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SPINNABLE CARBOXYMETHYLATED COTTON FIBERS AND THEIR PRODUCTION

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The invention herein described may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without the payment to us of any royalty thereon.

This invention relates to an improved process for carboxymethylating fibrous cellulosic materials and to the novel products produced thereby. In a particularly advantageous embodiment it provides spinnable carboxymethylated cotton fibers and a method for their production.

Various types of carboxymethylated celluloses have been known for over thirty years. The properties and advantages provided by the presence of carboxymethyl groups attached to cellulosic chains is well known.

Cotton cellulose is unique in that in addition to being composed of substantially pure alpha-cellulose; in its natural fibrous form, it has the properties a staple fiber must possess in order to be converted into yarns and fabrics by the conventional spinning methods and apparatus. These properties are hereinafter referred to as the properties of spinnable fibers.

While many processes for the chemical modification of cellulose fibers have been developed, the bulk of them are not suited for the production of spinnable cotton fibers. For example, while U. S. 2,448,153 discloses a process for the production of carboxymethylated celluloses containing 1 carboxymethyl group per 5 to 40 glucose units in a fibrous form; carboxymethylated cotton fibers so produced are not spinnable. While the cotton may be so treated in the form of yarn or threads and the carboxymethylated yarns or threads may be woven in the usual manner, they cannot be broken down into spinnable cotton fibers due to their adherence into mats. Similarly, a co-pending application of Daul and Reid, Serial No. 154,202, filed April 5, 1950, now Patent No. 2,617,707, employing the products of the above patent as the preferred starting material, discloses a process for the production of carboxymethylated celluloses containing more than 1 carboxymethyl group per 5 glucose units. The products of this process are fibrous and water soluble. However, like the former process, the latter is well suited for the production of yarns, threads, or textile, but not spinnable carboxymethylated cotton fibers.

Modern spinning and weaving practices have demonstrated remarkable advantages which can be obtained from a blend of two or more kinds of spinnable staple fibers.

We have discovered an improved method of

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conducting the carboxymethylation processes which has made possible the production of spinnable carboxymethylated staple fibers of cellulose containing up to about 1 carboxymethyl group per glucose unit. In addition to their particular advantage of being suitable for mixing with other staple fibers to form fiber blends having swelling, dyeing, ion-exchange, reactive (for example, for higher reactivity in crease-proofing process such as those disclosed in the co-pending application of Daul and Reid, Serial No. 156,032, filed April 14, 1950, now Patent No. 2,584,114), and the like properties best suited for a particular application, the spinnable carboxymethylated cellulose fibers produced by the process of this invention are more pliable, have a better hand and feel, a greater flexibility, and a more uniform and greater tensile strength than that of the carboxymethylcelluloses produced by any of the processes heretofore known.

As is described in the patent, cellulose carboxymethylated by the process of U. S. 2,448,153 to the extent of 1 carboxymethyl group per 5 to 40 glucose units is insoluble in water and aqueous alkaline solutions. Since this carboxymethylation is accomplished by the action of chloroacetic acid in the presence of concentrated aqueous solutions of alkali metal hydroxides (two water-soluble reagents); the patent logically teaches that, upon the attainment of the desired degree of reaction, the cellulosic materials are freed of reactants by mechanical means and water extraction. The co-pending application referred to above teaches that in the preferred "two-step" method of producing water-soluble carboxymethylated celluloses, the reagents used to carboxymethylate to below 1 carboxymethyl group per 5 glucose units (the first step), are removed in the same manner.

While extraction with an organic solvent rather than with water necessarily increases the expense of the process and the danger of fire, we have found that in the case of the removal of the reagents employed to carbomethylate a fibrous cellulosic material to the extent of 1 carboxymethyl group per 5 to 40 glucose units, the disadvantages are more than overcome by the advantageous results obtained. When the starting material is cotton fiber (in forms such as raw fiber, sliver, yarns, etc. that can be converted to spinnable fiber) the products are obtainable as spinnable cotton fibers as distinguished from non-spinnable ones; and, in any case, the products are more pliable, have a better hand and feel, a greater and more uniform tensile strength, and a greater

flexibility. These fibers were capable of being spun alone, or blended with other spinnable cellulose fibers and then spun.

The process of the present invention consists of: starting with a cellulosic material suitable for carboxymethylation by the process described in U. S. 2,448,153 in the form of raw fiber, sliver, roving, yarn, thread, or fabric; carboxymethylating said cellulosic material by the process of said patent to the extent of 1 carboxymethyl group per 5 to 40 glucose units; and removing the carboxymethylating reagents from the product by mechanical means and washing with liquid, water-miscible, organic solutions containing from about 1 to 30% water.

The mechanical means for removing the carboxymethylating reagents preferably comprise a pressing-out or a centrifuging-out of the reagents.

The organic solutions employed to extract the remaining carboxymethylating reagents from the product can suitably be solutions of any liquid water-miscible organic compound containing from about 1 to 30% water. Liquid water-miscible alkanones and alkanols of not more than 4 carbon atoms are preferred.

A particularly suitable method of conducting the extraction of the remaining carboxymethylation reagents comprises extracting a plurality of times with such an alkanone or alkanol containing about 5% water and about 5% of a water-miscible organic acid and then extracting with the alkanone or alkanol containing 5% water.

Acetone and methyl ethyl ketone are preferred alkanones for such employment, and methyl, ethyl, and isopropyl alcohol are preferred alkanols. Acetic and propionic acids are preferred acids.

In the production of fibrous water-soluble carboxymethylated celluloses, the process of the present invention consists of the "two-step" process of the application of Daul and Reid, Serial No. 154,202, filed April 5, 1950, in which the first step is conducted in the manner described above. This process has the unobvious result of producing products not only having more pliability, better hand and feel, a greater and more uniform tensile strength, and a greater flexibility, but products which exhibit no appreciable change in the diameter of the fibers. For example, while a water-soluble cotton yarn prepared by the process heretofore known often is 20% larger in gauge after carboxymethylation, the same yarn carboxymethylated to the same extent by the present process exhibits no appreciable amount of the undesired change in gauge.

The following examples are presented to illustrate in greater detail certain features involved in the practice of the present invention. However, as it is apparent that many modifications can suitably be made, the scope of the invention is defined by the claims and is not to be construed as being limited to the particular materials and conditions employed in the examples.

EXAMPLE 1

Five skeins of mercerized cotton thread were soaked in solutions of 10, 15, 20, 25, and 30% monochloroacetic acid in water containing a small amount of wetting agent to aid penetration. The skeins were centrifuged to about 50% wet pickup, based on the weight of the thread, then soaked in separate portions each of 50% sodium hydroxide solution. After one-half hour, the skeins were washed in water and neutralized with water containing 5% acetic acid, rewashed, and dried. The tensile strength, elongation, hand or feel, and substitution are shown in Table 1.

EXAMPLE 2

An identical set of samples was treated as described in Example 1 except that at the end of the reaction time of one-half hour, the samples were centrifuged free of part of the excess alkali and then washed several times with 95% ethyl alcohol containing about 5% acetic acid. They were then washed with hot 95% ethyl alcohol. The dried samples were tested in the same way as were the samples produced by the treatment described in Example 1. The results are shown in Table 1.

TABLE 1

Comparison of water-washed and alcohol-washed carboxymethylated cotton yarns

No.	MCA*, Percent	NaOH	Tenacity, Lb.	Elongation, Percent	Gauge, In.	Hand	Subst.***
WATER-WASHED [1]							
1	**0	50	10.2	10.5	0.0195	Soft	
2	10	50	7.3	11.8	0.0211	Sl. stiff	1:40
3	15	50	6.3	11.0	0.0220	Stiff	1:30
4	20	50	4.9	10.3	0.0238	Very stiff	1:20
5	25	50	4.2	10.6	0.0256	Brittle	1:17
6	30	50	2.5	12.1	0.0274	do	1:14
ALCOHOL-WASHED [2]							
7	**0	50	10.6	10.6	0.0195	Soft	
8	10	50	9.7	10.1	0.0208	do	1:20
9	15	50	9.1	10.5	0.0202	do	1:18
10	20	50	9.6	9.6	0.0204	do	1:15
11	25	50	10.2	11.4	0.0205	do	1:12
12	30	50	10.0	10.4	0.0208	do	1:10

[1] Samples from Example 1.
[2] Samples from Example 2.
*MCA represents monochloroacetic acid.
**Control samples.
***The substitution number indicates the average number of carboxymethyl groups pre glucose anhydride residues in the cellulose.

The results from Table 1 illustrate the advantages of the organic solvent wash over the water wash in respect to tensile strength, gauge, and hand.

EXAMPLE 3

Selected samples from Examples 1 and 2 were

retreated, individually, to make them soluble, as follows: The sample, in skein form, was impregnated with 50% monochloroacetic acid in water containing a small amount of wetting agent to aid penetration. They were then centrifuged to approximately 50% retention of liquid based on the weight of the sample and then soaked in separate portions of 50% sodium hydroxide for one-half hour. A ratio of approximately 8 parts of the alkaline solution to one part of the sample, by weight, was used. The samples were centrifuged to remove most of the excess alkali and then washed with alcohol, neutralized with alcohol containing 5% acetic acid and finally washed in hot alcohol. Results of tests on these samples and their corresponding numbers from Examples 1 and 2 are given in Table 2.

TABLE 2

Sample No.* in Table I	Tensile Strength, Lb.	Gauge, In.	Yarn Number	Substitution**
2	8.3	0.0242	2.22	1:2.7
4	4.4	0.0262	1.84	1:2
6	2.6	0.0299	1.28	1:1.6
8	9.5	0.0228	2.41	1:3
10	7.6	0.0220	2.34	1:2.4
12	6.3	0.0232	2.14	1:2.1

*Samples 2, 4, and 6 were water-washed after first treatment; 8, 10, and 12 were alcohol-washed.

**The substitution number indicates the average number of carboxymethyl groups per glucose anhydride unit in the cellulose.

EXAMPLE 4

Two skeins of viscose rayon were treated with 10% monochloroacetic acid, centrifuged, then washed in 50% sodium hydroxide for one-half hour. One sample (A), was washed in water, the other (B) in alcohol with 5% acetic acid added. Two skeins were treated with 30% monochloroacetic acid and 50% sodium hydroxide, one skein was put into water (C)—it dissolved completely. The other skein (D) was washed in alcohol and acetic acid.

Sample	Washing Treatment	Tenacity, Lb.	Gauge	Hand
A	Water	13.2	0.0392	Stiff.
B	Alcohol	10.5	0.0424	Soft.
C	Water	0		
D	Alcohol	10.6	0.0435	Rel. soft.

EXAMPLE 5

Two strips of eighty square cotton cloth were soaked in 30% monochloroacetic acid, centrifuged,, then soaked in 50% sodium hydroxide for one-half hour. One piece (A) was washed in water containing 5% acetic acid, the other piece (B) was washed in alcohol containing 5% acetic acid, then several times in 80% alcohol.

Sample	Washing Treatment	Tenacity*, Lb.	Substitution
Control		59.4	
A	Water	37.5	1:15
B	Alcohol	50.5	1:9

*1 x 10" strips broken on Scott tester (0-110 lb.).

EXAMPLE 6

Several yards of cotton sliver, extracted with acetone to remove waxes, was treated with 20% monochloroacetic acid solution and centrifuged followed by soaking in a 50% sodium hydroxide solution for 30 minutes. It was washed in alcohol, and neutralized with acetic acid in alcohol. It was retreated with 55% monochloroacetic acid and 50% sodium hydroxide for one-half hour, washed with alcohol and acidified with hydrochloric acid in alcohol, then converted to the ammonium salt with ammonium hydroxide in alcohol.

The sample had a soft hand, was water soluble, and could be easily carded.

Another sample washed with water after the first carboxymethylation treatment was so matted it could not be pulled apart easily.

The carboxymethylated cellulose products, produced according to the methods of the foregoing examples, were easily carded and spun.

Having thus described our invention, we claim:

1. In a process for the production of fibers containing one carboxymethyl group per each 5 to 40 glucose units by reacting a cellulosic material with aqueous monochloroacetic acid and an aqueous alkali metal hydroxide, the improvement which comprises: impregnating a cellulosic material composed of spinnable cellulosic fibers with aqueous monochloroacetic acid; further impregnating the so treated cellulosic material with an aqueous alkali metal hydroxide containing from 20 to 50% alkali metal hydroxide; allowing the reaction to proceed until one carboxymethyl group per 5 to 40 glucose units has been introduced; mechanically removing the aqueous reactants; washing the treated cellulosic material with a water-miscible organic liquid selected from the group consisting of alkanols and alkanones of not more than four carbon atoms, said organic liquid containing from 1 to 30% water; recovering a spinnable, strong, pliable, flexible carboxymethylated fiber; and spinning said carboxymethylated fiber.

2. In a process for the production of fibers containing one carboxymethyl group per each 10 to 20 glucose units by reacting a cellulosic material with aqueous monochloroacetic acid and an aqueous alkali metal hydroxide, the improvement which comprises: impregnating a cellulosic material composed of spinnable cellulosic fibers with aqueous monochloroacetic acid; further impregnating the so treated cellulosic material with an aqueous alkali metal hydroxide containing from 20 to 50% alkali metal hydroxide; allowing the reaction to proceed until one carboxymethyl group per 10 to 20 glucose units has been introduced; mechanically removing the aqueous reactants; washing the treated cellulosic material with a water-miscible organic liquid selected from the group consisting of alkanols and alkanones of not more than four carbon atoms, said organic liquid containing from 1 to 30% water; recovering a spinnable, strong, pliable, flexible carboxymethylated fiber; and spinning said carboxymethylated fiber.

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Number	Name	Date
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