process of producing resin-impregnated native cellulose fibers without materially reducing their strength which comprises treating native cellulose fibers with a liquid alkylenepolyamine from the group consisting of ethylenediamine, tetramethylenediamine, diethylenetriamine, and hexamethylenediamine until a substantially undegraded native cellulose fiber of reduced crystallinity is produced, impregnating said treated fibers with a urea-formaldehyde resin, and then drying the impregnated fibers.

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