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PROCESS FOR THE PRODUCTION OF ALKALI-SOLUBLE COTTON TEXTILE MATERIALS

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This invention relates to the production of alkali-soluble cotton textile materials. More specifically this invention describes a process for producing an alkali-soluble cotton textile material that retains the textile properties of the original unmodified material by virtue of an exceedingly mild chemical modification of the original textile material followed by an oxidizing treatment that employs, in combination, two oxidizing reagents in dilute aqueous solution. Oxidation with one oxidizing reagent in combination with a second oxidizing reagent in the practice of this invention is unexpectedly and strikingly synergistic.

It is well known that certain chemical modifications of cotton such as, for example, carboxymethylation and aminoethylation are effective for the production of water or alkali-soluble cotton textile material. It is also known that if the chemical modification treatments referred to above are followed by a subsequent oxidizing processing step using organic or inorganic oxidizing reagents, that the ultimate alkali-solubility of the treated material is enhanced to a considerable degree.

Conventional processes for the production of alkali-soluble cotton textile materials with solubilities in excess of 95% involve a chemical modification pretreatment of the textile material to produce a product with a degree of substitution of at least 0.4, followed by a rigorous oxidation treatment using either concentrated oxidizing reagents or, if dilute oxidizing reagents are employed unduly long oxidizing times and high oxidizing temperatures. The combination of chemical modification to produce a product with a high degree of substitution (the average number of ether groups substituted per anhydroglucose unit of the cellulose chain) followed by a vigorous oxidizing step gives rise, in the conventional processes, to serious loss of all desirable textile properties. The object of the present invention is to produce an alkali-soluble cotton textile material by employing (*a*) a chemical modification treatment carried to a very low degree of substitution (preferably no more than 0.1) and hence of small import insofar as the original characteristics of the untreated material is concerned and (*b*) a highly effective oxidation step carried out by the use, in combination, of two oxidizing reagents. A synergistic effect resulting from the use of mixed oxidizing reagents, permits the use of dilute aqueous oxidizing solutions, low oxidizing temperatures (room temperature), and relatively short treatment times. The combination of the chemical modification to a low degree of substitution and the highly effective oxidation step carried out with two oxidizing reagents used in relatively low concentrations which characterizes the process of this invention result in the preservation in the treated material of substantially all the desirable properties of the original untreated textile material.

The preservation of the original textile properties in an alkali-soluble textile material is most valuable and highly desirable since, even though for many uses the presence of the alkali-soluble material is transient, it is essential that the alkali-soluble product, while it exists in textile form, be capable of being processed on conventional textile machines. The obvious requisites are, of course, retention of strength, flexibility and abrasion resistance. A typical use for an alkali-soluble textile material is as a scaffolding or supporting foundation for the preparation of light or novelty yarns and fabrics. By alternating soluble textile yarn with nonsoluble textile yarns in weaving and then subjecting the woven product to dissolution, open-work fabrics and other novelty effects may be achieved. Knit socks may be produced in a continuous string each connected to its neighbors by a thread of soluble yarn. The socks after fabrication may then be readily separated by simple disintegration of the soluble connecting yarn. Soluble textile materials are also used as "backing" in the manufacture of lace. Other uses will be apparent to those skilled in the art.

In general the process of this invention is carried out by chemically modifying cotton textile material to produce alkali-soluble products. Aminoethylation and carboxymethylation are employed as the chemical modification step as the preferred chemical modification for the process of this invention as described in the specific examples that follow. Regardless of the chemical modification treatment employed the advantageous feature of the process of this invention is that the chemical modification need not be carried beyond a degree of substitution of about 0.33. The preferred range for this process is a degree of substitution of from about 0.01 to 0.1 average number of aminoethyl or carboxymethyl groups per anhydroglucose unit of the cellulose chain. Aside from the consideration of retaining the textile properties of the chemically modified material, the possibility of operating at a low degree of substitution possesses obvious economic advantages. Following the chemical modification step which step is to produce a material with a low degree of substitution and a material virtually unchanged with respect to textile properties, the chemically modified material is subjected to an oxidation step with a mixture of chromic and oxalic acid used in combination in an aqueous solution. The oxidizing step can be carried out at any temperature from 0 to 60° C., higher temperatures requiring shorter reaction times. The preferred treatment temperature is room temperature (20 to 25° C.). The preferred range of reagent concentration is from 1 to 10% by weight of each reactant (oxalic and chromic acid) in aqueous solution. The range 0.1% to 50% for chromic acid and from 0.1% to saturation for oxalic acid are operable, the higher concentrations requiring the shorter reaction times. The oxidizing step when carried out at room temperature within the preferred concentration range requires from 1 to 5 minutes.

There are three main points of attack by oxidizing agents on the cellulose molecule: (1) The aldehydic group on carbon atom 1 of the terminal anhydroglucose unit of the cellulose chain; however, in cotton with its relatively high degree of polymerization the number of these present is small and of little importance in this study. (2) The hydroxyl group on carbon atom 6 with formation of aldehyde or carboxyl group, depending upon reagent used. (3) The 2,3-dihydroxy or glycol group which may be oxidized either simultaneously or individually without ring cleavage to form ketonic groups or with

ring cleavage to form aldehyde groups. The latter may be further oxidized and converted to carboxyl groups.

Certain reagents in their reaction with cellulose result in almost exclusive oxidation at the 2,3 positions of the glucose residues to form aldehyde groups (reducing oxycellulose). The most notable of these reagents are periodic acid and lead tetraacetate. Chromic acid has been shown to react similarly but not quite as exclusively.

The most striking of the properties of reducing oxycellulose is alkali-solubility. Since the glycol units of cellulose are trans, complete oxidation is slow, and even impossible at times due to competing side reactions. However, oxidation to the extent of alkali-solubility is readily attained. The mechanism of this alkali-solubility, most widely accepted, is that of cleavage of the ether linkage beta to the strongly electronegative carbonyl group. The inductive effect of the carbonyl thus causes the hydrogen on the alpha-carbon atom to be removed by the strong base which is followed by an electron shift forming a double bond between the alpha and beta-carbon atoms with a simultaneous carbon-oxygen scission.

Partially etherified cottons offer two principal theoretical advantages over untreated cotton for the production of alkali-soluble derivatives by oxidation. These advantages are: (1) Presence of solubilizing groups which enhance alkali-solubility through greater solubility of the alkali-cleaved fragments. (2) Opening up of the crystalline regions of the fiber for more uniform and increased reaction. These properties are achieved by variations in the methods of preparation and chemical nature of the substituent group introduced.

Many etherified cottons bear a substituent group which in itself confers solubility to the derivative. Oxidation of unsubstituted 2,3 glycol units causes alkali-lability. The two effects added together result in high solubility from relatively low degree of reaction. A small amount of oxidation causing a limited amount of cleavage in alkali can be very effective if the cleaved fragments bear an alkali-solubilizing group. Thus, fragments of longer chain length than are usually soluble, will go into solution. Therefore, the alkali-solubility of oxidized partially etherified cotton theoretically combines disintegration with true macromolecular solution.

Although oxidation of cellulose with periodic acid proceeds uniformly throughout the fiber, most other reagents are limited in their reactivity to the accessible regions. Chromic acid, which is preferred for its lower cost and greater availability, is non-swelling and does not penetrate the ordered regions. Many of the partially etherified cottons are prepared under swelling conditions which greatly increase the accessibility of the crystalline regions of the fiber. Thus, just as mercerized cellulose is more readily oxidized, the rate and extent of oxidation of many of the etherified cottons are greatly increased.

In most cases the two effects work together, but by careful selection and comparison of results, the increase in alkali-solubility due to each can be demonstrated.

Having thus described in a general way the operation of the process of this invention, details of the process are listed below in specific examples which describe the application of the process to cotton textile materials.

Example 1

Samples of fabrics in form of 80 x 80 cotton print cloth were treated as follows: (*a*) carboxymethylated by treatment with 17% aqueous chloroacetic acid and 50% sodium hydroxide to a degree of substitution of 0.095, (*b*) aminoethylated by treatment with 20% aqueous 2-aminoethyl sulfuric acid and 40% sodium hydroxide to a degree of substitution of 0.104 (*c*) mercerized. The treated fabrics were then washed and dried. The fabrics were then oxidized with an aqueous solution containing 3% by weight of chromic acid and 3% by weight of oxalic acid according to the conditions listed in the table below, washed with water and dried. The last column in the table lists the solubilities of the treated products and the untreated product in hot 10% sodium hydroxide solution.

TABLE I

Fabric Oxidized	Conditions of Oxidation		Alkali-Solubility (Hot 10% NaOH)
	Time (min.)	Temp. (° C.)	
(*a*) Carboxymethylated cotton	1	25	Very soluble.
(*b*) Aminoethylated cotton	20	25	Do.
(*c*) Mercerized cotton	60	25	Insoluble.
Untreated cotton	60	25	Do.

Example 2

The retention of useful textile properties is illustrated by breaking strengths of the alkali-soluble products listed in Table II. Carboxymethylated cotton (degree of substitution=0.095) was oxidized according to the conditions listed in Table II.

TABLE II

Conditions of Oxidation				Percent Alkali-Solubility (Hot 10% NaOH)	Percent of Original Breaking Strength Retained
Solution		Time (min.)	Temp. (° C.)		
Percent Chromic Acid	Percent Oxalic Acid				
3	3	1	25	95.0	77.5
3	1	1	25	91.1	88.2
2	2	1	25	95.6	84.6
2	0.5	5	25	91.2	83.7
1	1	5	25	92.2	84.2

Example 3

The increased effectiveness of aqueous chromic acid-oxalic acid solution in contrast to that of chromic acid alone is illustrated by the following data. Samples of carboxymethylated cotton (degree of substitution=0.095) were treated with 3% by weight aqueous chromic acid solution at 25° C. for periods of 20 minutes and 30 minutes respectively. The sample treated for 20 minutes was partially soluble and the sample treated for 30 minutes was very soluble in hot 10% sodium hydroxide solution. The data in Example 2 show that an oxidation treatment using both chromic acid and oxalic acid in aqueous solution gives rise to a very soluble product after only 1 minute treatment time.

We claim:

1. A process for producing a cotton textile material, which prepared material is substantially completely soluble in 10% aqueous alkali and which prepared material retains, substantially unaltered, all the useful textile properties of the original unmodified material, comprising a mild chemical modification of the original cotton textile material to substitute therein a radical selected from the group consisting of aminoethyl and carboxymethyl to a degree of substitution of about from 0.01 to 0.1 average number of aminoethyl or carboxymethyl groups per anhydroglucose unit of the cellulose chain, and oxidation of the resulting chemically modified cotton textile material for from 1 to 5 minutes at room temperature with an aqueous solution containing about from 1 to 3 weight percent of chromic acid and about from 0.5 to 3 weight percent of oxalic acid.

2. A process for producing a cotton textile material, which prepared material is substantially completely soluble in 10% aqueous alkali and which prepared material retains, substantially unaltered, all the useful textile properties of the original unmodified material, comprising a mild chemical modification of the original cotton textile material by carboxymethylation thereof to a degree of substitution of about from 0.01 to 0.1 average number of carboxymethyl groups per anhydroglucose unit of the

cellulose chain, and oxidation of the resulting chemically modified cotton textile material for from 1 to 5 minutes at room temperature with an aqueous solution containing about from 1 to 3 weight percent of chromic acid and about from 0.5 to 3 weight percent of oxalic acid.

3. A process for producing a cotton textile material, which prepared material is substantially completely soluble in 10% aqueous alkali and which prepared material retains, substantially unaltered, all the useful textile properties of the original unmodified material, comprising a mild chemical modification of the original cotton textile material by aminoethylation thereof to a degree of substitution of about from 0.01 to 0.1 average number of aminoethyl groups per anhydroglucose unit of the cellulose chain, and oxidation of the resulting chemically

modified cotton textile material for from 1 to 5 minutes at room temperature with an aqueous solution containing about from 1 to 3 weight percent of chromic acid and about from 0.5 to 3 weight percent of oxalic acid.

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