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 yarns and threads and has among its objects the production of partially carboxymethylated cotton yarns and threads which disintegrate or are soluble in water and dilute alkaline solutions. Such yarns are useful in applications such as scaffolding fibers for novelty fabrics, knitting of socks together in the "string process," etc., where it is desirable to have a yarn which may be removed by washing at some stage in the manufacturing process.

The inventors have previously patented a process of making cotton textiles water-absorbent and rot-resistant by treatment of cotton with monochloroacetic acid and alkali metal hydroxides such as sodium hydroxide, in their patent, U. S. 2,446,153. The products of this patent contained one carboxymethyl group per from 40 to 5 glucose units. When cotton is carboxymethylated to a greater degree than one group per five glucose units, it swells in water and dilute alkali to such an extent that it either disintegrates or becomes soluble.

Commercially produced carboxymethylcellulose is generally in the form of the sodium salt and has from one carboxymethyl group per two glucose units to one to one substitution and is almost completely soluble in water. However, such materials in no way resemble cotton fibers.

The inventors have previously patented, in U. S. Patent 2,495,767, a process for the preparation of fibers from carboxymethylcellulose by extraction of a solution of the latter into a metal salt solution, such as aluminum sulphate. Some of the fibers so produced are soluble in alkaline solutions but these synthetic fibers do not resemble the modified cotton fibers described here.

The inventors have discovered a method of retaining the fibrous character of cotton yarns and threads and most of their tensile strength even though they have been treated severely enough to be soluble in water.

The invention takes advantage of an unexpected discovery that fibers, yarns, or threads, with or without tension, may be carboxymethylated sufficiently to be soluble in dilute alkali, 1% or less, or even in water, yet remain insoluble in the strong alkali needed for the carboxymethylation treatment.

An object of this invention is to produce a water-soluble and dilute alkali-soluble cotton or regenerated cellulose fiber, yarn or thread containing carboxymethyl substituents in a sufficiently high ratio to confer water-solubility, preferably at least one carboxymethyl group per three glucose units, by a method which retains the fibrous characteristics and most of the tensile strength of the fiber.

Another object of this invention is to convert the water-soluble fiber, yarn, or thread to a metal salt which is insoluble in water but soluble in dilute alkali.

A further object of this invention is to produce a water-soluble, dilute-alkali soluble cotton fiber having carboxymethyl substituents in the ratio of one carboxymethyl substituent to from one to three glucose units by a method which retains the fibrous character and most of the tensile strength of the cotton fiber.

Other objects are obvious from the detailed disclosure that follows.

Successful carboxymethylation to a greater degree than one group per five glucose units depends mainly upon keeping the water content of substances which contact the cellulosic materials, during or after treatment, below 60%. If the products of this invention should be washed with water to remove the alkali, they would disintegrate because of swelling and solubility in dilute alkali. However, if most of the excess alkali is removed by centrifuging, or by some other mechanical means, and the remainder neutralized with an acid, preferably acetic, in an aqueous solution of a water miscible organic solvent, such as acetone or alcohol, of concentrations of at least 60% of solvent, the cotton remains in a useful fibrous form and retains most of its strength.

By carefully adjusting the pH, the product may be retained in the form of the sodium salt, or if acidified first, may be converted to the ammonium salt with alcoholic ammonium hydroxide, or the pyridinium salt with pyridine in alcohol. Other salts may be formed similarly. If a fiber soluble only in alkali rather than water is desired, the material may be treated with solutions of soluble salts of copper, iron, lead, silver, mercury, or aluminum, etc., or with long chain organic bases which will form the corresponding water-insoluble salts of carboxymethylcellulose.

Organic materials such as long chain amines having from 10 to 20 carbon atoms, for example, octadecyl amine, will form water-insoluble salts of the carboxymethylcellulose and give a softer hand to the yarns and threads.
These products, though insoluble in water, may be solubilized with dilute alkaline solutions such as sodium carbonate, sodium hydroxide, ammonium hydroxide, etc.

Other organic solvents may be used provided they are soluble in or miscible with water. These will become apparent to those skilled in the art.

The products formed in the above procedure may be washed or extracted with alcohol or acetone until free of extraneous materials, then dried. Since the dried materials are usually somewhat stiffened, it is preferred to apply softening agents in non-aqueous solution such as triethanolamine in alcohol, textile oils, Turkey red oil, etc.

Products which are soluble in dilute alkali may be obtained by a single strong treatment of prephonably kier-bolted and mercerized cotton. However, if greater solubility is desired, as in water, it is preferred to start with a mild treatment, using from 10–30% monochloroacetic acid and 30–40% sodium hydroxide. Potassium hydroxide has been found to work in this reaction; however, stronger concentrations are required to produce the same results as with sodium hydroxide. It is possible, by increasing the temperature of the reaction with the alkali hydroxide, to expedite the treatment to a fraction of a minute. This causes some strength loss; however, we prefer to use room temperature and allow the reaction to proceed from 20–30 minutes or longer. The products of this reaction may be washed in water and are of a prior art. When these products are retreated with strong monochloroacetic acid, 50% or greater concentration, and sodium hydroxide of 40 to 50% strength, followed by neutralization in alcohol or acetone, solubility increases to the point where they disintegrate in water.

The following examples, which are not to be considered limiting, exhibit the invention in greater detail. It is understood, in the examples below, that “sewing thread” and “yarn” unless otherwise qualified mean cotton sewing thread and cotton yarn. Rayon means regenerated cellulose.

**Example I**

Approximately ten grams of cotton sliver, kier-bolted to remove waxes, etc., was soaked in 30% aqueous monochloroacetic acid containing 0.1% of a wetting agent (Aerosol OT), padded to remove excess, then treated with 40% sodium hydroxide for 45 minutes, and washed (with water) to remove free sodium hydroxide. Substitution was approximately one carboxymethyl group per twenty glucose units. This material was retreated with 50% monochloroacetic acid followed by 50% sodium hydroxide for one hour. It was neutralized with 5% acetic acid in a 60% ethyl alcohol aqueous solution; extracted-free of alcohol, then made into the ammonium salt with ammonium hydroxide in ethyl alcohol; washed with alcohol, and dried.

The product was still fibrous and had a substitution of one carboxymethyl group per three glucose units as determined by the copper content of its copper salt. It was soluble in 1% sodium hydroxide.

**Example II**

A 50-yarn skein of 12/5 sewing thread (kier-bolted) was soaked and padded with 15% monochloroacetic acid; then soaked in 50% sodium hydroxide for 20 minutes, washed until free of excess sodium hydroxide and dried. The carboxymethyl content was one group per ten glucose units as determined by analysis of the copper salt of the product. The skein was then padded with 50% monochloroacetic acid and treated with 50% sodium hydroxide for one hour after which it was extracted with 60% aqueous acetone neutralized with 5% acetic acid in 70% aqueous acetone, converted to the ammonium salt with ammonium hydroxide in acetone, then soaked in a 10% solution of triethanolamine in acetone centrifuged to about 50% retention, and dried. The dried product had a soft hand, retained 72% of its original tenes strength and was soluble in tap water at pH 7.5. It had a substitution of one carboxymethyl group per 2.5 glucose units.

**Example III**

Extracted two-ply 23's yarn, previously carboxymethylated to an extent of one carboxymethyl group per 20 glucose units with 24% chloroacetic acid and 40% sodium hydroxide, was retreated by soaking in 60% chloroacetic acid in 50% retention of liquid, washed (with wetting agent Aerosol OT), extracted to about 50% retention of solution, then soaked in 50% sodium hydroxide for 20 minutes, washed in 95% ethyl alcohol, neutralized with 10% acetic acid in 95% ethyl alcohol, then converted to the ammonium salt with alcoholic ammonium hydroxide and dried.

This yarn retained 85% of its tene strength, elongation increased 25%, and it had a substitution of one carboxymethyl group per three glucose units. It was completely soluble in water.

**Example IV**

Three samples of a few yards each of the products in the free acid form from the above Example III were soaked in 100 ml. portions of 10% solutions of aluminum sulfate, copper sulfate, and lead acetate. This made the corresponding aluminum, copper, and lead salts of carboxymethyl-cellulose in yarn form. The products could be washed in water but were soluble, or disintegrated, in 1% sodium hydroxide solution.

In cases where the carboxymethyl substitution is so great that the water in the salt solutions causes too great swelling the salts may be prepared in anhydrous solutions such as cupric chloride in ether, ferric chloride in benzene, etc.

**Example V**

A skein of 7's/2 ply mercerized sewing thread of 9 lb. tene strength which had been previously treated with 18% mono-chloroacetic acid and 40% sodium hydroxide to obtain a substitution of about one carboxymethyl group per 15 glucose units was soaked in a 50% aqueous solution of mono-chloroacetic acid containing 0.1% wetting agent (Aerosol OT). It was centrifuged to about 50% retention of liquid based on the weight of the thread. It was then treated with 50% sodium hydroxide solution for 30 minutes. The product was squeezed free of excess alkali, washed in 60% acetone in water, neutralized with 5% acetic acid in 60% aqueous acetone solution, then converted to the ammonium salt with ammonium hydroxide in 90% aqueous acetone. The dried product had 85% of its original strength and was soluble in water.

**Example VI**

A skein of 50 yards of 1100/2 tire-cord type rayon was soaked in a 50% solution of mono-chloroacetic acid in water containing 0.1% of a wetting agent (Aerosol OT). It was then centrifuged to about 50% pickup and treated with 50%
sodium hydroxide solution for 30 minutes. The product was centrifuged free of excess alkali, washed in 95% ethyl alcohol, and converted to the ammonium salt with alcoholic ammonium hydroxide. The product was dried at 80°C, in a blower oven. It was soluble in water and had 80% of its original strength.

It may be seen from the examples above that cotton or regenerated cellulose fibers, yarns, and threads may be carboxymethylated to an extent greater than one carboxymethyl substituent per five glucose units, yet retain their fibrinous character and tensile strength sufficient for further textile processing, if the procedures of the invention are carried out.

It is preferred to treat the cotton materials without tension, thereby allowing greater swelling and penetration of reagents, however, it is possible to treat under tension and obtain similar results.

It is also possible to place the treated sample under tension before drying to increase tensile strength and decrease elongation. This invention, in one form, is characterized as a process of making water-soluble and dilute alkali-soluble cotton or regenerated cellulose fibers, yarns, and threads containing carboxymethyl substituents in the ratio of more than one carboxymethyl group per five glucose units (sufficiently more to confer water-solubility), but retaining fibrinous characteristics and tensile strength, comprising impregnating a material of the group consisting of cotton regenerated cellulose and partially carboxymethylated cotton, with aqueous monochloracetic acid solution having a water content below 50%, centrifuging or squeezing to reduce the aqueous content, treating the impregnated material with alkali metal hydroxide of 45-50% concentration, then on completion of the reaction, reducing the alkali content by extraction with water miscible organic solvent containing not more than 40% water to remove alkali hydroxide or neutralizing with acid in organic solvent and drying. Since a product containing about one carboxymethyl group per five glucose units is the borderline case and is almost, but not quite, soluble in water, our preferred water soluble, fibrinous product contains at least one carboxymethyl group per three glucose units, as indicated by the above examples.

Having thus described our invention, we claim:
1. A process of producing a water-soluble cellulose textile, which process comprises: Wetting a cellulose textile of the group consisting of slivers, yarns, and threads of cotton, regenerated cellulose, and carboxymethylated cellulose containing less than 1 carboxymethyl group per 3 glucose units with aqueous at least 50% monochloracetic acid; mechanically reducing the amount of liquid retained by the so-wetted textile; wetting the resultant partially wet textile with aqueous 40 to 50% alkali metal hydroxide; maintaining the so-wetted textile for from about 20 to 60 minutes until the textile contains 1 carboxymethyl group per 1 to 3 glucose units; and substantially immediately removing the so-treated carboxymethylated textile from contact with alkali metal hydroxide by a mechanical reduction of the amount of liquid in contact with the textile, and by a neutralization of remaining alkali metal hydroxide with an acid in an aqueous inert water miscible organic solvent having a concentration of at least 60 percent of the organic solvent.

2. The process of claim 1 in which the product resulting therefrom is treated with ammonium hydroxide in an inert organic liquid medium to produce the ammonium salt.

3. The product of the process of claim 1, which is a carboxymethylated cellulose fiber containing one carboxymethyl group per one to three glucose units, which retains the fibrinous form and most of the tensile strength of the cellulose fiber but which is soluble in water and in weak alkali solutions.

4. The process in which the product produced by claim 1 is converted into a water-insoluble, dilute alkali soluble carboxymethylated cellulose by soaking said product in a solution of a salt of a metal of the group consisting of copper, iron, silver, mercury, lead, and aluminum.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

<table>
<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,236,645</td>
<td>Maxwell et al.</td>
<td>Apr. 1, 1941</td>
</tr>
<tr>
<td>2,278,613</td>
<td>Collings et al.</td>
<td>Apr. 7, 1942</td>
</tr>
<tr>
<td>2,448,183</td>
<td>Reid et al.</td>
<td>Aug. 31, 1948</td>
</tr>
<tr>
<td>2,510,353</td>
<td>Waldeck</td>
<td>June 6, 1950</td>
</tr>
<tr>
<td>2,524,524</td>
<td>Swinehart et al.</td>
<td>Sept. 26, 1950</td>
</tr>
</tbody>
</table>

OTHER REFERENCES

Textile Research Journal (2) September 1948, pages 551 to 556.