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PROCESS FOR PRODUCING TEXTILE CELLULOSE SULFO-ETHYL ETHER CATION-EXCHANGE MATERIAL

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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 chemically modified cellulose textile fibers and to a process for chemically modifying a cellulosic textile in the form of sliver, yarn, or fabric.

More particularly, the invention provides novel fibrous 2-sulfoalkyl ethers of cellulose and a process for their production.

While the value of a chemically modified cellulose in a fibrous form capable of existing as a fabric or in being converted to a fabric by the ordinary cellulosic fiber processing techniques and apparatus is readily apparent, no process for producing such a sulfoalkyl cellulose ether has heretofore been developed. The sulfo-substituted celluloses heretofore produced have been soft powders soluble in water and resembling in appearance and physical properties a synthetic linear polymer.

We have discovered that when a cellulosic textile containing reactive hydroxyl groups is impregnated with an aqueous alkali of mercerizing strength containing not more than about 15% of a sulfoalkylating agent, cured under moderate conditions, and washed free of alkali; the textile remains fibrous, is insoluble in water and is composed of a sulfoalkyl cellulose ether (in the form of its alkali metal salt). Such textiles have the valuable ion-exchange properties of an insoluble, strongly acidic material containing monobasic acid groups.

The textiles are preferably impregnated with the aqueous alkali containing the sulfoalkylating agent by contacting the textiles with enough of the alkali solution to wet substantially all of their fibers and substantially immediately removing the textiles from contact with any liquid in excess of the amount entrained. Such an impregnation can suitably be accomplished by swabbing portions of the liquid onto a textile suspended in a position in which any liquid not entrained by the textile will run off, or by impregnating the textile by padding or by using squeeze rolls in a conventional textile impregnating procedure.

The textile fibers provided by this invention have valuable properties in addition to their ion-

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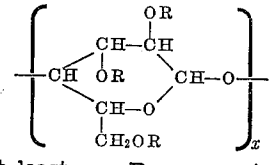
exchange properties. For example, they can be blended by conventional fiber processing procedures into yarns and fabrics having strong cation affinity, and thus having enhanced properties of dyeing with basic dyes and of undergoing fabric modifications generally. The textile fibers provided by this invention have the property of combining with ammonium ions and the ions of other nitrogenous bases, including the ions of methylene blue, and the materials so produced have improved resistance to burning. Fabrics provided by this invention have an organdy-like stiffness and appearance and have a high degree of reactivity with the basic reagents such as salts of the metals used to impart rot resistance, insecticidal properties, and the like.

The cellulosic textiles which can be converted to fibrous 2-sulfoalkyl ethers by the process of this invention are textiles of alpha-cellulose and its derivatives having the formula,



in which at least one R represents a hydrogen atom and the other R is a monovalent radical, preferably an aminoalkyl, carboxyalkyl, or acyl radical. The subscript x represents a large whole number. They can be so sulfoalkylated in the form of sliver, rovings, yarns, or fabrics. In certain cases where the cellulose textile tends to react with alkalies of mercerizing strength to form alkali-celluloses, e. g. fibrous partially esterified celluloses, they tend to be sulfoalkylated by the replacement of groups other than hydrogen atoms in the positions designated by R. Examples of suitable cellulosic textiles for sulfoalkylation by the process of the invention include cotton textiles and textiles of aminoethyl, diethylamine, carboxymethyl, carboxylated, phosphorylated and the like modified celluloses in the form of sliver, roving, yarn, or fabric.

The sulfoalkylating agents which are suitable for employment in the process of the invention are the anions of the 2-haloalkanesulfonic acids, the 2-sulfatoalkanesulfonic acids and the 1-alkenesulfonic acids of low enough molecular weight

to be at least partially soluble in aqueous alkalies of mercerizing strength. Particularly preferred sulfoalkylating agents are 2-chloroethanesulfonic acid anion, ethionic acid anion and ethylenesulfonic acid anion which may be dissolved in the aqueous alkali in the form of the acids, salts, or anhydrides and converted to the respective anions in situ.

In certain cases a sulfoalkylating agent which is too insoluble in the aqueous alkali to provide the desired degree of substitution can advantageously be applied to the cellulosic textile in the form of a water solution after which the sulfoalkylation reaction can be completed by impregnating the wetted textile with a strong aqueous alkali, and curing and washing the wet textile in the above manner.

While up to about 15%, by weight as the alkali salt, based on the weight of the alkali solution, of sulfoalkylating agent may be used; about 10% has been found to be particularly suitable when the textile is impregnated at about room temperature. The use of 2-chloroethanesulfonic acid anion in such concentration in a 29% sodium hydroxide solution has been found to produce a fibrous 2-sulfoethyl cellulose in the form of a fabric having substantially the same breaking strength as the unmodified cellulosic fabric.

The curing temperatures can suitably range from about 50° to the decomposition temperature of the salts of the sulfoalkyl cellulose ethers and they can be cured at such temperatures for from 1 to 30 minutes. The preferred curing temperatures are from about 70 to 100° for times of from about 4 to 30 minutes. Particularly suitable results from sodium hydroxide solutions of from 28 to 30% continuing from 5 to 10% sodium 2-chloroethanesulfonic acid have been attained by curing in a forced draft oven for 15 minutes at 70° C., for 5 minutes at 100° C., and on steam heated cans for 4 minutes at a surface temperature of 85° C.

The process may be conducted in a batch-wise or continuous manner employing the conventional apparatus for treating cellulosic textiles.

The alkali solutions may be applied over the temperature ranges commonly used in mercerization processes, but their application at about room temperature is effective and convenient and therefore is preferred. While lithium or potassium hydroxide can be used, sodium hydroxide is economical and highly effective, and its employment is preferred.

The impregnation of the textile with the aqueous alkali solution may be preceded by or accompanied by treatments with any of the commonly employed wetting or dispersing agents, e. g., phenolic compounds, such as cresylic acid, with or without solvents such as hexanol to increase the wetting power, sulfonated acids, sulfuric esters of aliphatic alcohols, etc.

The following examples are presented to illustrate various phases of the invention in detail. However, since many variations in materials and modes of operation are within its scope, the invention is not to be construed as being limited to the particular substances and conditions recited in the examples.

EXAMPLE I

Batch-wise treatment of a fabric

A piece of cotton fabric was pinned into a sleeve and fitted over a stainless steel beaker. The fabric was then swabbed with a solution composed of 61 g. of water, 29 g. of sodium hydroxide (cooled) and 10 g. of the sodium salt of 2-chloroethylsulfonic acid, heated in a forced draft oven at 85° C. for 10 minutes, washed in tap water until free of sodium hydroxide, and air dried. The product was a fabric having more stiffness than the original material. Its cation-exchange capacity was about 580 milli-equivalents per kg.

EXAMPLE II

Continuous treatment of a fabric

A roll of cotton fabric 12 inches wide and 150 yards long was padded with a solution composed of 5185 g. water, 2465 g. sodium hydroxide, and 850 g. of the sodium salt of 2-chloroethylsulfonic acid, $ClCH_2CH_2SO_3Na$ (added last to the cooled solution). The pick-up was 146 percent. The fabric was passed over steam cans with a surface temperature of about 85° at such a speed that the fabric was in contact with the cans for about 4 minutes. The fabric was then washed; and dried by passing over the steam cans again. The product was a stiff organdy-like fabric having a cation-exchange capacity of about 510 milli-equilavents per kg. and a sulfur content of 1.7 percent.

The fabric employed was a 78 square print cloth which prior to sulfoalkylation had a breaking strength of 34 pounds per 78 filling yarns and 46 pounds per 78 warp yarns. The fibrous sulfoethyl cellulose ether (in the form of the sodium salt) fabric prepared from it had a breaking strength of 30 and 51 pounds, respectively.

EXAMPLE III

Batch-wise treatment of sliver

A roll of 1.5 pounds of cotton sliver in the form in which it came from the card was placed in cans and wetted with 22 pounds of a solution composed of 69.6 parts of water, 25 parts of sodium hydroxide, 5 parts of 2-chloroethanesulfonic acid and 0.4 part of a wetting agent of the cresylic acid type. After the sliver was completely and uniformly wetted, it was put through squeeze rolls and heated in a drying oven for 30 minutes at 100° C. It was then washed by putting it through water and passing it to squeeze rolls.

The product was a fibrous 2-sulfoethyl cellulose ether (in the form of the sodium salt) in the form of a sliver which could be directly spun into yarn, or be put through an opener, converted into picker lap, carded, drawn, and spun into yarn.

EXAMPLE IV

Use of ethylenesulfonic acid anion

A piece of cotton fabric was pinned into a sleeve and fitted over a stainless steel beaker. The fabric was then swabbed with a solution composed of 65 g. of water, 25 g. sodium hydroxide, and 10 g. of the sodium salt of ethylenesulfonic acid, $CH_2{=}CHSO_3Na$, heated in a forced draft oven at 100° C. for 10 minutes, washed and dried. The cation-exchange capacity of the resulting fabric was 486 milli-equivalents per kg.

EXAMPLE V

Use of ethionic acid anion

A piece of cotton fabric was treated in a manner similar to that described in Example 4, except that a solution composed of 60 parts by weight of water, 25 parts sodium hydroxide and 15 parts of sodium ethionate,

$NaO_3SOCH_2CH_2OSO_2Na$

was used. It was cured for 10 minutes at 100° C. The cation-exchange capacity of the resulting fabric was 430 milli-equivalents per kg.

EXAMPLE VI

Use of various curing conditions and concentrations of sulfoalkylating agents

Identical samples of cotton were treated by the procedure of Example I varied only as indicated in the concentration of 2-chlorethanesulfonic acid anion and of the sodium hydroxide and cured under the indicated conditions. The ion exchange properties of each treated sample, calculated upon a dry basis, are reported in the following table.

Temp., ° C.	Time in Minutes	5% $ClCH_2CH_2SO_3Na$			10% $ClCH_2CH_2SO_3Na$		
		25% NaOH	29% NaOH	33% NaOH	25% NaOH	29% NaOH	33% NaOH
70	5	232	195	251	223	267	299
	10	302	283	336	239	363	429
	15	485	374	489	399	624	574
	20	487	441	508	574	675	611
	25	492	449	491	600	612	626
85	5	327	342	399	414	426	458
	10	487	489	535	566	682	584
	15	533	509	522	587	643	551
	20	500	460	485	574	620	514
	25	487	420	449	542	540	529
90	5	397	434	415	495	543	496
	10	470	538	493	617	634	596
	15	476	514	453	606	612	547
	20	431	405	395	555	555	452
	25	430	371	323	529	511	383
100	5	379	404	463	324	534	435
	10	494	502	464	632	632	627
	15	439	418	333	576	555	513
	20	357	345	258	465	438	391
	25	362	266	220	431	389	273

Having thus described our invention, we claim:

A process for the production of a cellulosic textile having cation-exchange properties and containing textile fibers of water-insoluble 2-sulfoethyl ethers of cellulose, comprising impregnating a cellulosic textile containing reactive hydroxyl groups with an aqueous solution of an alkali metal hydroxide of mercerizing strength containing from about 5 to 15%, based on the weight of the said alkali metal hydroxide solution, of the sodium salt of a sulfoethylating agent of the group consisting of 2-chloroethanesulfonic acid, ethionic acid and ethylenesulfonic acid by contacting the textile with enough of the alkaline liquid to wet substantially all of the fibers and substantially immediately removing the textile from contact with any of the liquid in excess of the amount entrained, heating the wet textile at a temperature above about 50° C. but below the decomposition temperature of the formed sodium salt of the sulfoethyl cellulose ether for from about 1 to 30 minutes, and washing the so-treated textile free of alkali.

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