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PROCESS OF REACTING PARTIALLY SWOLLEN COTTON TEXTILES WITH AQUEOUS SOLUTIONS OF SPECIFIC ALDEHYDES CONTAINING ACID CATALYSTS TO PRODUCE WET AND DRY CREASE RESISTANCE

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This invention relates to an improved process for the treatment of cotton textiles with formaldehyde.

The processes that have been known heretofore are not satisfactory for use on cotton textiles because of the great loss of strength that is brought about. An object of the present invention is to provide a process for reacting formaldehyde with cotton textiles without excessive reduction of the strength of the cotton fiber or fibrous product. Another object of the present invention is to provide an improved practical process for producing cotton textiles which are relatively non-shrinkable and which have a high degree of dry and wet wrinkle recovery, and which at the same time have good tearing and tensile strengths. Still another object of this invention is to produce crosslinked cotton textiles with the above named properties which have moisture regain values of about 7% or greater.

To achieve the object of this invention the cotton textiles is allowed to steep in a solution containing water, a water-soluble organic liquid, formaldehyde, and a mineral acid catalyst under such conditions that the reaction of formaldehyde with the cotton textile reaches the desired stage. To stop the reaction at the desired stage the cotton textile is washed free of unreacted formaldehyde and acid or the acid is neutralized with a suitable base before drying it.

In carrying out the process of this invention the proportion of water to water-soluble organic liquid is the factor which determines to a large extent the final properties of the product. The proportion of water to water-soluble liquid must be such that the cotton cellulose is not in a fully swollen state, but in a partially swollen state. The proportion of water should range about from 8% to 40%, based on the weight of the solution. It is also very important that the cotton fiber is not in a completely dry condition at the time it is reacted with the formaldehyde. Therefore, it is necessary to have sufficient water-soluble organic liquid present to prevent the complete swelling which would be obtained if the system were entirely aqueous. The preferred proportion of water-soluble organic liquid lies in the range of about 50% to 90% based on the total weight of the solution, including water, water-soluble organic liquid, formaldehyde, and mineral acid.

The rate of reaction of formaldehyde with the cotton

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cellulose depends on the concentration of mineral acid and formaldehyde in the treating solution and upon temperature. The concentration of formaldehyde and mineral acid can be varied over a considerable range, but relatively low concentrations of mineral acid (1%–17.2%) and formaldehyde (1%–10%) have been found to be adequate. The temperature at which the reaction is carried out will also affect the rate of reaction of formaldehyde with the cotton cellulose. The time required decreases rapidly with an increase in temperature. The reaction may be carried out at temperatures ranging from slightly above the freezing point of the solution to about 45° C. The preferable range is about 25° C. to 35° C. The strength of the modified cotton textile is greatly reduced at temperatures substantially above 70° C. The time of reaction may be varied from about 3 minutes to several hours, the longer times generally being required at the lower temperatures.

After the reaction has been carried to the desired stage it is desirable to wash the product thoroughly to free it of unreacted formaldehyde and acid. At some stage during the washing it is preferable to add in an alkaline substance such as sodium carbonate to the wash water to neutralize the acids.

The cotton textiles processed according to this invention may be in the form of loose fibers, yarns, or fabrics. The cotton textiles may be processed on existing textile machinery such as a jig or "J-Box," or they may be processed by festooning. The type of equipment used for processing is not an important feature of this invention. The process using the jig is preferred for fabric. When the process is carried out at the higher temperatures the reaction proceeds at such a rate that a continuous process may be used. Yarn can be readily treated according to this invention in a package dye machine. Aldehydes other than formaldehyde which react with cellulose to crosslink it may be used in this process. Such aldehydes include glyoxal, glutaraldehyde, adipaldehyde, and α-hydroxy adipaldehyde, acetaldehyde and benzaldehyde. Aldehyde derivatives, such as dimethylol ethylene urea may also be used.

Water-soluble solvents useful in this invention are organic compounds which have relatively little (as compared to water) or no swelling action on cotton cellulose fibers. Water must be soluble in these liquids to the extent of at least 5%. Examples of useful water-soluble liquids are: acetone, dioxane, diethylene glycol, dimethyl ether, tetrahydrofurane, organic acids such as acetic, formic, propionic, and lactic acids. Mixtures of organic compounds such as benzene in acetic acid and xylene in tetrahydrofurane are useful liquids. With these mixtures it is important that water will dissolve in them to the extent of at least 5% of the weight of the mixture. Acetic acid is the preferred water soluble organic liquid for use in this invention.

Catalysts suitable for use in this invention include mineral acids of the group consisting of hydrochloric acid, sulfuric acid, and phosphoric acid. The reaction rate is greatest at a particular temperature and reagent concentration when hydrochloric acid is used.

The products obtained by the process described herein have excellent wet and dry crease resistance. Both of

these qualities are necessary for a fabric if the fabric is to dry smooth and unwrinkled after washing and tumble drying. When cotton fabrics or fibers are reacted with formaldehyde and an acid catalyst by the drying and curing process, they have good wet and dry crease recovery, but suffer a great loss in strength. In addition, the reproducibility of the process is difficult and not practical. An advantage of the process of this invention is the greater tear and tensile strength retention of the product. This improved strength retention is made possible by allowing the reaction of formaldehyde with cotton to take place while the cellulosic material is wet with the treating solution at a temperature not exceeding 45° C., and is in a partially swollen state. Temperatures much above 45° C. destroy the strength of the cotton. For example, at a temperature of 75° C., over 75% of the strength of cotton is lost in about 5 minutes, whereas the strength of regenerated cellulose is not greatly affected at the higher temperatures. Another advantage of the process is that various degrees of dry crease recovery can be obtained merely by changing the concentration of water in the solutions. At the lower concentrations of water (8% to 30%) excellent dry crease recovery as well as excellent wet crease recovery can be obtained. As the water concentration is increased the dry crease recovery of fabric products show less improvement over the control, and finally with over about 50% water in the system no improvement at all is obtained in dry crease recovery, although the wet crease recovery is still very good. An object of this invention is to produce cotton fabrics with good wet and dry crease recovery. It is evident that properties of the final fabric product are dependent on the degree of fiber swelling at the time the reaction takes place, which in turn are determined by the amount of water present. For instance, cotton fabric soaked for 5 days in a solution containing 3.6% formaldehyde, 3.7% hydrochloric acid, and 92.7% water contained only 0.4% combined formaldehyde, and had no improvement in dry crease recovery. Bone dry cotton fabric soaked for 5 days in an anhydrous solution containing the same concentrations of formaldehyde and hydrogen chloride (the remainder being acetic acid) contained combined formaldehyde but was extremely degraded, the fabric retaining only about 15% of its original strength. On the other hand, cotton fabric soaked for only one hour in a solution containing 3.6% formaldehyde, 3.7% hydrochloric acid, 17.7% water, and 75% acetic acid contained 0.8–1.0% combined formaldehyde and had excellent wet and dry crease recovery, and about 70% strength retention. This again illustrates the advantage of carrying out the reaction within specified limits of water concentration.

Softening agents such as silicones, polyethylene, polyacrylonitrile, or long chain fatty acid derivatives may be used to improve the strength, abrasion resistance and hand of the product. Up to 90% Elmendorf tearing strength retention has been obtained by this process by using a softener as an after treatment. The softeners may also be applied to the fabrics before treating with formaldehyde.

Cotton fabrics produced by this process have the quality of drying smooth after repeated laundering whether they are drip-dried, line-dried, or tumble-dried. Other properties such as fiber density, moisture regain, water of inhibition, and dyeability are affected by the treatment. For example, moisture regain of treated fabrics was generally greater than that of the untreated fabrics. The extent to which these properties are changed is again dependent on the degree of fiber swelling at the time the reaction of formaldehyde with the cellulose takes place.

The following examples illustrate the methods of carrying out the invention but the invention is not restricted to these examples. Treated fabrics were tested by the standard methods of the American Society for Testing Materials, Philadelphia. Breaking strength was determined by the one inch strip method, tearing strength by the Elmendorf method, and dry crease recovery by the Monsanto method. Wet crease recovery was carried out by first thoroughly wetting the sample with water, blotting, and then measuring the crease recovery of the wet sample by the Monsanto method. The percentages are by weight.

EXAMPLE 1

A series of solutions was prepared containing varying amounts of formaldehyde, hydrochloric acid, water, and acetic acid. The composition of these solutions are shown in Table I.

Table I

Solution No.	Calculated Amount of Water in Final Solution, Percent [1]	HCHO, Percent	HCl, Percent	Acetic Acid, Percent	Acetic Anhydride, Percent
1	92.7	3.6	3.7		
2	68.0	7.5	17.2	7.3	
3	42.7	3.6	3.7	50.0	
4	42.7	7.5	17.2	32.6	
5	30.0	7.5	9.4	53.1	
6	21.0	3.6	3.7	71.7	
7	17.7	3.6	3.7	75.0	
8	12.6	3.6	3.7	80.0	
9	9.0	3.6	3.7	[2] 60.0	20
10	0.0	3.6	3.7	[2] 8.0	72

[1] The amount of water indicated includes a small amount of methanol which was in the formaldehyde as a stabilizer.
[2] The percent acetic acid here does not include that formed from the reaction of water and acetic anhydride.

The solutions were prepared by mixing glacial acetic acid, 36% aqueous formaldehyde, and 37% hydrochloric acid in the ratio required to give the desired concentrations. In some of the solutions containing a high concentration of water, it was necessary to add water in addition to that present in the formaldehyde and hydrochloride acid to obtain the desired water concentration. In some of the solutions containing low concentrations of water, it was necessary to add enough acetic anhydride to react with a portion of the water in the formaldehyde and hydrochloric acid to obtain the desired water concentration.

The water concentration in the series was varied from 92.7% (where no acetic acid was used) to 0.0% (where only acetic acid was used as the solvent). The concentration of formaldehyde was varied from 3.6% to 7.5%, and that of the hydrochloric acid from 3.7% to 17.2%.

Several samples of bleached unmercerized cotton print cloth were immersed in each solution. A sample was removed from each solution at time intervals varying from 3 minutes to 6 hours in the more reactive solutions and up to 5 days in the less reactive solutions. All of the reactions were carried out by allowing the samples to steep in the solutions at room temperature (about 27° C.). After the samples of fabric had been removed from the reaction media, they were washed thoroughly with water to remove unreacted formaldehyde and acids. The amount of combined formaldehyde in the cotton was determined, as well as physical properties such as wet and dry crease recovery and tearing strength. The properties of some of these samples are shown in Table II.

Table II.—Physical Properties of Formaldehyde Treated Bleached Cotton Print Cloth

Reaction Time, Hrs.	Physical Properties at various times and solution concentrations				
	Combined HCHO, Percent	Tearing Strength (Warp) gms.	Crease Recovery Angle (Warp + Fill)		Moisture Regain, Percent
			Dry	Wet	
SOLUTION NO. 2					
2	0.78	405	201	319	9.4
3	0.87	385	202	299	9.0
SOLUTION NO. 5					
½	1.05	450	241	287	
1	1.20	415	239	296	
2	1.42	370	245	296	
SOLUTION NO. 7					
½	0.81	480	256	270	7.8
1½	1.33	400	272	291	8.0
4	1.70	330	279	304	8.7
SOLUTION NO. 8					
½	0.67	555	248	279	
1	1.12	365	269	280	
4	1.88	300	301	310	
SOLUTION NO. 9					
½	0.65	440	223	236	7.5
1½	1.07	325	260	284	7.4
4	1.52	245	298	298	7.5
CONTROL (UNTREATED PRINT CLOTH)					
		1,050	188	152	6.7

The data shows that after two or three hours reaction time in solution No. 2 there is not much improvement in the dry crease recovery even at the higher formaldehyde and hydrochloric acid concentrations. This was due to the high degree of swelling in the completely aqueous system. The dry crease recovery began to increase as the water concentration was reduced. Good wet crease recovery was also obtained. Moisture regain values varied from about 7.0% to about 9.4%. The moisture regain of the untreated fabric was 6.7%. In this experiment optimum fabric properties were obtained when using solutions 5 through 8, at water concentrations of 30% to 12.6%. Print cloth reacted for two hours in solution No. 4, contained 1.84% combined formaldehyde and had dry crease recovery angle of 249° and a wet angle 360°. Bone dry print cloth reacted for 3 days in solution No. 10 contained only 0.17% combined formaldehyde and had a dry crease recovery angle of only 156° and a wet crease recovery angle of only 180°; the tearing strength was only 215 grams. The disadvantage of using a completely aqueous or completely anhydrous system is readily apparent if good wet and dry crease recovery and good strength are desired.

Print cloth was also reacted at time intervals of 3, 10, and 20 minutes in the solutions of Table I. This cloth had formaldehyde contents varying from 0.25% to .75% and had wet and dry crease recovery.

EXAMPLE 2

A series of solutions were prepared containing 3.6% formaldehyde, 3.0% hydrochloric acid, 16.4% water,

and 77% acetic acid. Samples of bleached print cloth, bleached broadcloth, and mercerized bleached print cloth were steeped in these solutions at temperatures varying from about 20° C. to about 45° C. at time intervals varying from 5 minutes to 90 minutes. After the samples were allowed to react for the required length of time they were removed from the solutions and washed thoroughly with water to remove unreacted formaldehyde and acids. The amount of combined formaldehyde was determined as well as tearing strength and wet and dry crease recovery angles. The results of some of these tests are shown in Table III. The advantage of using mercerized fabric is evident from the greater strength retained.

Table III.—The Effect of Temperature and Time on Properties of Formaldehyde Treated Cotton Fabrics

Cotton Fabric, Type	Temperature, ° C.	Time, Minutes	Combined HCHO, Percent	Tearing Strength (Warp), gms.	Wrinkle Recovery Angle (Warp + Fill)	
					Dry	Wet
Bleached print cloth	20	30	0.57	465	210	232
	20	90	1.10	315	257	290
	35	5	0.50	500	232	244
	35	10	0.68	490	244	274
	35	30	1.06	340	262	302
	45	5	0.84	360	258	278
	45	10	1.10	325	277	298
	45	20	1.36	255	280	303
Mercerized print cloth	25	30	0.72	805	232	294
	25	60	1.02	670	249	288
	35	10	0.71	760	228	287
	35	30	1.29	620	262	313
	45	10	1.26	655	265	299
Bleached broadcloth	35	10	0.72	360	248	302
	45	5	0.85	350	269	305
Untreated control, bleached print cloth				1,050	188	152
Mercerized control, print cloth				1,150	195	199
Untreated control, bleached broadcloth				950	184	204

EXAMPLE 3

A pilot plant run was carried out as follows:

A solution was prepared containing 2,140 ml. of 37% aqueous formaldehyde, 2,380 ml. of 36% hydrochloric acid, and 17,780 ml. of glacial acetic acid. The solution contained about 3.7% formaldehyde, 3.6% hydrochloric acid, 12.1% water, and 80.6% acetic acid. A piece of broadcloth, print cloth, and mercerized print cloth were sewed together making a total of 50 yards of 18" width fabric. The fabric was treated with the solution for one hour at room temperature (about 27° C.) using a jig. The reaction was stopped by first washing the fabric in water containing sodium carbonate, and then rinsing well with cold water, and finally with hot water and drying on a tenter. Best results were obtained on the mercerized print cloth, which had a formaldehyde content of 1.12%, a dry crease recovery angle of 250°, a wet crease recovery angle of 300°, and a tearing strength of 630 grams. The tearing strength was increased to 800 grams by applying 0.3 to 0.4% polyethylene softener to the treated fabric. This was a 75% strength retention based on the bleached control fabric and a 70% strength retention based on the mercerized control fabric.

EXAMPLE 4

A pilot plant run was carried out as follows:

A solution was prepared containing 2,132 ml. of 36%

aqueous formaldehyde, 2,378 ml. of 37% hydrochloric acid, 13,742 ml. of acetic acid, and 3,138 ml. of acetic anhydride. The acetic anhydride reacted with a portion of the water to give a solution containing 3.6% formaldehyde, 3.7% hydrochloric acid, 10.0% water, and 82.7% acetic acid.

Fifty yards of fabric (consisting of 20 yards of bleached print cloth, 12 yards of mercerized print cloth, and bleached broadcloth) were treated with this solution in the same manner described in Example 3. Best results were obtained on the mercerized print cloth, which had a formaldehyde content of 0.96%, a dry crease recovery angle of 260°, a wet crease recovery angle of 280°, a tearing strength of 785 grams, and a breaking strength of 32 lbs. After 1% of a silicone softener was applied to the treated mercerized print cloth, it had tearing strength of 940 grams and a breaking strength of 36.3 lbs. This was a 95% tearing strength retention and a 70% breaking strength retention based on the unmercerized control. This also was an 87% tearing strength retention and a 64% breaking strength retention based on the mercerized control.

EXAMPLE 5

A solution was prepared containing 3.6% formaldehyde, 9.4% sulfuric acid, 17.7% water and 69.3% acetic acid. A piece of bleached cotton print cloth was immersed in the solution for 1 hour at room temperature (about 27° C.). The fabric was then removed from the solution and washed free of unreacted formaldehyde and acids, and dried. The fabric contained 1.94% formaldehyde, and had a dry crease recovery angle of 275° and a wet crease recovery angle of 269°.

EXAMPLE 6

A solution was prepared containing 3.6% formaldehyde, 2.9% hydrochloric acid, 16.9% water, and 76.6% acetic acid. A piece of mercerized cotton print cloth was immersed in the solution for 1 hour and then removed and washed thoroughly with water. The fabric contained 0.94% formaldehyde, had a dry crease recovery of 244°, a wet crease recovery of 288°, and a breaking strength of 36.5 lbs. The breaking strength of the mercerized control fabric was 52.4 lbs. The treated fabric retained 70% of its breaking strength. The treated fabric was subjected to 20 home launderings using a detergent. The dry crease recovery was then 232°, and the wet crease recovery was 273°. The fabric lost only 5% of its crease recovery. The breaking strength after the 20 launderings was 40.4 lbs.—a 77% strength retention based on the mercerized control fabric.

EXAMPLE 7

Each of four samples of mercerized cotton broadcloth was treated with a different softening and/or water repelling agent. These agents were (1) a 1% aqueous solution of Sapamine WL (acid salt of a complex amino organic compound), (2) a 1% solution of Sapamine WL followed by the application of a 3% aqueous emulsion of Zelan AP, (3) a 1% aqueous emulsion of Primenit VS (N,N-octadecyl ethylene urea), (4) a 1% aqueous emulsion of a silicone. Each of these agents was applied to a sample of fabric by standard procedures. Then each softened or water repellent sample was immersed in a solution equivalent to solution No. 7 in Table I of Example I, and allowed to react for one hour at room temperature (27° C.). The samples were removed and washed free of excess formaldehyde and acid. The wet and dry crease recovery angles using the different softening and water repelling agents are shown in Table IV.

Table IV

Agent	Wet Wrinkle Recovery, Degrees	Dry Wrinkle Recovery, Degrees
Sapamine WL	330	246
Sapamine WL+Zelan AP	348	263
Primenit VS	322	280
Silicone	324	288

We claim:

1. A process comprising steeping a cotton textile in a solution containing, based on the weight of the solution, about from 50% to 90% of an organic water-soluble liquid in which water is soluble to the extent of at least 5% and selected from the group consisting of acetone, dioxane, diethylene glycol, dimethyl ether, tetrahydrofurane, formic acid, acetic acid, propionic acid, lactic acid, a mixture of benzene in acetic acid, and a mixture of xylene in tetrahydrofurane, about from 1% to 10% of an aldehyde selected from the group consisting of formaldehyde, glyoxal, glutaraldehyde, adipaldehyde, α-hydroxy adipaldehyde, acetaldehyde, and benzaldehyde, about from 8% to 40% of water, and about from 1% to 17.2% of a mineral acid catalyst selected from the group consisting of hydrochloric acid, sulfuric acid, and phosphoric acid at a temperature not exceeding about 45° C. to partially swell and react the cotton cellulose with the aldehyde, and removing all steeping solution from the thus-treated cotton textile to obtain a modified cotton textile characterized in that it has a combined aldehyde content of at least 0.25% based on the weight of the textile, a moisture regain value of at least 7% based on the weight of the textile, a breaking strength of at least 50% of the original untreated textile, and possessing both wet and dry wrinkle recovery.

2. The process of claim 1 wherein the organic water-soluble liquid is acetic acid.

3. The process of claim 1 wherein the aldehyde is formaldehyde.

4. The process of claim 1 wherein the mineral acid catalyst is hydrochloric acid.

5. The process of claim 1 wherein the temperature ranges about from 20° C. to 45° C.

6. A process comprising steeping a cotton textile in a solution containing, based on the weight of the solution, about from 50% to 90% of acetic acid, about from 1% to 10% of formaldehyde, about from 8% to 40% of water, and about from 1% to 17.2% of hydrochloric acid at a temperature of about from 20° C. to 45° C. to partially swell and react the cotton cellulose with the formaldehyde, and washing the thus-steeped cotton textile free from the steeping solution with water to obtain a modified cotton textile characterized in that it has a combined formaldehyde content of at least 0.25% based on the weight of the textile, a moisture regain value of at least 7% based on the weight of the textile, a breaking strength of at least 50% of the original untreated textile, and possessing both wet and dry wrinkle recovery.

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