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FURTHER AMINIZED AMINOALKYLATED
CELLULOSES BY REACTING WITH ETH-
YLENIMINE

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This invention 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 use of any royalty thereon.

This invention relates to cellulose derivatives which contain nitrogen in the form of amino groups and have ion-exchange properties which are not substantially altered by each used and regeneration.

The invention particularly relates to a process for producing a cellulose derivative which has a higher nitrogen content than that obtainable by the 2-aminoethylsulfuric acid process, which nitrogen is in a form more firmly bound than the nitrogen in compositions containing the same amount of nitrogen produced by the ethylenimine process.

One of the methods heretofore used to introduce amino groups involves the reaction of cellulose with an aminoalkylation agent such as a haloethylamino hydrohalide or with 2-aminoethylsulfuric acid in the presence of an alkali metal hydroxide. It has been well established that such reactions produce aminoalkyl cellulose ethers. Such aminoalkylated celluloses have proven to be resistant to the action of acids and bases. However, when more than about 1% nitrogen is so introduced, the ethers become more and more soluble in water, and the cellulosic fibrous character is lost in that cellulosic fabrics so treated become stiff and boardy.

Another method heretofore used to introduce amino groups involves the reaction of cellulose with imines such as ethylenimine. Chemists have been unable to conclusively establish whether all of the imine polymerizes upon the surfaces of the cellulosic fibers or whether some of it reacts to form aminoalkyl cellulose ethers. However, while up to about 10% nitrogen has in some manner been combined with, or on, cellulose by such a treatment, very little of the nitrogen is firmly bound. Even when the nitrogen content is low, upon treatment with aqueous acids or bases, a substantial amount of the amino nitrogen is lost.

The cellulosic derivatives containing amino groups and retaining a cellulosic fibrous character have been found to exhibit particularly valuable anion-exchange properties. Hoffpauir and Guthrie reported, *J. Biol. Chem.* 178, 207-212, that in the preparation of oilseed proteins, "Aminized cotton fabric was the most satisfactory anion-exchange material for the preparation of

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protein, since a higher pH could be obtained with it and the ash and phosphorus content of the preparation were lower than that obtained with either of the commercial anion-exchange resins."

5 The aminized cotton fabrics they used were prepared by reacting cellulose with 2-aminoethylsulfuric acid in the presence of sodium hydroxide by the process of Patent 2,459,222 and contained 0.8% nitrogen.

10 We have found that while introducing additional amino groups by reacting an aminoalkylated cellulose with 2-aminoethylsulfuric acid in the presence of an alkali metal hydroxide, or introducing additional amino groups by reacting the composition produced by the reaction of
15 cellulose with ethylenimine with additional portions of ethylenimine, tends to produce products which are soluble in water or easily decomposed by aqueous acids or bases; surprisingly, if an
20 aminoalkylated cellulose is reacted with an alkyl-
enimine, a totally different type of product is produced. The product produced by this latter method retains a cellulosic fibrous character, and is more resistant to the action of aqueous acids
25 and bases than is a product containing a like amount of nitrogen produced by the ethylenimine method. It is therefore apparent that reacting an aminoalkylated cellulose with ethylenimine produces a different substance than is produced
30 by retreating cellulose one or more times with either an aminoalkylating agent such as 2-aminoethylsulfuric acid or with an alkyl-
enimine such as ethylenimine.

While the invention is not to be construed as
35 being dependent upon the occurrence of a particular series of reactions, a possible explanation of the difference in the respective further aminized products is the following. Aminoalkylated celluloses contain aminoalkyl groups attached to the cellulosic nucleus by the relatively stable
40 ether linkage. When the ethylenimine is in contact with cellulose it is reasonable that the polymerization of ethylenimine predominates, and the relatively soluble polyethylenimine molecules form on the surfaces of the cellulosic material. On the other hand, when the ethylenimine is in contact with aminoalkylated cellulose,
45 it is reasonable that the reaction of the amino groups of the cellulose derivative with the ethylenimine predominates, and the aminoethyl groups on the cellulosic nucleus are converted to poly(ethyleneamino)aminoethyl groups. The occurrence of the above series of reactions would
50 account for the fact that the reaction of amino-

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alkylated celluloses with 2-aminoethylsulfuric acid lead to the production of water soluble compounds. When an aminoalkylated cellulose is so reacted, more and more of the cellulosic hydroxyl groups are converted to aminoethoxy groups.

We have demonstrated that subjecting an aminoethylated cotton fabric to two further aminizations with the vapors of ethylenimine can produce an ion-exchange fabric which after use and regeneration has a capacity of substantially 2000 milli-equivalents per kilogram and which retains a substantially unchanged ion-exchange capacity through at least four use and regeneration cycles.

The further aminization process of this invention can be suitably applied to any form of an aminoalkylated cellulose, for example to aminoalkylated cotton, aminoalkylated alpha-cellulose, aminoalkylated viscose rayon, and the like. Preferred starting materials comprise an aminoethylated cellulose containing from about 0.5 to 1.8% nitrogen; and such starting materials are preferably further aminized according to our invention until they contain from about 2 to 5% nitrogen.

A preferred embodiment of the invention is in the further aminization of aminoalkylated cotton cellulose in the form of yarn, particularly when the yarn is treated as such or while made up into a fabric. However, in general, any of the aminoalkylated celluloses can be further aminized by the process of the invention in the form of raw fibers, sliver, or in a disintegrated or powdered form.

The reaction is preferably conducted by contacting the aminoalkylated cellulose with the vapors of ethylenimine at a temperature below the decomposition temperature of the cellulosic material. However, in the further aminization of certain aminoalkylated celluloses, the ethylenimine can be dissolved in a solvent inert to the aminoalkylated cellulose and the reaction conducted in solution, for example in a solution containing an imine such as N-cetyl ethylenimine in benzene, toluene, xylene, or other liquid hydrocarbons.

Ethylenimine is the preferred alkylenimine for employment in the process of the invention. However, alkylenimines such as 2-methylethylenimine, 2,2-dimethylethylenimine and, in general, the homologs of ethylenimine can suitably be employed.

The reaction can be conducted at any temperature from about room temperature to the decomposition temperature of the cellulosic material. However, temperatures of from about 50 to 100° C. constitute a preferred range of temperatures for employment in the process of the invention.

In conducting the process in the preferred manner, i. e., in contacting the aminoalkylated cellulose with the vapors of the imine, it is preferred to employ less than an equal part of weight of ethylenimine. The use of amounts of from about 10 to 20% based upon the weight of the aminoalkylated cellulose have been found to be particularly suitable where the cellulosic material is placed in an evacuated chamber in which the imine is allowed to evaporate.

Where it is desired to produce a product having a relatively high nitrogen content, the reaction is preferably accomplished in several steps, contacting the aminoalkylated cellulose with the preferred amount of imine in each step.

The time necessary to accomplish a given degree of further aminization, of course varies widely depending upon the temperature and amount.

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of imine used. In general it has been found desirable to employ temperatures below about 100° C. and times of greater than about 6 hours for each treatment.

The following examples are presented to illustrate in detail certain phases of the invention. However, as it is apparent that other materials, reactions, conditions, and operative steps can be used, the scope of the invention is defined by the appended claims, and the invention is not to be construed as being limited to the particular substances or operations recited in the examples.

Example 1

Bleached cotton sheeting was padded with a solution composed of 55 parts by weight of water, 25 parts sodium hydroxide and 20 parts of 2-aminoethyl sulfuric acid. The pickup of solution after passing the squeeze rolls of the padder was about twice the weight of the original fabric. The moistened fabric was then heated in an oven for one hour at 100° C., washed and dried. At this stage in the process the fabric had an anion-exchange capacity of 570 milliequivalents per kg. and a nitrogen content of 0.85 percent.

The fabric was now placed in a vacuum chamber heated to 70° C. After the chamber had been evacuated, ethylenimine was introduced dropwise into the chamber through an addition tube in such a way that it vaporized at once. The weight of ethylenimine used was 16 percent of the weight of the fabric. After the fabric had reacted for three days with the ethylenimine vapor, it was removed and analyzed. It had an anion-exchange capacity of 1260 milliequivalents per kg. and a nitrogen content of 2.59 percent. After it had been used once to remove hydrochloric acid from dilute aqueous solution, being regenerated with dilute ammonium hydroxide solution, it had an anion-exchange capacity of 1200 and a nitrogen content of 2.14 percent. After it had been used four times to remove hydrochloric acid from dilute aqueous solution, it had an anion-exchange capacity of 1140 milliequivalents per kg. and a nitrogen content of 2.21 percent. Some of the fabric was boiled for 6 hours with 2 percent sodium hydroxide solution. After this it had an anion-exchange capacity of 1960 and a nitrogen content of 1.95 percent.

In order to obtain an even higher anion-exchange capacity, the fabric was treated a second time with ethylenimine by the method described above. The ion-exchange capacity was now 2070 milliequivalents per kg. and the nitrogen content was 4.63 percent. After it had been used once to remove hydrochloric acid from dilute aqueous solution, being regenerated with dilute ammonium hydroxide solution, it had an anion-exchange capacity of 1830 and a nitrogen content of 3.63 percent. After 4 cycles as an anion-exchanger its capacity was 1830 milliequivalents per kg. and its nitrogen content was 3.77 percent. After boiling with sodium hydroxide solution as previously described its anion-exchange capacity was 1480 milliequivalents per kg. and its nitrogen content was 2.79 percent.

For comparative purposes the same fabric was put twice through the portion of the process using 2-aminoethylsulfuric acid. Its anion-exchange capacity was 1060 milliequivalents per kg. and its nitrogen content was 1.58 percent. After boiling with sodium hydroxide solution as previously described, the values were .900 and 1.39 respectively. This fabric was again put through the part of the process using 2-aminoethylsulfuric acid, making a total of 3 times. It now had an anion-

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exchange capacity of 1290 and a nitrogen content of 1.97 but was stiff and boardy and beginning to lose its fabric structure. After boiling with sodium hydroxide solution as previously described, the values were 1050 and 1.55 respectively.

For comparative purposes some of the original untreated fabric was cured with sodium hydroxide solution alone to give a control fabric and this was then processed with ethylenimine only at the 16 percent level as previously described. The anion-exchange capacity was 770 milliequivalents per kg. and the nitrogen content was 2.20 percent. After it had been used once to remove hydrochloric acid from dilute aqueous solution, being regenerated with dilute ammonium hydroxide solution, it had an anion-exchange capacity of 570 and a nitrogen content of 1.09 percent. After 4 regeneration cycles the values were 520 and 1.03 respectively. After boiling with sodium hydroxide solution as described previously the values were 380 and 0.75 respectively. When the control fabric was processed twice with ethylenimine alone at the 16 percent level as previously described the values were 1310 and 3.38 respectively, but these fell to 950 and 1.70 after one use and to 890 and 1.65 after four regeneration cycles. After boiling with sodium hydroxide solution as previously described the values were 680 and 1.26 respectively.

A summary of the ion-exchange capacity of the materials made in the above examples is given in the following table:

Description of Fabric	Two AESA ¹	Three AESA	One AESA, One Imine ¹	One AESA, Two Imine	Two Imine
Original.....	1,060	1,290	1,260	2,070	1,310
After 1 cycle....	-----	-----	1,200	1,830	950
After 4 cycles....	-----	-----	1,140	1,830	890
Boiled with NaOH.....	900	1,050	1,060	1,480	680

¹AESA represents 2-aminoethylsulfuric acid and Imine represents ethylenimine.

Example 2

Coarse cotton bagging was put through the 2-aminoethylsulfuric acid process 5 times using a solution composed of 65 parts water, 25 parts sodium hydroxide and 10 parts 2-aminoethylsulfuric acid. This was to determine how high

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an anion-exchange capacity could be reached by this process alone. The anion-exchange capacity was 1210 milliequivalents per kg. and the nitrogen content was 1.71 percent. The fabric was, however, stiff and boardy and beginning to show signs of going into solution. It was now processed with the vapor of ethylenimine at the 16 percent level in a manner similar to that described in Example 1. The anion-exchange capacity was now 2700 and the nitrogen content 5.00 percent.

Having thus described our invention, we claim:

1. A process for the production of a cellulosic anion-exchange material which comprises further aminizing an aminoethylated cellulose containing from about 0.5 to 1.8% nitrogen by reacting it with the vapors of ethylenimine until the reaction product contains from about 2 to 5% nitrogen.

2. The process of claim 1 in which the aminoethylated cotton cellulose further aminized is in the form of a fabric.

3. The process of claim 1 in which aminoethylated cellulose is further aminized by subjecting the aminoethylated cellulose to a series of further aminization treatments using about 15%, by weight, of ethylenimine vapors and a temperature of about 70° C. in each treatment.

4. A process of producing an ion-exchange fabric which even after use and regeneration for at least four cycles has an ion-exchange capacity of at least about 1400 milli-equivalents, and which possesses cellulosic fibrous character comprising: reacting aminoethylated cotton fabric containing 0.5 to 1.8% nitrogen with ethylenimine until the fabric contains from 2 to 5% nitrogen, the aminoethylated cotton being one obtained by treating cotton fabric with aminoethylsulfuric acid and sodium hydroxide.

5. The process of claim 4 in which the ethylenimine is in the form of a vapor.

6. The process of claim 4 in which the ethylenimine is dissolved in an organic solvent.

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References Cited in the file of this patent

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Number	Name	Date
2,097,120	Fink et al.	Oct. 26, 1937
2,459,222	Guthrie	Jan. 18, 1949