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INTRODUCTION OF AMINO GROUPS INTO CELLULOSE

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This application is made under the act of March 3, 1883, as amended by the act of April 30, 1928, and the invention herein described, if patented, may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment to me of any royalty thereon.

This invention relates to a process of introducing amino groups into cellulose.

Cellulose textiles do not ordinarily dye well with acid dyes. It is known that amino groups may be introduced into cellulose, and that the cellulose textiles, such as cotton or viscose rayon textiles, thereby be rendered capable of fast dyeing with acid dyes.

An improvement over known processes may be accomplished by wetting cellulose textiles, such as cotton fabrics, with an aqueous solution of a haloethylamino hydrohalide, in particular, 2-chloroethylamine hydrochloride or 2-bromoethylamine hydrobromide (about 8 percent concentration preferred), drying the textile, then treating it with a saturated sodium hydroxide solution (about 50 percent strength, at a temperature of about 100° C., for about 1 minute, preferred), and then washing the fabric to free it of the sodium hydroxide. This subject matter is further disclosed and claimed in my copending application Serial No. 754,584, filed June 13, 1947, which has become abandoned.

The above process, although expeditious, utilizes a quite expensive amino adding agent and introduces a maximum of about only 0.23 percent nitrogen into the cellulose.

The present invention accomplishes the incorporation of a greater amount of nitrogen into the cellulose, thus enhancing the acid-dyeing characteristics, does so expeditiously, and utilizes a more economical amino adding agent.

In general, according to this invention, the cellulose is wetted with an aqueous solution of sodium hydroxide (mercerization strength of about 25 percent preferred), containing also 2-aminoethylsulfuric acid (preferably about 10 percent). The treated cellulose is heated at a temperature from 70° to 110° C. for a minimum period from 40 minutes to 9 hours, the higher temperatures being used with the shorter periods, the preferred temperature and period being about 100° C. and about 40 minutes, following which the cellulose is washed to remove the sodium hydroxide. Nitrogen up to about 0.60 percent is readily introduced by this procedure, and the treated fabric dyes darkly and fast with acid wool dyes.

The 2-aminoethylsulfuric acid is readily produced by reacting the relatively cheap products, fuming sulfuric acid and ethanol amine.

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To exhibit the invention in greater detail, a number of experiments were conducted in which the material used was a commercial broadcloth, 4 yds. per lb., 108 by 60 thread count, that had been singed, desized, kierboiled, and bleached. The 2-aminoethylsulfuric acid used was made by treating 10-ml. portions of ethanol amine, cooled in ice-salt mixture, with 20 ml. of fuming sulfuric acid (dropwise). After addition of a little water to the reaction mixture, the substance was precipitated with an excess of ethyl alcohol. The substance was separated by filtration, redissolved in water and reprecipitated with alcohol, giving a yield of about 15 g.

The fabric was cut into several 12-cm. in width strips lengthwise of the warp. Each strip was pinned into a sleeve 32 cm. in circumference and slipped over a stainless steel beaker of 32 cm. outside circumference. A 12 x 30 cm. area (3.7 g. dry wt.) of each of the fabrics was then moistened with solution of the sodium hydroxide and 2-aminoethylsulfuric acid using a glass wool swab and the beaker and fabric heated in a forced draft oven, various temperatures for various times being employed with different fabrics.

The solutions used were: (A) 18.75 g. sodium hydroxide, 48.75 ml. water, and 7.5 g. of 2-aminoethylsulfuric acid; (B) 18.75 g. sodium hydroxide, 54.0 ml. water, and 2.25 g. 2-aminoethylsulfuric acid; (C) 67.5 g. of 50 percent sodium hydroxide and 7.5 g. of 2-aminoethylsulfuric acid; and (D) 72.75 g. 50 percent sodium hydroxide and 2.25 g. 2-aminoethylsulfuric acid. Appropriate controls were included. It was necessary to apply solutions C and D to the fabric hot in order to keep the material in solution. The take-ups of solutions A and B were about 8.5 g. and for C and D about 12.5 g.

The fabrics thus treated were heated in a forced draft drying oven and then washed at least 45 minutes on the beaker in running tap water and then with two or more changes of distilled water. During the heating the solutions dried on the cellulose.

The introduction of amino groups was measured by Kjeldahl nitrogen determinations. For this, the material was digested in the usual manner using mercury as a catalyst. The ammonia was distilled into an excess of dilute acid and determined colorimetrically using Nessler's reagent. Moisture determinations were made so that the nitrogen values could be converted to the dry basis.

The results are summarized in the table. Dyeing tests with Kiton fast red were in agreement with the total nitrogen values, the fabrics containing 0.5 to 0.6 percent nitrogen dyeing a dark red, those with 0.2 percent nitrogen a lighter red.

Table

Solution	Percentage of—		Temperatures and times of heating						
			90° C.		100° C.		110° C.		70° C.
	NaOH	2-aminoethylsulfuric acid	20 min., nitrogen introduced, percent	40 min., nitrogen introduced, percent	20 min., nitrogen introduced, percent	40 min., nitrogen introduced, percent	20 min., nitrogen introduced, percent	40 min., nitrogen introduced, percent	9 hr., nitrogen introduced, percent
A	25	10	0.15	0.37	0.23	0.56	0.47	0.62	0.59
B	25	3	0.03	0.20	0.13	0.23	0.20	0.24	0.25
C	50	10	0.07	0.31	0.13	0.30	0.34	0.36	0.28
D	50	3	0.08	0.20	0.16	0.18	0.20	0.21	0.15
Control	25	0	0.01					0.02	0.02
Do	50	0	0.01					0.02	0.02

Tests indicate that the breaking strength is only slightly decreased by the procedure, the average breaking test for the various treated examples of the table being about 48 lbs. per 100 warp threads as compared to 51 lbs. for the untreated fabrics.

Taking into consideration both total nitrogen values and the breaking strength values, the condition of choice appears to be 25 percent sodium hydroxide with heating for 40 minutes at 100° C.

For the purpose of testing the effect of sodium hydroxide concentrations further, solutions containing 10 percent 2-aminoethylsulfuric acid in 30, 25, 23, 21, 19 and 17 percent sodium hydroxide were tried, and heating at 100° C. for 40 minutes. The total nitrogen values obtained on the dry basis were 0.51, 0.59, 0.57, 0.54, 0.47, and 0.46 percent, respectively. This shows that 25 percent sodium hydroxide is the concentration of choice, although small variations from this concentration are of little importance.

Increasing the heating time beyond 40 minutes does not greatly increase the nitrogen percent, since 16 hours at 100° using 10 percent 2-aminoethylsulfuric acid in 25 percent sodium hydroxide gave only 0.64 percent nitrogen compared with 0.56 percent for the 40-minute period. The fabric heated for 16 hours had a breaking strength of 37 lbs. per 100 warp threads. It will be noted from the table that the heating temperature may be lowered to 70° C. if the time is extended to 9 hours. However, in other experiments 50° C. for 45 hours gave a nitrogen value of only 0.24 percent and 40° C. for 71 hours gave 0.18 percent. Allowing the wetted fabric to stand in a closed container for several hours before baking did not increase the nitrogen value.

The 2-aminoethylsulfuric acid need not be isolated. In one experiment 10 ml. of ethanolamine was treated with 20 ml. of fuming sulfuric acid in the usual manner. The reaction mixture was diluted with water and neutralized with strong sodium hydroxide solution. It heated and reacted vigorously. After cooling, 58 g. of solid sodium hydroxide was added followed by water to make a total of 230 g. Although much sodium sulfate separated from this solution, the supernatant liquid was quite effective. A fabric giving a dark dyeing reaction after treatment with this liquid at 110° C. for 40 minutes was obtained. Its total nitrogen content on the dry basis was 0.52 percent. After the liquid had stood for 3 weeks at room temperature, a fabric treated with it in the same manner, containing 0.41 percent nitrogen, was obtained.

The treatment with 2-aminoethylsulfuric acid and sodium hydroxide works on viscose rayon. Acetate rayon must be soaked in the solution for about 40 minutes to de-acetylate it prior to baking.

Repeated treatments of the same piece of fabric with 2-aminoethylsulfuric acid have been tried. A parchment-like material having some fabric structure was obtained. Its nitrogen content was 1.84 percent on the dry basis.

Sodium hydroxide solutions containing 2-aminoethylsulfuric acid may be used to print patterns on fabrics. If used in connection with another sodium hydroxide solution containing monochloroacetic acid (see British Patent No. 231,803 of 1925), acid carboxyl groups may be introduced into portions of fabric while amino groups are introduced into other portions. When fabrics so printed are dyed with a basic dye like methylene blue and then with an acid dye like Kiton fast red, two-colored printing results.

The most outstanding property of the fabric treated with the 2-aminoethylsulfuric acid and sodium hydroxide is its dyeing with acid dyes. The aminized fabric also dyes well with a chrome dye such as alizarine blue black B while the untreated fabric does not. The amino groups of the treated fabric exhibit the expected properties of amino groups, outstanding of which is the capacity to take up acids. The aminized fabric takes up hydrochloric acid from dilute solution in amounts commensurate with its amino content measured by total nitrogen values. It is dyed yellow with picric acid. When placed in dilute phosphoric acid, it takes up, and retains after thorough washing, enough of this acid to give a black ash showing no afterglow when the fabric is burned. When the fabric is placed in 1 percent sodium dichromate solution and thoroughly washed, it retains enough chromic acid to become a brownish yellow, while untreated fabric, or fabric treated with sodium hydroxide alone, remains white. The aminized fabric treated with sodium dichromate showed rot resistance in a soil burial test. Rot resistance may also be obtained by treating the aminized fabric with a 1 percent solution of mercuric chloride. When placed in 0.5 N potassium permanganate, acidified with a little acetic acid, the aminized fabric turns a dark brown. This color is not removed by thorough washing.

Another property of the fabric worthy of note is its slight but noticeable water repellency. A drop of water placed on the aminized fabric does not soak in for some time, while control fabric treated with sodium hydroxide alone or untreated fabric wets at once. The aminized fabric has a

somewhat higher moisture content than the control fabric treated with sodium hydroxide alone, and a much greater moisture content than the untreated fabric.

The amino groups are presumably introduced into the fabric as amino ethoxyl groups, replacing some of the hydroxyl groups of the cellulose. This involves an ether linkage which should be quite stable to hydrolytic agents. It may be calculated that 0.56 percent nitrogen on the dry weight basis is equivalent to about one amino group for every 15 glucose units in the cellulose molecule. Based on uptake of treating solution and weight of fabric taken, the efficiency of introduction of amino groups based on the take-up of the fabric is about 25 percent for 2-aminoethylsulfuric acid.

Having thus described the invention, what is claimed is:

1. A process of introducing amino groups into cellulose comprising treating the cellulose with an aqueous solution of sodium hydroxide and 2-aminoethylsulfuric acid, heating the treated cellulose at a temperature from 70° to 110° C. for a minimum period from 40 minutes to 9 hours, the higher temperatures being used with the shorted periods, and then washing the cellulose to remove sodium hydroxide.

2. The process of claim 1 wherein the treating solution contains about 10 percent of the 2-aminoethylsulfuric acid.

3. The process of claim 2 wherein the temperature is about 100° C. and the period about 40 minutes.

4. The process of claim 3 wherein the treating solution contains about 25 percent of the sodium hydroxide.

5. The process of claim 4 wherein the solution is dried on the cellulose during the heating.

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