

UNITED STATES PATENT OFFICE

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PROCESS OF MAKING COTTON TEXTILES WATER-ABSORBENT AND ROT-RESISTANT

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1 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 us of any royalty thereon.

This invention relates to textiles, and has among its objects the production of cotton textiles which are swellable when wetted, highly water absorbent and rot resistant.

In general, according to the invention, a cotton textile is soaked with monochloroacetic acid and then treated with a solution of an alkali metal hydroxide, such as sodium hydroxide, varying in concentration between 20 percent to 50 percent, to give a resulting textile containing about one carboxymethyl substituent per 40 to 5 glucose units, the higher carboxymethyl substitution going with the higher concentration of NaOH, which is swellable when wetted, and is water absorbent, the degree of swellability and absorbency being controlled by the strength of the hydroxide used and consequent degree of carboxymethyl substitution. The textile can be rendered rot resistant by treating it further with solutions of certain metallic salts in such manner that insoluble metal salts of the carboxymethyl groups present in the textile are formed. A salt which yields copper ions in solution thus to produce the copper salts of the carboxymethyl groups is quite satisfactory. However, other metallic salts, such as those which yield iron, silver, nickel, mercury, lead or aluminum ions, may be employed. Treatment with a metallic salt also affects the manner of swellability, as later will be shown.

The swellable and water-absorbent fabrics of the invention, with or without treatment to ren-

2 and therefore may be used as a waterproof wall. The water-absorbent property renders the textile useful in the production of toweling, surgical bandages and sponges, and the like.

5 In case the metallic salt employed is a salt of copper, it is unexpected that the resulting rot-proof textile is highly swellable. The copper-cellulosic salt is itself almost entirely insoluble in water, whence it would be expected that the textile with the copper substituted carboxymethyl groups would swell but little.

10 The following examples exhibit the invention in greater detail.

EXAMPLE I

15 Three skeins of similar No. 12 soft cotton seine twine (samples numbered 1, 2 and 3) were made up and treated with boiling ethyl alcohol to remove waxes. The wax extraction is not necessary but helps to insure good penetration. The skeins were then soaked in a 40% solution of monochloroacetic acid, pressed out, and mercerized under tension with, respectively, 20%, 24%, and 28% sodium hydroxide for a period of one hour.

25 The samples were then thoroughly washed and treated with an excess of a 10% solution of copper sulfate, and again washed. Part of each sample was analyzed for copper to determine the carboxyl content. The samples were then exposed to the action of micro-organisms by weighting and submerging in the water of Bayou St. John, New Orleans, Louisiana. The average temperature of the bayou was 58° F. Control samples of untreated twine and twine treated with copper naphthenate were also exposed and portions of the samples were removed at various time intervals for testing. Tensile strength in lbs. per twine were determined, the results being given in Table 1.

Table 1

Twine sample	NaOH percent	Cu percent	Tensile strength, lbs. per twine					
			Exposed 0 wk.	Exposed 2 wks.	Exposed 4 wks.	Exposed 6 wks.	Exposed 8 wks.	Exposed 11 wks.
Untreated control.....	-----	0.00	30.2	13.4	00.0	-----	-----	-----
Cu naphthenate control.....	-----	1.00	34.1	36.8	29.8	22.9	15.9	6.7
No. 1.....	20	0.35	30.2	30.8	20.8	15.7	14.5	3.0
No. 2.....	24	0.80	31.0	29.6	19.3	13.1	7.3	2.9
No. 3.....	28	2.20	28.6	27.2	18.7	14.4	7.8	3.2

der them rot-resistant, are useful in the production of such articles as tents, water pressure hose, and the like, since the cloth due to swelling of the yarn becomes leak proof when wet.

EXAMPLE II

To show the effect of varying the metallic salt employed, 21 skeins of cotton thread were soaked

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in 40% monochloroacetic acid overnight with a wetting agent to aid penetration. Seven skeins were mercerized with 25% sodium hydroxide, seven with 28% sodium hydroxide, and seven with 30% sodium hydroxide for a period of one hour. The skeins were then washed thoroughly with the addition of a small amount of acid to aid in obtaining neutrality. One each of the seven skeins of each group was treated with an excess of a copper sulfate solution, a ferric chloride solution, a silver nitrate solution, a nickel chloride solution, a mercuric chloride solution, a lead acetate solution, and an aluminum sulfate solution to give complete metallic substitution in the carboxymethyl groups present. After treatment, the samples were washed and dried. Sets of threads taken from the samples were then buried in soil containing highly active cellulose-destroying organisms and samples were removed at various intervals of time for testing. The results are given in Table 2.

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absorbency being based on the weight of the dry yarn.

Table 3

Sample	NaOH percent	Cu, percent	Water Absorbency, percent	Leakage, ml.	
				1st 10 min.	2d 10 min.
Mercerized control	-----	0.0	50.7	7.33	6.33
No. 4.....	32	0.0	75.8	0.48	0.40
No. 5.....	35	0.0	98.1	0.0	0.0
No. 6.....	40	0.0	181.8	0.0	0.0
No. 7.....	40	2.4	116.9	0.33	0.29

Small portions of sample No. 4 and sample No. 5 were further treated with an excess of copper sulfate and analyzed. They contained 0.5 percent and 0.72 percent of copper, corresponding to carboxymethyl substituents in the ratio one to 40 and one to 20 glucose units, respectively.

Sample No. 6 swelled so much that its usefulness

Table 2

Metallic salt used	NaOH, per cent	Tensile strength, lbs. per thread						
		Exposed 0 wk.	Exposed 1 wk.	Exposed 2 wks.	Exposed 3 wks.	Exposed 4.5 wks.	Exposed 7.5 wks.	Exposed 10.5 wks.
Untreated.....	-----	15.5	0.0	-----	-----	-----	-----	-----
Copper sulfate.....	25	15.7	8.2	0.0	-----	-----	-----	-----
Do.....	28	16.2	6.7	0.0	-----	-----	-----	-----
Do.....	30	16.5	7.2	0.0	-----	-----	-----	-----
Ferric chloride.....	25	14.7	5.4	0.0	-----	-----	-----	-----
Do.....	28	15.6	5.2	0.0	-----	-----	-----	-----
Do.....	30	14.8	8.7	0.0	-----	-----	-----	-----
Silver nitrate.....	25	15.5	15.8	15.0	13.0	11.2	0.0	-----
Do.....	28	15.6	14.6	15.1	13.9	11.4	7.0	0.0
Do.....	30	14.9	13.8	12.6	12.8	12.2	6.5	0.0
Nickel chloride.....	25	17.0	6.6	0.0	-----	-----	-----	-----
Do.....	28	16.2	8.4	0.0	-----	-----	-----	-----
Do.....	30	15.0	7.6	0.0	-----	-----	-----	-----
Mercuric chloride.....	25	16.3	15.8	16.1	16.7	16.7	7.5	0.0
Do.....	28	16.1	16.7	16.5	16.4	17.4	16.3	0.0
Do.....	30	15.2	16.6	16.6	17.3	17.3	16.7	0.0
Lead acetate.....	25	17.1	16.5	12.7	0.0	-----	-----	-----
Do.....	28	15.9	17.3	10.4	7.9	0.0	-----	-----
Do.....	30	14.8	16.2	11.5	7.4	0.0	-----	-----
Aluminum sulfate.....	25	16.2	7.1	0.0	-----	-----	-----	-----
Do.....	28	15.9	5.4	0.0	-----	-----	-----	-----
Do.....	30	16.4	6.3	0.0	-----	-----	-----	-----

EXAMPLE III

To show the effects of the treatment relating to water-absorbency and swellability, three skeins of cotton yarn were soaked in a 40% solution of monochloroacetic acid containing a wetting agent to assure good penetration and were then treated with 32%, 35% and 40% sodium hydroxide solution, respectively, for one-half hour. The samples are numbered 4, 5 and 6 in Table 4. Part of the sample treated with the 40% sodium hydroxide solution was further treated with an excess of copper sulfate solution (numbered 7 in the table), and it contained 2.4% copper which indicates that there is approximately one carboxyl group per every 5 glucose units of the cellulose.

Various samples were tested for water absorption by soaking them in water for 24 hours and then centrifuging at 1850 times gravity for 20 minutes to remove absorbed water. They were also tested for swelling by placing a sufficient number of dry yarns lengthwise in an orifice so that about 34% free air space remained and testing the water leakage through the packed orifice for two successive ten-minute periods under 50 lbs. per sq. in. pressure. The results are given in Table 3 and illustrate the high absorbency and swelling properties of the material, the percent

might be limited for many purposes. However, sample No. 7, which was made from sample No. 6, does not have the excessive swelling fault, but still has excellent swelling properties, as well as rot resistancy. The table also shows that even as little as approximately one carboxyl group per 40 glucose units, as in the case of sample No. 4, imparts good swelling properties.

Not only can yarns and threads be processed according to the invention, but cotton cloth may also be so processed, as for example, by treating it with monochloroacetic acid and then mercerizing it with or without tension, followed, if desired, by the treatment with metallic salts in a manner similar to the treatment heretofore set forth relative to the yarns and threads.

Table 4 gives the results obtained by treatment of a number of samples of khaki-dyed, herringbone twill. The permeability to air was measured on a standard machine, and the results are given in cubic feet of air passed per minute through a square foot of the material. The samples were also tested on the Suter hydrostatic pressure machine with a 4½" circular opening, under a 6" pressure head for 5 minutes, and the milliliters of water passing through the cloth measured.

Table 4

Sample	NaOH, percent	Cu, percent	Air perme- ability, cu. ft. per min. per sq. ft.	Water per- meability, ml.
Control not treated (No. 8)-----	0	0	16.8	10,430
Control mercerized (No. 9)-----	50	0	11.0	8,980
No. 10-----	28	1.0	64.00	334
No. 11-----	44	1.0	15.2	3
No. 12-----	44	3.02	72.0	6,120
No. 13-----	50	2.55	62.0	7,270

¹ Copper equivalent 1.43.

² Copper equivalent 3.02.

Mercerization of the cloth in a conventional manner (sample No. 9) permanently swells the cloth fibers so that both air and water permeability are reduced somewhat over those of the cloth not treated (sample No. 8). Increasing the strength of the sodium hydroxide solution used, however, (sample No. 10 and sample No. 11) greatly decreases the water permeability. The air permeability is, however, somewhat increased because the dry cloth, when mercerized with the higher strength sodium hydroxide solution, is stiffer due to the greater amount of carboxymethyl groups added. Treating with copper salt (sample No. 12 and sample No. 13) tends to increase water permeability over corresponding samples not so treated, because the treatment tends to render the cloth porous.

Having thus described the invention, what is claimed is:

1. A process comprising impregnating a cotton textile with chloracetic acid, treating the impregnated textile with a solution of an alkali metal hydroxide ranging in concentration between 20% and 50% to give a fabric having carboxymethyl substituents in the ratio of one to from 40 to 5 glucose units, and then treating the textile with a solution of a salt which yields metal ions in the solution and produces a non-soluble metal salt of the carboxymethyl groups, the said salt being selected from the class consisting of salts of copper, iron, silver, nickel, mercury, lead and aluminum.

2. The process of claim 1 in which the salt is a salt of copper.

3. The process of claim 1 in which the salt is copper sulfate.

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The following references are of record in the file of this patent:

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