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PROCESS OF MAKING ALKALI-INSOLUBLE CELLULOSE GLYCOLIC ACID ETHER FABRIC

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The present invention relates to the partial and uniform etherification of fibrous cellulose by treatment with chloroacetic acid.

Glycolic acid ethers of cellulose have been prepared by the use of chloroacetic acid and sodium hydroxide, and it has been suggested to impregnate cellulosic fabrics with a solution of monochloroacetic acid or a solution of the sodium salt thereof and to then dry the impregnated cloth and causticize it with a sodium hydroxide solution at room temperature for a period of time from 5 minutes to several hours. Also, it has been suggested to first causticize the fabric and then impregnate it with sodium chloroacetate or chloroacetic acid, following which the fabric thus impregnated was to be heated for a period of time from 10 minutes to an hour at a temperature of 50 to 100° C.

There were serious disadvantages encountered in all of these previous attempts to convert the cellulose fiber into glycolic acid ethers of cellulose. Thus when the free acid was used to impregnate the fabric, it caused severe corrosion of the equipment, and if the acid was dried into the fabric, it caused considerable loss of tensile strength in the finished product. If the acid-treated goods were causticized immediately after the impregnation, without previous drying, a product with satisfactory properties resulted but of a much lower degree of substitution than one would expect to obtain with the concentration of the acid employed. This meant an economic loss and a high cost for the process in question.

If the fabric were impregnated with a sodium chloroacetate solution and then dried, the subsequent causticizing of the goods became impractical because the sodium hydroxide solution did not uniformly wet out the fabric, and a spotty and uneven treatment resulted which gave an unsatisfactory product. Attempts were made to partially dry the fabric impregnated with sodium chloroacetate solution before causticizing, but it was found non-feasible to partially dry the fabrics uniformly within a narrow range of moisture content. Furthermore, if not completely dry, the sodium chloroacetate hydrolyzed on storage, splitting off sodium chloride and liberating hydroxyacetic acid.

Wetting agents did not appreciably increase the wetability of the dried sodium chloroacetate-impregnated fabrics when such agents were introduced either into the sodium chloroacetate bath or into the sodium hydroxide solution.

While it is possible to obtain a satisfactory product by first causticizing the fabric and then, without drying, impregnating with a chloroacetic acid or sodium chloroacetate solution, this method was found unsatisfactory because of the corrosion of equipment by the acid and the excessive amount of chloroacetic acid or chloroacetate required to obtain a sufficient degree of substitution. To obtain a substitution of one glycolic acid group to each 15–25 glucose units, it was either necessary to employ a vast excess of chloroacetic acid or chloroacetate, or it

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required a correspondingly long reaction time of from 30 minutes to several hours, or even days.

The present invention overcomes the defects of the prior art by employing a solution of the ammonium salt of chloroacetic acid, drying the impregnated fabric completely and then causticizing it with a hot (40 to 55%) sodium hydroxide solution. The dry ammonium chloroacetate-containing fabric is rapidly and completely wetted by the hot sodium hydroxide solution with evolution of ammonia. Satisfactory degree of substitution, i. e. one glycolic acid group to each 15–25 glucose units, was obtained within 45–65 seconds when chloroacetic acid in form of ammonium chloroacetate was used in quantities of 5 to 10% on the weight of the dry fabric. The ammonium chloroacetate-impregnated fabrics when dried may be stored for prolonged periods of time without showing appreciable hydrolyzation of the chloroacetic acid and consequent loss of reactivity. The maximum rate of reaction was observed when the sodium hydroxide concentration was between 45 to 55% and the temperature of the sodium hydroxide was held between 55 to 85° C.

The following method was used for determining the degree of substitution:

The treated fabric is rinsed in 2% acetic acid solution and then in distilled water to remove the acetic acid. The excess water is removed from the fabric by centrifuging it in a basket-type centrifuge. The moist fabric, without drying, is then immersed for 24 hours in a 2% copper sulphate solution. The excess copper sulphate is removed by rinsing with distilled water. The fabric is dried by pressing it in a flat bed press. It is then conditioned for 4 hours in a constant temperature and humidity room at 70° F. and 65% relative humidity. A suitable sized sample (10–12 gms.) of the copper-containing fabric is then cut into approximately 1" square pieces and the copper extracted from the material with a 5% sulphuric acid solution. The copper present may be determined either by gravimetric, volumetric or colorimetric methods. In the present work, the colorimetric method was employed by the use of a suitable electrophotometer. In order to obtain increased precision, the color of the copper solution was intensified with tetraethylenepentamine. The calculation of the degree of substitution was based on the assumption that each mole of copper has combined with 2 glycolic acid carboxyls.

Example 1

Fabric: Cotton sheeting 39" wide; thread count: 96 x 100; weight: 4.10 yds./lb. The fabric was desized, scoured and bleached before it was subjected to our process.

Preparation of ammonium chloroacetate solution:

	Lbs.
Water	83.25
Monochloroacetic acid—Tech. Grade (98% $\text{ClCH}_2\text{—COOH}$)	10.00
Ammonia 26° Bé. (29.4% NH_3)	6.75
Total	100.00

Dissolve the monochloroacetic acid in the water, add the ammonia and mix thoroughly. The above quantity of ammonia used represents a 10% excess over the stoichiometric amount required for neutralizing the monochloroacetic acid. This was found advantageous to compensate for the losses of the ammonia during the drying operation.

Impregnation.—The fabric was impregnated with the ammonium monochloroacetate solution in a standard textile padder, set for a double immersion and equipped with squeeze rolls, between immersions and after the second immersion. The squeeze rolls, after the second

immersion, were adjusted to allow a weight of salt solution about equal to that of the weight of the dry fabric to be retained in the fabric. The impregnated fabric, after padding, was dried immediately in a clip-tenter at between 120 to 138° C. for approximately 1 minute. A "bone-dry" fabric was obtained.

Causticizing.—The equipment used for the causticizing was a standard textile padder set for a double immersion and equipped with squeeze rolls between immersions and after the second immersion. A 50% sodium hydroxide solution was used in the immersion tanks as the causticizing liquor. The liquor was heated to about 60° C. and held at that temperature throughout the run with the aid of steam coils in the immersion tanks. The fabric leaving the padder was picked up in a 20 yard long clip-tenter and held under sufficient weft tension to hold the fabric taut yet not to cause it to rip at the selvages. The padder and the tenter were operated synchronously at a rate of about 20 yds./minute, which corresponded to a total contact time of 65 seconds with the sodium hydroxide solution. As the fabric emerged from the causticizing bath, it was squeezed to expel all but about 90 to 110% of sodium hydroxide solution calculated on the weight of the dry fabric.

Washing and drying.—The causticized fabric reaching the end of the tenter frame was immediately washed with a very large excess of hot water (80 to 95° C.) and then with cold water in a standard "open-width" textile washer, until all excess NaOH was removed. The washing was considered completed when the fabric was neutral to phenolphthalein. The fabric was then dried without tension in a loop drier. In order to obtain a fabric with satisfactory dimensional stability, i. e. within 2% shrinkage or stretch, the fabric passed through a tenter frame equipped with steam jets at a tension corresponding with "zero width" in accordance with established practice in the art.

The product obtained in the above process was the sodium salt of the glycolic acid ether of the cotton cellulose.

Degree of substitution:

1 glycolic ether to 25 glucose units

Dimensional stability:

Shrinkage, 1.8% after one standard AATCC #3 wash test

Tensile strength:

Original fabric, 58 lbs./inch

Treated fabric, 63 lbs./inch

Elongation at break:

Original fabric, 7%

Treated fabric, 18%

Handle of the fabric:

Stiff, wiry feel

Uniformity of treatment:

Uniform as demonstrated by the even dyeing obtained with methylene blue.

Example II

Fabric: Cotton print cloth 40" wide; thread count: 48 x 48; weight: 2.85 yds./lb. The fabric was desized, scoured and bleached before impregnating it with the ammonium chloroacetate solution.

The process used in this example was the same as that used in Example I.

Degree of substitution:

1 glycolic ether to 18 glucose units

Dimensional stability:

Shrinkage 2% after one standard AATCC #3 wash test

Tensile strength:

Original fabric, 73 lbs./inch

Treated fabric, 90 lbs./inch

Elongation at break:

Original fabric, 6%

Treated fabric, 27%

Handle of the fabric:

Stiff, wiry feel

Uniformity of treatment:

Uniform as demonstrated by even dyeing obtained by the use of methylene blue.

Example III

Fabric: Same as in Example II.

Process analogous to Example II. After washing the fabric free of sodium hydroxide, it was rinsed with an excess of a 2% acetic acid and dried. In this manner, the free glycolic acid ether was obtained. The tensile strength, the elongation and the dimensional stability of the fabric showed only insignificant variations from those of the sodium salt of Example II. The handle of the fabric, however, was full and much softer than that of Example II.

Example IV

Fabric: Same as in Example II.

Process analogous to Example III. The souring of the fabric after washing was accomplished with a 4% solution of oxalic acid followed by a rinse with de-ionized water. In this manner, we succeeded in removing the traces of iron and other metals picked up by the carboxyls of the glycolic acid ether of the cellulose during processing. The resulting product had essentially the same properties as that obtained in Example III, with the exception that it was noticeably whiter due to the absence of the colored metal compounds.

Example V

Fabric: Linen suiting 48" wide; thread count: 25 x 20; weight: 3.43 yds./lb. The fabric was desized, scoured, bleached and mercerized without tension before subjecting it to our process.

The process used was the same as in Example I.

Degree of substitution:

1 glycolic acid ether to 15 glucose units

Dimensional stability:

Shrinkage, 4% after one standard AATCC #3 wash test

Tensile strength:

Original fabric, 63.27 lbs./inch

Treated fabric, 95.9 lbs./inch

Elongation at break:

Original fabric, 27%

Treated fabric, 19.5%

Handle of the fabric:

Stiff, wiry feel.

Example VI

Fabric same as in Example V. The process used was the same as in Example IV.

The handle of the fabric in this case was much softer than of the product obtained in Example V.

Tensile strength:

Original fabric, 63.27 lbs./inch

Treated fabric, 84 lbs./inch

Elongation at break:

Original fabric, 27%

Treated fabric, 10%

The fabric obtained in the above examples dyed with methylene blue shows that the treatment when carried out in accordance with this invention is uniform throughout the fabric from end to end and from side to center. As checked by the copper method, the glycolic acid substitution shows no noticeable variations in different sections of the same fabric. Employing the same quantity ammonium chloroacetate per weight of fabric, the rate of substitution increases with increasing thickness of weave. Bleached mercerized linen gives a higher degree of substitution than a corresponding cotton fabric.

The sodium salts obtained in accordance with the above examples are considerably stiffer, more wiry, than the corresponding untreated fabrics. The "handle" of the fabric is improved if the glycolic acid ether is liberated by souring it with a dilute acid solution and then drying it. The free glycolic acid ether of cellulose has a pleasing "handle" and shows a fullness and "life" entirely different from that of the original untreated fabric. The free carboxyl groups are capable of reacting with metals forming colorless or colored compounds depending on the metal. Both the sodium salt and the free acid show exceptionally high degrees of wetability with water. Results similar to those obtained with ammonium chloroacetate were obtained also by the use of the ammonium salts of α -chloropropionic acid and α -bromobutyric acid. Using these longer chain acids, the formation of the glucose ether was somewhat slower and less complete. The products obtained, however, showed uniform treatment. Monochloroacetic acid salts of volatile amino compounds, such as methyl and ethyl amine, were substituted for ammonia in some experiments. The resulting products were similar to those obtained with ammonium chloroacetate. However, the degree of substitution was somewhat less than that obtained with the ammonium salt. The foregoing use of α -chloropropionic acid and α -bromobutyric acid, as well as the monochloroacetic acid salts of volatile amino compounds such as methyl and ethyl amine, are to be regarded in a broad sense as equivalents of the ammonium salts of the monochloroacetic acid.

We claim:

1. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric corresponding with 5% to 10% of chloroacetic acid calculated on the weight of the dry fabric, drying the fabric, impregnating the dried fabric with a 40 to 55% aqueous solution of sodium hydroxide at temperatures about 55 to 85° C., retaining about 90 to 110% sodium hydroxide solution calculated on the weight of the dry fabric, permitting the sodium hydroxide solution to remain in contact with the fabric for a period of from 45 seconds to 3 minutes, removing the sodium hydroxide with excess water, and then drying the fabric.

2. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric corresponding with 5% to 10% of chloroacetic acid calculated on the weight of the dry fabric, drying the fabric, impregnating the dried fabric with a 40 to 55% aqueous solution of sodium hydroxide at approximately 60° C., permitting the sodium hydroxide solution to remain in contact with the fabric for a period of from 45 seconds to 3 minutes, removing the sodium hydroxide with excess water, and then drying the fabric.

3. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric corresponding with 5% to 10% of chloroacetic acid calculated on the weight of the dry fabric, drying the fabric, impregnating the dried fabric with 40 to 55% aqueous solution of sodium hydroxide at approximately 60° C., retaining about 90 to 110% of sodium hydroxide solution calculated on the weight of the dry fabric, permitting the sodium hydroxide solution to remain in contact with the fabric for about 65 seconds, removing the sodium hydroxide with excess water, and then drying the fabric.

4. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric and corresponding with 5% to 10% of chloroacetate acid calculated on the weight of the dry fabric, drying the fabric, passing the dried fabric at a rate of 20 yds./minute through a causticizing bath of 40 to 55% aqueous solution of sodium hydroxide at temperatures about 55 to 85° C., squeezing it immediately as it emerges from the causticizing bath to expel all but about 90 to 110% of sodium hydroxide solution calculated on the weight of the dry fabric, permitting the sodium hydroxide solution to remain in contact with the fabric for a period of from 45 seconds to 3 minutes, removing the sodium hydroxide with excess water, and then drying the fabric.

5. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric and corresponding with 5% to 10% of chloroacetate acid calculated on the weight of the dry fabric, drying the fabric, passing the dried fabric at a rate of 20 yds./minute through a causticizing bath of 40 to 55% aqueous solution of sodium hydroxide at temperatures about 55 to 85° C., squeezing it immediately as it emerges from the causticizing bath to expel all but about 90 to 110% of sodium hydroxide solution calculated on the weight of the dry fabric, permitting the sodium hydroxide solution to remain in contact with the fabric for a period of from 45 seconds to 3 minutes while holding the fabric under weft tension, removing the sodium hydroxide with excess water, and then drying the fabric.

6. A process of preparing alkali-insoluble glycolic acid ethers of fibrous cellulose comprising impregnating the cellulose fabric with an aqueous solution of ammonium monochloroacetate, retaining in the fabric an amount of the solution about equal to the weight of the dry fabric and corresponding with 5% to 10% of chloroacetate acid calculated on the weight of the dry fabric, drying the fabric, passing the dried fabric at a rate of 20 yds./minute through a causticizing bath of 40 to 55% aqueous solution of sodium hydroxide at temperatures about 55 to 85° C., squeezing it immediately as it emerges from the causticizing bath to expel all but about 90 to 110% of sodium hydroxide solution calculated on the weight of the dry fabric, permitting the sodium hydroxide solution to remain in contact with the fabric for a period of from 45 seconds to 3 minutes while holding the fabric under weft tension, removing the sodium hydroxide with excess water, rinsing the fabric with an excess of a weak acid, and then drying the fabric.

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