

United States Patent Office

2,824,779

Patented Feb. 25, 1958

1

2,824,779

CARBAMOYLETHYL, CARBOXYETHYL, AND AMINOETHYL CELLULOSE ETHER TEXTILE FIBERS AND PROCESS OF MAKING THE SAME

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No Drawing. Application March 9, 1955
Serial No. 493,313

10 Claims. (Cl. 8—117)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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This invention relates to the production and use of cellulosic textile fibers containing carbamoylethyl radicals ($-\text{CH}_2\text{CH}_2\text{CONH}_2$), and other beta-substituted ethyl radicals, attached to oxygen atoms of cellulose molecules of the fibers.

Among the textile fibers (i. e., fibers which have been woven, or are capable of being woven) the native or natural vegetable textile fibers are unique. Chemically they are substantially the same as various man-made textile fibers. They are composed of cellulose in the form of high polymers in which anhydroglucose units are the recurring structural units. However, the natural vegetable textile fibers have a unique combination of many desirable textile properties, due to the complex laminated structures in which their cellulose molecules are arranged. For example, in the American Dyestuff Reporter, February 15, 1954, pages 2 to 10, it is pointed out that the natural textile fibers, such as cotton fibers, possess a combination of over fifty properties to which their outstanding performance under all types of service conditions are due. The article also points out that, when the proper conditions for reaction are found, native vegetable fibers can be chemically modified, so that they acquire certain new fiber properties while retaining the intrinsic structure that gives them a combination of desirable textile properties.

It has previously been discovered that cellulose can be caused to react with acrylamide, when the cellulose is immersed in a liquid containing a strongly basic water-soluble hydroxide and acrylamide and maintained at temperatures between about 0° and 40° C. However, the products of such a reaction are not textile fibers. Even when the cellulose employed is a natural vegetable textile fiber, the products of the immersion reaction are aqueous media-soluble cellulose ethers which are only useful as organic chemicals.

The primary object of this invention is to provide a process of chemically modifying textile fibers composed of cellulosic molecules arranged in the complex laminated structure characteristic of natural vegetable textile fibers, to produce textile fibers that have substantially the same molecular arrangement and textile properties, but have different chemical properties. A further object is to provide a process of etherifying cellulose hydroxy

2

groups while they are attached to cellulose molecules that are arranged in the complex laminated structure characteristic of natural vegetable textile fibers, so that the hydrogen atoms of such hydroxy groups are replaced by beta-substituted ethyl radicals. A further object is to provide a process of etherifying cellulosic textile fibers that approaches the simplicity and ease of operation found in the conventional additive finishing processes. A further object is to provide novel etherified cellulosic textile fibers, composed of cellulose molecules and etherified cellulose molecules arranged in the complex laminated structure characteristic of natural vegetable textile fibers, in which fibers the radicals that replace hydrogen atoms of cellulose hydroxy groups consist essentially of: carbamoylethyl radicals; carboxyethyl radicals; aminoethyl radicals; a mixture of carbamoyl and carboxyethyl radicals; a mixture of carbamoyl and aminoethyl radicals; a mixture of carbamoylethyl, carboxyethyl and aminoethyl radicals; or beta-substituted ethyl radicals of the formula $-\text{CH}_2\text{CH}_2-\text{A}$ where A represents an N-substituted carbamoyl group, an esterified carboxyl group, or an N-substituted amino group.

In general, in accordance with the present invention, cellulosic textile fibers composed of cellulosic molecules arranged in the complex laminated structure characteristic of natural vegetable textile fibers, are produced by: wetting cellulosic textile fibers composed of hydroxyl group-containing cellulosic molecules arranged in the complex laminated structure characteristic of natural vegetable textile fibers with an inert solvent, which is unreactive toward cellulose, containing from about 1.0 to 12 weight percent of a dissolved alkali hydroxide or a quaternary ammonium hydroxide and from about 1.0 to 55.2 weight percent (as shown in Table II, below) of dissolved acrylamide; mechanically freeing the wetted fibers of substantially all of the liquid in excess of the amount retained by the porous portions of the fibers; and heating the so-treated fibers at a temperature above the freezing point of the liquid but below the temperature at which the thermal degradation of the fibers becomes appreciable, until etherification occurs. The tendency of the reaction to form only carbamoylethyl cellulose ethers (e. g. to convert cotton fibers to etherified fibers in which the radicals that replace hydrogen atoms of cellulose hydroxy groups consist only of carbamoylethyl radicals) is enhanced by heating the fibers that have been wetted with and freed of the excess liquid to a temperature above about 100° C. for less than about 20 minutes. The etherification reaction appears to go to substantial completion within about 20 minutes, even at about 60° C., and, in general, the reaction proceeds only as long as the fibers are moist. The tendency of the reaction to form only carbamoylethyl cellulose ethers is further enhanced by the employment of a quaternary ammonium hydroxide as the strong base.

In general, the etherified cellulosic textile fibers produced in accordance with this invention retain substantially all of the textile properties that characterize the natural vegetable textile fibers, and are useful wherever a natural vegetable textile fiber is useful. For example, a cotton cloth carbamoylethylated to a nitrogen content of 3.6 percent (corresponding to about 1 carbamoylethyl radical per 2 anhydroglucose units) is almost indis-

3

tinguishable from the untreated cloth, on the basis of hand, feel, and appearance, and can be used wherever the untreated cloth is used. However, such an etherified cotton cloth, and all of the etherified cellulosic textile fibers produced in accordance with this invention, exhibit properties such as dyestuff affinity, moisture affinity, insulating properties, chemical activity, and the like, resembling those of wool or synthetic textile fibers.

Substantially any cellulosic textile fibers composed of cellulosic molecules containing cellulose hydroxy groups arranged in the complex laminated structure characteristic of the natural vegetable textile fibers, can be etherified to produce etherified cellulosic textile fibers in accordance with this invention. In addition, substantially any cellulosic fibers containing cellulose hydroxy groups can be etherified by the simple process provided by this invention.

The fibers can be treated in the form of free fibers, sliver, yarn, thread or fabric. The apparatus and handling techniques usually employed for the chemical treatment of textile fibers can be used. In general, the employment of the fibers in the form of spun textiles such as threads or cloth is preferred.

Illustrative examples of fibers which can be employed include cotton, flax, ramie, and the like natural vegetable textile fibers; mercerized, partially acetylated, partially cyanoethylated, or the like chemically modified natural vegetable textile fibers that contain cellulose OH groups and the intrinsic elements of the structure of natural vegetable textile fibers; and, derived or regenerated cellulosic textile fibers, such as the fibers regenerated from the natural vegetable textile fibers by the cuprammonium or the viscose process, or the like derived or regenerated cellulosic textile fibers that are derived from natural vegetable textile fibers, contain cellulose OH groups, and have a structure that retains the intrinsic elements of the structure of the natural vegetable textile fibers but is produced by a disruption and rearrangement of the intrinsic elements of the structure of natural vegetable textile fibers. The natural vegetable textile fibers are particularly suitable fibers for employment in the present process.

Substantially any inert solvent, which is substantially unreactive toward cellulose and is appreciably miscible with acrylamide and the strong base used as a catalyst, can be used as the reactant-containing liquid, i. e., the liquid which contains the acrylamide and the basic catalyst. Illustrative examples of suitable liquids include water or aqueous bases; molten acrylamide; liquid amines, such as pyridine, piperidine and the like; hydrocarbons such as benzene, toluene, hexane and the like; ethers such as diethyl, diphenyl, dioxane, and the like; and ketones such as acetone, methyl ethyl ketone, methyl butyl ketone and the like. Water is a preferred liquid for employment in the present process.

Substantially any strong base capable of dissolving along with acrylamide in an effective concentration, in the reactant-containing liquid, can be used as the catalyst. Illustrative examples of suitable strong bases, include: the quaternary ammonium hydroxides such as benzyl trimethyl ammonium hydroxide, dibenzyl dimethyl ammonium hydroxide, tetraethyl ammonium hydroxide, and the like; the alkali metal hydroxides; mixtures of the quaternary ammonium hydroxides, the alkali metal hydroxides, or the quaternary ammonium hydroxides and the alkali metal hydroxides; and the like strong bases. The use of the quaternary ammonium hydroxides, particularly benzyl trimethyl ammonium hydroxides such as those available under the trade name Triton B, is preferred.

In addition to the acrylamide and the basic catalyst, the reactant-containing liquid can contain textile fiber treating agents; such as softening agents, lubricating agents, flammability retarding agents, and the like, which

4

are unreactive toward the acrylamide and the basic catalyst.

At the time the fibers are wetted with the reactant-containing liquid, the latter can be maintained at substantially any temperature above its freezing point and below its boiling point; but, in general, the liquid is preferably maintained at about room temperature (i. e. from about 20° to 30° C.). Where the reactant-containing liquid is maintained at a temperature appreciably higher than room temperature, the wetted fibers are preferably substantially immediately freed of excess liquid.

The step of mechanically removing, from fibers wetted with the reactant-containing liquid, substantially all of the liquid in excess of the amount retained by the porous portions of the fibers, is an important element of the present process. If the fibers are reacted with the acrylamide for a substantial length of time in the presence of a materially greater amount of the solution than is necessary to wet out the fibers, the reaction tends to produce a water soluble cellulose ether having none of the textile properties characteristic of natural vegetable textile fibers. In general, it is preferable to wet the fibers with the reactant-containing liquid by a "controlled impregnation," i. e., by a procedure equivalent to a textile padding operation in that the fibers are wetted with and freed of the excess liquid by mechanical means, which procedure is controlled so that, substantially immediately after the fibers have been uniformly wetted, a proportion of the entrained liquid that is about equal to that which is usually removed by the squeeze rolls of a textile padder, is removed from the wetted fibers. The wetting of the fibers can be accomplished by the usual immersion and/or spraying techniques, and the freeing of the wetted fibers of the excess liquid can be accomplished by the usual squeezing and/or centrifuging techniques controlled to reduce the wet pickup of the fibers to from about 60 to 150% of their weight of reactant-containing liquid.

The proportionate amount of catalyst contained by the reactant-containing liquid can be varied widely. Both the catalyst and the acrylamide can be incorporated in the liquid in the form of solutions, emulsions or dispersions of compounds in a liquid in which they are appreciably soluble. The proportion of the catalyst is not critical, but the use of a proportion materially smaller than about 1.0% of the weight of the reactant-containing liquid tends to result in an undesirably slow reaction at the moderate or lower reaction temperatures; and the use of a proportion materially greater than about 12% provides little or no increase in rate of reaction, and tends to cause the more rapid depletion of the textile properties characteristic of natural vegetable textile fibers, due to a reaction between the catalyst and cellulose.

In general, the proportion of acrylamide in the reactant-containing liquid should be such that the amount of liquid left in contact with the fibers, preferably from about 70 to 110 parts of liquid per 100 parts of fibers, contains a slight molar excess of acrylamide for the amount of cellulose OH groups it is desired to convert to carbamoylethyl ether groups. The use of an acrylamide concentration of as little as 1% by weight of the reactant-containing liquid imparts an appreciable change to cotton textile fibers. In the case of cotton fibers (where about 70 to 110% of liquid is left in contact with the fibers after the mechanical removal of excess liquid) and acrylamide content of 25% by weight of the liquid provides an adequate molar excess of acrylamide for the conversion of about 1 cellulose OH group per 5 or 6 anhydroglucose units of the fibers.

The fibers can be reacted with the acrylamide contained in the amount of reactant-containing liquid retained in the porous portions of the fibers at substantially any temperatures above the freezing point of the liquid and below the degradation temperature of the fibers. However, in order to use up most of the acrylamide in a reasonable time,

the reaction is preferably conducted at a temperature of from about 60° to 150° C. In general, reaction times of from about 2 to 15 minutes, with the longer times being used with the lower temperatures, are sufficient to convert the acrylamide to O-linked carbamoyl ethyl radicals. Where a high degree of etherification is desired, the fibers can be subjected to a plurality of controlled impregnations and heatings with the heatings conducted so that the fibers are partially or substantially completely dried between each controlled impregnation.

Where it is desired to conduct the etherification so that carbamoyl ethyl radicals are substantially the only radicals introduced by the reaction, the fibers are preferably wetted with a reactant-containing liquid containing a relatively high proportion of acrylamide and from about 1 to 12 weight percent of dissolved quaternary ammonium hydroxide. The proportion of the acrylamide can exceed that which is soluble in the reactant-containing liquid as long as a flowable emulsion or suspension is produced. Where an aqueous reactant-containing liquid is employed, the use of a substantially saturated solution of the acrylamide dissolved in a water solution of the quaternary ammonium hydroxide, is preferred. After the controlled impregnation of the fibers, the latter are preferably heated at from about 90° to 140° C. for from about 3 to 8 minutes. When cotton fibers are etherified so that carbamoyl ethyl radicals are substantially the only radicals introduced, the fibers exhibit an enhanced but mild affinity for either acid wool dyes which are not cellulose dyes or basic dyes which are not cellulose dyes, and also dyes readily with cotton dyes.

Where it is desired to conduct the etherification so that both carbamoyl ethyl and carboxyethyl radicals are introduced by the reaction, the fibers are preferably wetted with a reactant-containing liquid containing from about 2 to 12 weight percent of dissolved alkali metal hydroxide and from about 1.0 to 55.2 weight percent of dissolved acrylamide. With the lower concentrations of alkali (i. e., from about 1.0 to 4 weight percent) only a very small amount of carboxyethyl groups are formed, but with the higher concentrations of alkali greater amounts of carboxyethyl groups are formed. After the controlled impregnation of the fibers, the latter are preferably heated to from about 90° to 140° C. for from about 3 to 8 minutes. When the fibers are etherified so that both carbamoyl ethyl and carboxyethyl radicals are introduced, they exhibit little, if any, affinity for the acid wool dyes but exhibit a strongly enhanced affinity for the basic dyes. They also dye readily with cotton dyes.

Both the carbamoyl ethyl and the carboxyethyl radicals introduced into cellulosic textile fibers in accordance with this invention, can readily be caused to undergo the reactions characteristic of carbamoyl or carboxyl groups. As was discussed above, the carbamoyl ethylation reaction with the amount of liquid reactant brought into contact with the fibers by a controlled impregnation (i. e., the amount retained in the porous portions of the fibers) appears to introduce ether groups primarily in the porous portions of fibers. We have also discovered that, when cellulosic textile fibers which have been so carbamoyl ethylated and/or carboxyethylated, are subjected to a further reaction with a compound capable of reacting with a carbamoyl or a carboxyl group, this compound will react with these groups even if it is also reactive with cellulose, if it is used as a liquid reactant in an amount which is just retained by the porous portions of the fibers. The resultant fibers retain most of their desirable natural textile properties, but exhibit new chemical properties due to the incorporation of beta-substituted ethyl ether groups. Thus, the present invention provides a two step process for the production of cellulosic textile fibers containing etherified cellulose molecules in which the radicals that replace cellulose hydroxy groups contain beta-substituted ethyl radicals of the formula $-\text{CH}_2\text{CH}_2-\text{A}$ where A represents an N-substituted carbamoyl group, an O-sub-

stituted carboxyl group, an amino group, or an N-substituted amino group.

Illustrative examples of compositions capable of reacting with either or both carboxyethyl and carbamoyl ethyl groupings include: aliphatic aldehydes such as formaldehyde, acetaldehyde, butyraldehyde and the like; aqueous hypohalites such as sodium hypochlorite, potassium hypobromite and the like; aqueous alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and the like; alcohols such as the butyl alcohols, the fatty oil alcohols and the like; and methylol group-containing compositions such as the further polymerizable methylol phosphorus polymers described in our copending applications Serial Nos. 378,437, now U. S. Patent 2,809,941; 393,020; 421,212; and 467,899 filed September 3, 1954; November 18, 1953; April 5, 1954; and November 9, 1954.

Textile chemists have long sought for processes of attaching amino groups to cellulosic molecules to render them capable of undergoing fast dyeings with acid wool dyes. Numerous processes for accomplishing such an "aminization" have been developed. However, in general, the prior aminization processes cause an appreciable increase in the stiffness of cellulosic textile fibers. We have now discovered that, by means of the two step reaction process described above, the aminization can be accomplished without causing an appreciable increase in stiffness. To accomplish this, fibers which have been carbamoyl ethylated in accordance with the present process are subjected to a reaction with the amount of an aqueous hypohalite solution retained in the porous portions of the fibers, for example, by means of an ordinary aqueous hypohalite bleaching process. Where the carbamoyl ethylation is conducted under conditions conducive to the formation of both carbamoyl ethyl and carboxyethyl ether groups, the aminized fibers produced by such a hypohalite reaction not only exhibit wool like dyeing properties, but also exhibit an increased affinity for water and basic dyes, due to the presence of carboxyethyl groupings.

The proportion of carboxyethyl groupings present in cellulosic textile fibers that have been carbamoyl ethylated in accordance with the present invention and/or in cellulosic textile fibers that have been aminized in accordance with the present invention, can be increased by reacting the fibers with an aqueous alkali metal hydroxide. The aqueous alkali metal hydroxide reaction can be accomplished by a wide variety of procedures including the ordinary mercerization procedure.

The following examples are illustrative of the details of at least one method of practicing the invention.

EXAMPLE 1

Carbamoyl ethylation

The cellulosic textile fibers used were cotton fibers in the form of 48 x 48 sheeting which had been scoured by the usual procedures.

The reactant-containing liquids used were aqueous solutions containing the weight percentages of acrylamide and either sodium hydroxide or the quaternary ammonium hydroxides available under the trade name Triton B indicated under "Solution composition" in Table I.

Samples of the cloths were wetted and mechanically freed of excess reactant-containing liquid by passing the samples through a conventional textile padder having squeeze rolls set to leave the wet pickups indicated under "Wet pickup" in the following table. The so-impregnated clothes were then heated at 115° C. for the times indicated under "Heating time" in Table I.

The treated samples were washed, dried and tested for nitrogen content and warp breaking strength by conventional analytical methods. The proportions of nitrogen introduced by the treatment and the breaking strengths in pounds and in percent retained by the treated samples

are indicated under "Nitrogen" and "Breaking strength" in Table I.

nary ammonium hydroxide catalyzed carbamoylethylation process described in Example 1.

TABLE I

Sample No.	Solution Composition			Wet Pickup, Percent	Heating time, min.	Breaking strength		Nitrogen, Percent
	Acrylamide, percent	NaOH, percent	Triton B, percent			lbs.	Percent retained	
Untreated control.....					0	55.8		0.05
1-----	0	0	5	73	5	55.2	99	0.03
2-----	25	0	5	72	5	52.8	95	0.98
3-----	0	0	5	74	10	53.6	96	0.04
4-----	25	0	5	70	10	55.5	99	0.72
5-----	0	0	10	73	5	52.7	94	0.04
6-----	25	0	10	71	5	50.0	90	1.20
7-----	0	0	10	70	10	53.6	96	0.04
8-----	25	0	10	74	10	50.6	91	1.18
9-----	0	5	0	77	5	52.9	95	
10-----	25	5	0	81	5	45.8	82	1.13
11-----	0	5	0	77	10	53.3	96	
12-----	25	5	0	82	10	46.7	84	1.17
13-----	0	10	0	84	5	54.8	98	
14-----	25	10	0	93	5	47.5	85	0.94
15-----	0	10	0	84	10	54.8	98	
16-----	25	10	0	90	10	47.7	85	0.89

EXAMPLE 2

Carbamoylethylation with more concentrated reactants

Additional samples of the cotton sheeting were carbamoylethylated by the procedure described in Example 1 using reactant-containing liquids of the composition indicated in Table II, applied to a wet pickup of about 80%. The nitrogen contents of the so-treated samples are indicated in Table II.

TABLE II

Sample No.	Composition				Nitrogen, percent
	Acrylamide, percent	NaOH, percent	Triton B, percent	H ₂ O, percent	
1-----	0	12.9	0	87.1	
2-----	14.5	12.9	0	72.6	0.39
3-----	55.2	2.3	0	42.5	1.85
4-----	55.2	0	2.3	42.5	1.28

EXAMPLE 3

Carbamoylethylation in two steps

Samples of the same cotton sheeting were carbamoylethylated by padding the fabrics in aqueous solutions containing acrylamide and a catalyst, then heating at 125° C. and at 140° C. for 4 minutes in a forced air oven. Samples 1, 2, and 3 of Table III were prepared by padding in the acrylamide containing solutions, drying at elevated temperatures then washing, whereas samples 4, 5, and 6 were prepared by retreating a portion of samples 1, 2, and 3 respectively, under the conditions given in the table.

TABLE III

Sample No.	Concentration of Reagents in Treating Solutions			Wet pickup of solution, percent	Drying temp., ° C.	Nitrogen content of finished fabric, percent	Breaking strength of finished fabric	
	Acrylamide, percent	Triton B, percent	NaOH, percent				lb.	retention, percent
1-----	25	0	4	80	125	1.7	51.3	92
2-----	25	5	0	73	125	1.0	59.5	106
3-----	48	0	4	81	125	2.2	51.8	93
4*-----	25	0	4	80	140	2.4	45.2	81
5*-----	25	5	0	73	140	1.3	50.4	90
6*-----	48	0	4	81	140	3.6	47.1	84

*Samples 4, 5, and 6 are retreatments of samples 1, 2, and 3 respectively.

EXAMPLE 4

Carbamoyl-, and aminoethylation

A sample of the same cotton sheeting was carbamoylethylated to a nitrogen content of 1.18% by the quater-

That carbamoylethylated cloth was padded with an aqueous 2.62% solution of sodium hypochlorite, using a conventional textile padder adjusted to leave a wet pickup of about 100%. The damp cloth was heated for 5 minutes at 110° C. in a forced draft oven and then was water washed and dried.

The so-treated cloth exhibited pronounced wool-like dyeing properties and was appreciably less stiff than a similar cloth aminoethylated to a much lower nitrogen content by a process involving reacting the cloth with 2-aminoethyl sulfuric acid in the presence of aqueous sodium hydroxide. Yet, the cloth treated in accordance with the present invention exhibited an affinity for acid wool dyes which are not cellulose dyes which was comparable to that of cloth that was aminoethylated by the aminoethyl sulfuric acid reaction.

When a sample of the above described carbamoylethylated cloth and a sample of the untreated cotton cloth from which the carbamoylethylated cloth was prepared were reacted with aqueous hypochlorite solutions of the same concentration (2.62%) by immersing the samples in the solution maintained at 80° C. for 5 minutes, in both cases, the cloths disintegrated.

An additional sample of the same cotton sheeting which had been carbamoylethylated to a nitrogen content of 1.28% by the quaternary ammonium hydroxide catalyzed carbamoylethylation process described in Example 2, was padded to a wet pickup of about 80% with an aqueous 0.52% sodium hypochlorite solution and was heated for 10 minutes to 105° C. The so-treated cloth exhibited a good hand and feel, and a strong affinity for acid wool dyes which are not cellulose dyes.

The cloth treated in accordance with the present process exhibited a reduction in warp breaking strength of only about 13% as compared to 28% when a piece of the same fabric was immersed in a 0.52% sodium hypochlorite solution maintained at only 80° C. for 10 minutes.

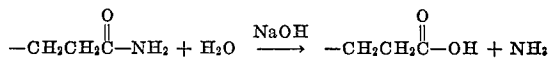
EXAMPLE 5

Comparative dyeings

Cotton and cotton etherified with carbamoyl ethyl and carboxyethyl radicals.—An 80 x 80 cotton print cloth was carbamoyl ethylated to a nitrogen content of 1.4% by the procedure described in Example 1 using aqueous 4% sodium hydroxide as the catalyst, a heating temperature of 125° C. and a heating time of 6 minutes. A control fabric was prepared by padding a piece of the same cloth with aqueous 4% sodium hydroxide and heating it in the same manner. Pieces of the etherified and control cloths were dyed in the same bath containing methylene blue (a basic dye which is not a cellulosic dye). The etherified cloth received a color which was appreciably darker than that received by the control cloth.

Other pieces of the etherified cloth and the control were soaked for about 65 hours in an aqueous 0.5% sodium hydroxide solution, washed free of lye, and then dyed in the manner described above. The lye treated etherified cloth received a much darker color than the lye treated control cloth, which received about the same color as the untreated control cloth.

As will be apparent to those skilled in the art, the nitrogen content indicates the attachment of carbamoyl ethyl radicals to the cotton during the etherification process and the increased affinity for the basic dye indicates that, in the lye catalyzed carbamoyl ethylation reaction, some of the carbamoyl ethyl radicals were converted to carboxyethyl radicals. In the lye soaking treatment, more of the radicals were so converted, probably in accordance with the equation:



Other pieces of the etherified cloth prepared using Triton B as catalyst and control cloth were dyed in a dyebath containing an acid wool dye which is not a cellulosic dye (Kiton Fast Red 3GLL). Neither cloth received a strong color, but the etherified cloth received a somewhat darker color than the control cloth.

As will be apparent to those skilled in the art, the absence of a strong affinity for the acid dye indicates the absence of basic groups such as amino groups and the slight affinity of the etherified cloth indicates that the attachment of the substantially neutral carbamoyl ethyl radicals imparted a somewhat increased affinity for acid dyes.

A piece of the etherified cloth containing both carbamoyl ethyl and carboxyethyl radicals prepared by the lye catalyzed carbamoyl ethylation described above was immersed in about 20 parts of an aqueous 0.65% sodium hypochlorite solution per part of cloth, and heated for 9 minutes. A piece of the control cloth prepared as described above was similarly treated with hypochlorite. The hypochlorite treated cloths were water washed and dyed in a dyebath containing Kiton Fast Red. The hypochlorite treated etherified cloth dyed a dark red, while the hypochlorite treated control fabric received substantially no color.

As will be apparent to those skilled in the art, the strong affinity for the acid dye indicates that the hypochlorite treatment had introduced amino groups into the etherified cloth, probably by a Hofmann degradation reaction of the carbamoyl ethyl groups, so that the so-treated cloth contained carbamoyl ethyl groups, carboxyethyl and aminoethyl groups.

Carbamoyl ethylated cloth in which substantially all of the ether groups are carbamoyl ethyl radicals.—A piece of 80 x 80 print cotton cloth was carbamoyl ethylated to a nitrogen content of 1.0% by the process described in Example 1, using aqueous 5% Triton B as the catalyst, a heating temperature of 105° C. and a heating time of 10 minutes. A control sample was prepared by padding

a piece of the same cloth with aqueous 5% Triton B and heating it in the same manner.

With both methylene blue and Kiton Fast Red the carbamoyl ethylated cloth dyed to a light color which was somewhat but not materially greater than the color received by the control cloth when the cloths were dyed as described above.

As will be apparent to those skilled in the art, the absence of strong affinity for either the basic or acid dyes indicates that substantially all of the nitrogen was present in the form of carbamoyl groups and that the cloth contained no appreciable proportion of carboxyethyl groups.

After a treatment with aqueous about 0.65% hypochlorite, in the manner described above, the hypochlorite treated carbamoyl ethyl cloth dyed a dark red with Kiton Fast Red; indicating the formation of aminoethyl groups as described above.

EXAMPLE 6

Ethers containing O-substituted carboxyl groups

A sample of cotton print cloth etherified with carboxyethyl radicals substantially free of other ether radicals was prepared in the manner described in Example 5. The etherified cloth was immersed for 15 minutes in an aqueous solution containing enough sodium hydroxide to produce a pH of 12. The cloth lowered the pH of the solution to 8.

As will be apparent to those skilled in the art the experiment demonstrates the capability of the cloth to act as a cation exchange material; and the conversion of carboxyl groups of the etherified cloth to sodium carboxyl groups ($-\text{CH}_2\text{CH}_2\text{COONa}$).

EXAMPLE 7

Ethers containing N-substituted amino groups

A sample of cotton print cloth etherified with aminoethyl radicals substantially free of carboxyl radicals was prepared in the manner described in Example 5. The etherified cloth was immersed for an hour in an aqueous solution containing 1% copper acetate and 0.25% acetic acid. After being removed and rinsed with water, the fabric contained an appreciable amount of copper and exhibited a blue color characteristic of a copper-amine complex.

We claim:

1. A process for carbamoyl ethylating cellulosic textile fibers containing at least 1 free hydroxyl group per 5 to 6 anhydroglucose units which comprises reacting said fibers with about from 60 to 150% of the weight of the fibers of a solution comprising 1–55.2% of acrylamide and 1 to 12 weight percent of a strong base from the group consisting of an alkali metal hydroxide and a quaternary ammonium hydroxide until there is introduced into the cellulose molecules about from 1 carbamoyl ethyl group per 6 anhydroglucose units to 1 carbamoyl ethyl group per 2 anhydroglucose units.

2. A process for producing carbamoyl ethylated cellulosic textile fibers the cellulose molecules of which are arranged in the complex laminated structure characteristic of natural vegetable textile fibers, said fibers containing at least 1 free hydroxyl group per 5 to 6 anhydroglucose units, which comprises wetting cellulosic textile fibers which are arranged in the said complex laminated structure characteristic of natural vegetable textile fibers with a solution, in a solvent which is inert to cellulose, containing about from 1 to 12 weight percent of a dissolved strong base from the group consisting of an alkali metal hydroxide and a quaternary ammonium hydroxide and about from 1 to 55.2 weight percent dissolved acrylamide, mechanically freeing the wetted fibers of substantially all of the liquid in excess of about from 60 to 150% of the weight of the fibers, and then heating the fibers at a temperature of about from 60° to 150° C. for

about from 2 to 15 minutes until there is introduced into the cellulose molecules about from 1 carbamoylethyl group per 6 anhydroglucose units to 1 carbamoylethyl group per 2 anhydroglucose units.

3. The process of claim 2 wherein the strong base is an alkali metal hydroxide.

4. The process of claim 2 wherein the strong base is a quaternary ammonium hydroxide.

5. Carbamoylethylated cotton textile fibers in which the cellulose molecules of the fibers are arranged in the complex laminated structure characteristic of natural cotton textile fibers and in which the cellulose molecules contain about from 1 carbamoylethyl group per 6 anhydroglucose units to 1 carbamoylethyl group per 2 anhydroglucose units.

6. A process for producing etherified cellulose textile fibers the cellulose molecules of which are arranged in the complex laminated structure characteristic of natural vegetable textile fibers in which about from 1 hydroxyl group per 6 anhydroglucose units to 1 hydroxyl group per 2 anhydroglucose units are etherified by carbamoylethyl and carboxyethyl groups, which process comprises wetting cellulosic textile fibers the cellulose molecules of which are arranged in the said complex laminated structure characteristic of natural vegetable textile fibers and which contain at least 1 free hydroxyl group per 5 to 6 anhydroglucose units with a solution, in a solvent which is inert to cellulose, said solution containing about from 1 to 12 weight percent of a dissolved strong base from the group consisting of an alkali metal hydroxide and a quaternary ammonium hydroxide and about from 1 to 55.2 weight percent dissolved acrylamide, mechanically freeing the wetted fibers of substantially all of the liquid in excess of about from 60 to 150% of the weight of the fibers, then heating the fibers at a temperature of about from 60° to 150° C. for about from 2 to 15 minutes, until there is introduced into the cellulose molecules about from 1 carbamoylethyl group per 6 anhydroglucose units to 1 carbamoylethyl group per 2 anhydroglucose units, and then further treating the fibers with a dilute aqueous solution of an alkali metal hydroxide until a portion of the carbamoyl radicals have been converted to carboxyl radicals.

7. A process for producing cellulosic textile fibers containing aminoethylated cellulose molecules, said cellulose molecules being arranged in the complex laminated structure characteristic of natural vegetable textile fibers in which about from 1 hydroxyl group per 6 anhydroglucose units to 1 hydroxyl group per 2 anhydroglucose units are etherified by aminoethyl groups, which process

comprises wetting cellulosic textile fibers containing at least 1 free hydroxyl group per 5 to 6 anhydroglucose units, the cellulose molecules of which are arranged in the said complex laminated structure characteristic of natural vegetable textile fibers with a solution, in a solvent which is inert to cellulose, said solution containing about from 1 to 12 weight percent of a dissolved strong base from the group consisting of an alkali metal hydroxide and a quaternary ammonium hydroxide and about from 1 to 55.2 weight percent dissolved acrylamide, mechanically freeing the wetted fibers of substantially all of the liquid in excess of about from 60 to 150% of the weight of the fibers, then heating the fibers at a temperature of about from 60° to 150° C. for about from 2 to 15 minutes, until there is introduced into the cellulose molecules about from 1 carbamoylethyl group per 6 anhydroglucose units to 1 carbamoylethyl group per 2 anhydroglucose units, then wetting the fibers with about from 60 to 150% of the weight of the fibers with an aqueous solution of sodium hypochlorite, and then heating the so-wetted fibers to convert a portion of the carbamoyl groups to amino groups.

8. Etherified cellulose textile fibers the cellulose molecules of which are arranged in the complex laminated structure characteristic of natural vegetable textile fibers in which a total of about from 1 hydroxyl group per 6 anhydroglucose units to 1 hydroxyl group per 2 anhydroglucose units are etherified by carbamoylethyl and carboxyethyl groups.

9. Etherified cellulose textile fibers the cellulose molecules of which are arranged in the complex laminated structure characteristic of natural vegetable textile fibers in which a total of about from 1 hydroxyl group per 6 anhydroglucose units to 1 hydroxyl group per 2 anhydroglucose units are etherified by carbamoylethyl and aminoethyl groups.

10. Etherified cellulose textile fibers the cellulose molecules of which are arranged in the complex laminated structure characteristic of natural vegetable textile fibers in which a total of about from 1 hydroxyl group per 6 anhydroglucose units to 1 hydroxyl group per 2 anhydroglucose units are etherified by carbamoylethyl, aminoethyl, and carboxyethyl groups.

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