

Aug. 9, 1966

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CONTINUOUS METHOD OF IMPARTING WET AND DRY GREASE
RESISTANCE TO CELLULOSIC MATERIALS THROUGH
REACTION WITH FORMALDEHYDE

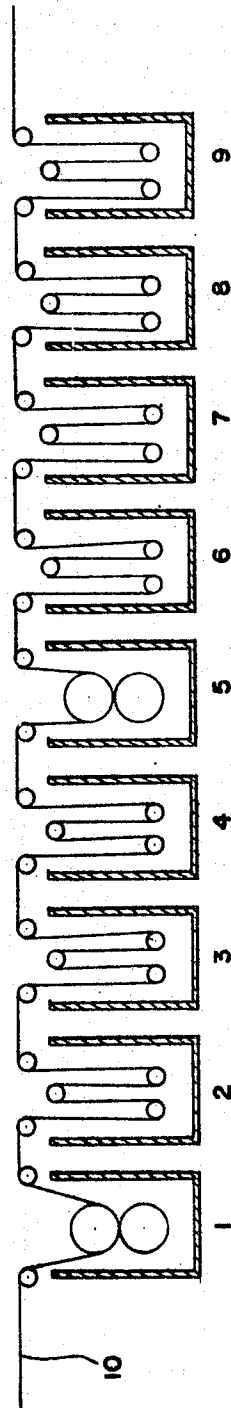
3,265,463

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FIG. 1.

CONTINUOUS RANGE FOR FORMALDEHYDE FINISHING



1. CATALYST PAD

2. FORMALDEHYDE REACTOR

3. WASHING OPERATION

4. DRIER

5. PAD FOR LATENT CATALYST OR
TEXTILE AUXILIARIES

6. DRIER

7. CURING OVEN

8. WASHING OPERATION

9. SANFORIZER

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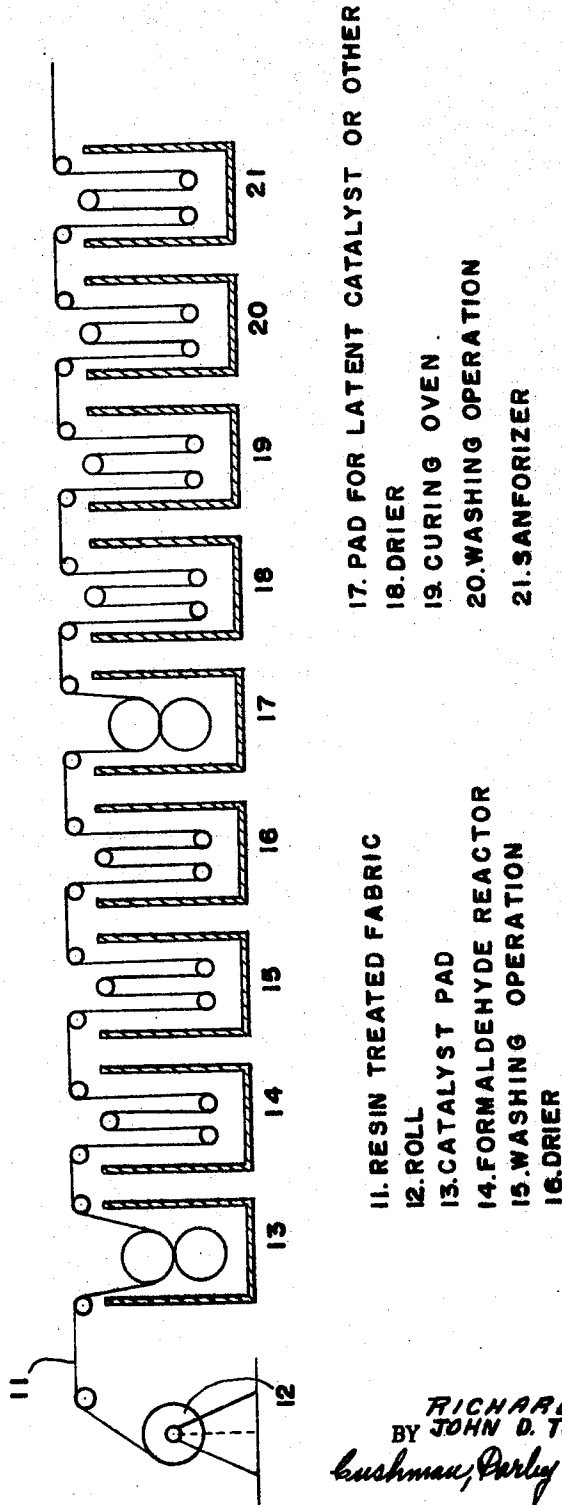
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FIG. 2.

CONTINUOUS RANGE FOR RESIN FORMALDEHYDE FINISHING



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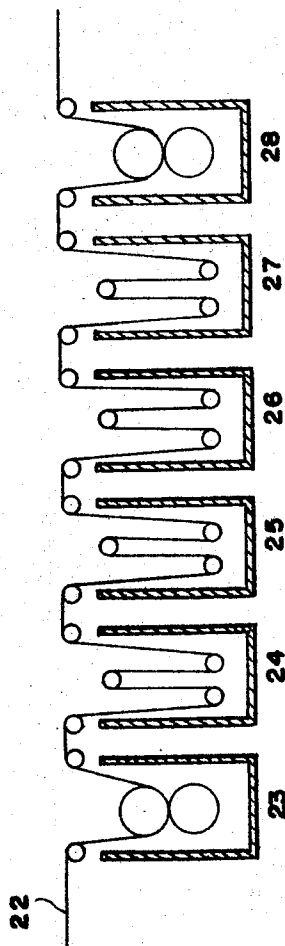
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FIG. 3.

CONTINUOUS RANGE FOR FORMALDEHYDE FINISHES



23. CATALYST PAD

24. FORMALDEHYDE REACTOR

25. WASHING OPERATION

26. DRIER

27. SANFORIZER

28. PADD FOR LATENT CATALYST

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3,265,463 CONTINUOUS METHOD OF IMPARTING WET AND DRY CREASE RESISTANCE TO CELLULOSIC MATERIALS THROUGH REACTION WITH FORMALDEHYDE

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The present invention relates to a continuous method for treating cellulosic fabrics with formaldehyde.

The treatment of cellulosic materials with formaldehyde has been known for well over one hundred years. Formaldehyde due to its cross-linking of cellulosic chains results in a significant increase in wet and dry wrinkle resistance. However, in order to obtain wrinkle resistant properties by such treatment other physical properties of the cellulosic fabric such as tensile strength, elongation and abrasion resistance are adversely affected to a significant extent. For example, the tensile strength can be reduced as much as 50% to 65% or greater.

Accordingly, it is an object of the present invention to enhance the wrinkle resistance of cellulose by the use of formaldehyde without significantly altering the other physical properties such as tensile strength, abrasion resistance, elongation, hand and appearance.

Another object is to control the amount of cross-linking within cellulosic materials that have been treated with formaldehyde.

A further object is to treat cellulosic fabrics which have been subjected to formaldehyde in such a fashion that pleats or creases can be placed in the fabrics after the fabrics have been made into wearing apparel.

An additional object is to treat fabrics containing cellulose fibers in such a fashion that wash and wear fabrics can be achieved without the use of a resin.

Yet another object is to improve the wrinkle recovery properties of cellulosic fabrics without seriously affecting other physical properties such as tensile strength, abrasion resistance, hand and appearance.

A still further object is to eliminate the post curing operation with formaldehyde treated fabrics containing cellulosic fibers and thereby greatly enhancing the dimensional stability of the treated fabrics while the tensile strength and abrasion resistance are not changed significantly.

Yet another object is to permanently stabilize cellulosic fabrics that have been treated with formaldehyde.

An additional object is to dimensionally stabilize formaldehyde treated cellulosic fabrics which are mechanically embossed. The embossing can be done prior or subsequent to the formaldehyde treatment.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by utilizing the procedures discussed hereinafter. Basically these procedures include two chemical reactions. The first is reacting formaldehyde with cellulose in the wet state to give acetal cross-links and hemiacetal groups. The second is the cross-linking reaction of these hemiacetal groups by the addition of a latent catalyst and curing. During the first reaction the wet crease recovery and the

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dimensional stability of the fabric are enhanced. During the second step there is a substantial increase in both wet and dry wrinkle recovery. By appropriate modification of the process as set forth below cellulosic fabrics can be pleated or creased after the fabrics have been made into apparel, e.g. garments.

In the drawings:

FIGURE 1 is a schematic diagram of one method of continuous operation according to the invention;

FIGURE 2 is a schematic diagram of a different continuous operation according to the invention; and

FIGURE 3 is a schematic diagram of a third type of continuous operation.

The properties imparted by the processes of the present invention such as wrinkle resistance, dimensional stability and pleating after the fabric has been made into apparel are all permanently imbedded into the fabric. Thus, these properties have proven stable up to eleven sanforized washings.

As previously set forth the present invention enables the union of cellulose with formaldehyde to enhance the wrinkle resistance properties and dimensional stability without significantly altering the other physical properties such as the tensile strength, abrasion resistance, hand and appearance. The present invention employs a method of controlling the amount of cross-linking within cellulosic materials in a fashion to minimize the loss in tensile strength and reduction in abrasion caused by excessive cross-linking.

As the cellulosic fabric there can be employed cotton, linen, hemp, juice, ramie, sisal, rayons, e.g., regenerated cellulose (both viscose and cuprammonium), cellulose acetate, cellulose acetate-propionate, cellulose acetate-butyrate and ethyl cellulose and mixture of such cellulosic fabrics with each other or other fabrics, e.g., nylon, acrylonitrile fibers or polyester (Dacron) fabrics. The invention is particularly applicable to the treatment of cotton fabric material such as cotton cloth.

The cellulosic material in a wet state goes into either a dehydrating medium or an anhydrous medium containing formaldehyde. Either the formaldehyde containing medium or the original wetting solution can contain an acid. The result of this treatment is to significantly enhance the wet wrinkle properties of the cellulosic material with a minimum amount of strength degradation. During the course of the wet stage reaction wet wrinkle recovery is increased with no significant increase in dry wrinkle recovery. Under the reaction conditions used herein formaldehyde reacts and is present in three forms; namely as acetal linkages, hemiacetal groups and free formaldehyde. The actual linkages are formed in those regions where the cellulosic chains are in close proximity to each other. The hemiacetals are potential cross-linkers but because of the swollen condition of the cellulosic chains the distance between the reactive groups is too great to permit the hemiacetal groups to cross link. Also there is present in the fabric unreacted amounts of formaldehyde.

If this fabric containing the acetals, hemiacetals and free formaldehyde is washed, for example in cold water, the free and some of the hemiacetal formaldehyde is removed. The hemiacetal formaldehyde remaining can then be cross-linked if the fabric is treated with a latent catalyst, e.g., magnesium chloride, dried and cured. In the drying operation the distance between the cellulosic chains are reduced sufficiently to enable the hemiacetal groups to cross-link. When the fabric is cured or heated up to about 300° F. (149° C.) or more the latent catalyst is activated and a secondary reaction and/or the conversion of the hemiacetal to the acetal is accomplished. At this point the dry wrinkle recovery of the fabric is

markedly increased and there is an increase in wet wrinkle recovery.

If it is desired to put permanent pleats or creases in cellulosic fabrics which have been made up into apparel the cellulosic fabrics are padded with an aqueous solution of an acid, e.g., hydrochloric acid, reacted in a reactor containing a dehydrated or anhydrous medium with formaldehyde, washed in cold water to remove excess formaldehyde and dehydrating material, dried, latent catalyst, e.g. magnesium chloride, applied and the product dried at a low temperature, e.g. 20 to 100° C. After the fabric has been fashioned into an apparel, the fabric can be creased or pleated with a hot iron. These pleats or creases are permanent. In addition to the formation of permanent pleats and crease, the fabric itself will have a significant increase in dry wrinkle properties.

In this procedure the secondary step or final cross-linking of the hemiacetals is made after the fabric has been fashioned into its final form. Cross-linking in this state gives the fabric a memory so that after washing and drying this memory brings the fabric to the position it had when the final reaction or cross-linking of the hemiacetals was made.

According to the present invention the cellulosic fabrics are first treated with a relatively dilute aqueous system of acid or water alone and substantially immediately thereafter treating the cellulosic fabric with a formaldehyde solution of substantially lower water content. The amount of water retained by the fabric in this step should be between 10 and 100%, preferably 60-70%, by weight of the fabric. The formaldehyde content of the formaldehyde solution is usually 5-10%, but can be lower, e.g. 3%, or higher, e.g. 15% or 20%.

As the acid there can be used an aqueous solution of a strong acid or the salt of a weak base with a strong acid, e.g. phosphoric acid, hydrochloric acid, hydrobromic acid, sulfuric acid, trichloroacetic acid, formic acid, toluene sulfonic acid, ammonium chloride and ammonium sulfate. The acid strength can vary from moderate concentrations, e.g. 20% to as low as 0.01%, but preferably is between 0.5 and 6%. The preferred acid is hydrochloric acid.

After the treatment with the formaldehyde solution the fabrics are washed in cold water and then dried. Either after the cold wash or the drying operation a latent catalyst, e.g. magnesium chloride, is padded onto the fabric. The fabric is then dried and postcured.

Unless otherwise indicated all parts and percentages are by weight.

There are three basic methods for carrying out the present invention.

METHOD 1

The cellulosic fabric to be treated is padded, e.g. to a 60 or 70% weight pick up of an aqueous solution containing an acid of the type set forth supra, e.g. a mineral acid such as hydrochloric acid or sulfuric acid or a strong organic acid such as chloroacetic acid. The acid concentration can be varied between 0.01% and 20% as previously set forth. The acid treated fabric is then reacted in a dehydrating or anhydrous medium containing 3 to 20%, preferably 5 to 10%, of formaldehyde by weight. Thus the formaldehyde can be dissolved in an anhydrous solution of glacial acetic acid containing traces of acetic anhydride.

In place of glacial acetic acid there can be used a highly dehydrating medium such as an aqueous solution containing 40 to 70% of calcium chloride hexahydrate (equivalent to 20 to 35% anhydrous calcium chloride) and the 5 to 10% of formaldehyde by weight. The fabric after being treated in this manner is then washed with cold water and dried. After drying 0.5 to 6%, preferably 2 to 4%, by weight of the fabric of a latent catalyst is applied to the surface of the fabric. Suitable latent catalysts include magnesium chloride, zinc nitrate,

amine hydrochlorides, e.g. aniline hydrochloride, ethylamine hydrochloride, ethylene diamine hydrochloride and other latent catalysts known to be suitable for curing melamine-formaldehyde or urea-formaldehyde resins.

The fabric is then dried and cured. This procedure is illustrated in FIGURE 1 wherein cotton cloth 10 is continuously passed substantially instantaneously through aqueous hydrochloric or other acid in tank 1 where the cloth picks up 60-70% by weight of the solution. The cloth then is passed through the formaldehyde reactor 2 containing formaldehyde dissolved in glacial acetic acid having traces of acetic anhydride (or alternatively a formaldehyde solution in 60% aqueous calcium chloride hexahydrate). The cloth is then washed with cold water in washing operation 3 and dried in drier 4 at a temperature below 150° C. Upon drying a latent catalyst, e.g. magnesium chloride, is applied to the surface of the fabric in padder 5. The fabric is dried in drier 6, at a temperature below 150° C., cured at a temperature of at least 150° C. in curing oven 7, washed in washing operation 8 and passed through sanforizer 9.

Tables 1 and 2 show the results obtained when utilizing method 1 in the manner shown in FIGURE 1.

In Table 1 in step I the cotton fabric was padded with 3% aqueous hydrochloric acid at room temperature to a 60% wet pickup and almost instantaneously thereafter was reacted in a solution containing 7% formaldehyde and 60% calcium chloride hexahydrate for 16 seconds at 50° C. After reaction with formaldehyde, the fabric was washed in cold water and dried at 110° C. for several minutes.

In step II (the secondary reaction) the dried fabric was padded with 2% aqueous magnesium chloride, dried at 300° F. for 1.5 minutes and then cured at 350° F. for 1.5 minutes.

TABLE 1

	After Step I	After Step II
Tensile Strength, p.s.i. Warp.....	61	53
Tensile Strength, p.s.i. Filling.....	52	44
Flex Abrasion:		
Warp.....	2,000+	2,000+
Filling.....	2,000+	2,000+
Crease Resistance Dry (Monsanto).....	2.9 x 3.0	3.0 x 3.1
After 5 Sanforized Washes (Monsanto).....	2.8 x 2.8	2.9 x 3.1
Crease Resistance Wet (Monsanto).....	2.8 x 2.9	3.2 x 3.1
After 5 Sanforized Washes (Monsanto).....	3.1 x 3.1	3.1 x 3.3
Tear, Warp/Filling.....	5.5 x 5.0	5.0 x 4.0
Shrinkage:		
Initial.....	+0.42 x 1.94	+2.50 x 2.50
After 5 Sanforized Washes.....	+0.28 x 1.67	+2.50 x 2.50
After 10 Sanforized Washes.....	0 x 1.67	+2.22 x 2.50
Formaldehyde Content, Percent.....	0.112	0.100

It will be noted that there is a considerable increase in formaldehyde content as a result of the post curing. Table 1 shows the effect of post curing on the physical properties of cotton fabrics that have been treated with formaldehyde in the wet state.

Table 2 shows the effect of the two step formaldehyde process on the wrinkle recovery and tensile strength of cotton fabrics.

In Table 2 in step I the dry cotton fabric was padded with aqueous hydrochloric acid at room temperature to a 60% wet pickup. In sample 1 the acid was of 1% concentration and in sample 2 the acid was of 3% concentration. Then the samples were reacted in an aqueous solution containing 5% formaldehyde, 1% hydrochloric acid and 70% calcium chloride hexahydrate for 30 seconds at 50° C.

In step II the treated fabric was washed in cold water for 5 minutes, dried and padded through an aqueous solution containing 2% magnesium chloride. The fabric was dried for 1.5 minutes at 300° F. and cured for 1.5 minutes at 350° F.

TABLE 2

Sample	After Step I			After Step II		
	Tensile, p.s.i. (F)	DWR-WXF	WWR-WXF	Tensile, p.s.i. (F)	DWR-WXF	WWR-WXF
1-----	36	2.65 x 2.55	3.48 x 3.3	36	3.0 x 3.0	3.4 x 3.4
2-----	32	2.72 x 2.85	3.32 x 3.32	34	3.1 x 3.1	3.5 x 3.5

The term DWR signifies dry wrinkle resistance, the term WWR signifies wet wrinkle resistance, WXF denotes warp X filler and F denotes filler.

METHOD 2

The cellulosic fabric to be treated is padded to a 10 to 100%, preferably 60 to 70%, weight pickup of a water solution containing a wetting agent, preferably in an amount of 0.1-1%. While anionic and cationic wetting agents can be employed the preferred wetting agents are nonionic in character.

Typical examples of nonionic wetting agents are alkyl-aryl polyether alcohols such as Triton 155, a p-isooctylphenol condensed with 10 ethylene oxide units, Arlacel C (sorbitan sesquioleate), Brij 35 (polyethylene glycol lauryl ether), Ethofats (polyethylene esters of fatty acids or rosin acids, e.g., Ethofat 3, 7, 11, 13, 15 and 19), Ethomids, e.g., Ethomid 8, 10, 12 and 14, Igepal CA (alkylphenyl polyethylene glycol ether), Myri (polyethylene glycol stearate), Ninol 1281 (fatty acid ethanolamide), Nonionic 218 (tertiary dodecyl polyethylene glycol thioether), Pluronic (condensation products of ethylene oxide and propylene oxide having molecular weights of 400 to 4000), Span 20 (sorbitan monolaurate), Span 40 (sorbitan monopalmitate), Span 60 (sorbitan monostearate), Span 80 (sorbitan monooleate), Sterox CD (polyethylene glycol ester of tall oil acids), Triton X-100 (p-octylphenyl polyethylene glycol ether), Tween 20 (tris polyoxyethylene sorbitan monolaurate) and Tweens 40, 60 and 80 (the palmitates, stearates and oleates corresponding to the laurate of Tween 20).

There can also be employed anionic surface active agents such as alkyl and aryl sulfates and sulfonates, e.g., sodium alkyl benzene sulfonates having 10 to 18 carbon atoms, sodium lauryl sulfate, Aerosol OT (sodium salt of dioctyl sulfocuccinate), sodium oleyl isothionate, sodium N-methyl-N-oleyl laurate, sodium salt of propylated naphthalene sulfonic acid, sodium salt of sulfonated monoglyceride of coconut fatty acids, Areskap 100 (sodium salt of butylphenylphenol sulfonic acid), sodium lignin sulfonate, sodium dodecyl benzene sulfonate, sodium tetradecyl sulfate and sodium dihexyl sulfosuccinate. As cationic surface active agents there can be used lauryl trimethyl ammonium chloride, cetyl pyridinium chloride and octadecyl trimethyl ammonium chloride.

Then the wet fabric is reacted in a dehydrating solution containing, for example 5 to 20% of formaldehyde together with 0.01 to 20%, preferably 0.5 to 6% of an acid of the type previously set forth, e.g. a mineral acid such as hydrochloric or sulfuric or a strong organic acid such as chloroacetic acid. The dehydrating solution can be either a 50 to 70% aqueous calcium chloride hexahydrate solution or glacial acetic acid.

The reaction time is dependent on both the temperature and concentration of the acid catalysts in the reactor and can be controlled in conventional manner. After the fabric leaves the reactor it is washed with cold water. The washing system for the calcium chloride medium can contain a small amount of a sequestering agent along with soda ash or other water soluble alkali, e.g., sodium hydroxide or potassium carbonate, to neutral any excess acid from the reactor. Plain water also can be used for the washing system. After washing the fabric is dried. Then a solution of 2 to 4% of a latent catalyst, e.g. magnesium chloride, is padded onto the fabric either in the wet or dry state. The fabric is then dried and cured.

The process is basically that illustrated in FIGURE 1 except that a wetting agent is present in tank 1 and the acid is introduced in the formaldehyde reactor 2 rather than previously.

Table 3 shows the effect of this two step formaldehyde process on the physical properties of cotton fabrics. The fabric was first padded with water containing 1% of Triton 155 (higher alkylphenyl monoether of polyethylene glycol) to a 60-70% pickup. It was then reacted for 17 seconds at 50° C. in an aqueous solution containing 3% hydrochloric acid, 10% formaldehyde and 70% calcium chloride hexahydrate. The fabric was washed in cold water and dried at 110° C. Then the fabric was padded through an aqueous solution of 3% magnesium chloride, dried at 300° F. for about 1½ minutes and cured at 350° F. for 1½ minutes.

The cotton fabric employed had a tensile strength of 41 p.s.i. in the filling and 2.35 dry crease angle (dry wrinkle recovery) prior to the finishing treatment described supra.

TABLE 3

	Fabric with treatment	After 10 sanforized washings
Tensile strength, p.s.i. (filling)-----	26	-----
Abrasion resistance (filling)-----	550	-----
Dry wrinkle recovery (filling)-----	3.47	3.55
Wet wrinkle recovery (filling)-----	3.45	3.44
Stabilization (percent shrinkage)-----	1 0.36 x 0.28	0.56 x 0.36

¹ Warp x filling.

METHOD 3

The cellulosic fabrics or fabrics containing cellulosic fibers are treated with a small amount, e.g. 0.5 to 8%, of a starch, e.g. corn, rice, potato, tapioca or wheat starch, or one of the curable crease-proofing resins. These include the urea-aldehyde, e.g., urea-formaldehyde resin, dimethylolurea, dimethyl ether of urea-formaldehyde resin, aminotriazine-aldehyde resins, e.g., melamine-formaldehyde resins including alkylated melamine-formaldehyde, trimethylol melamine, methylated trimethylol melamine, tetrahydro-5-hydroxy-2 (1 H)-pyrimidone-formaldehyde resin, cyclic ethylene urea-formaldehyde, e.g., dimethylol ethylene urea, uron-formaldehyde resins, e.g., dimethylol uron, Aerotex 23 (a triazine-formaldehyde resin believed to be a melamine-formaldehyde type resin), Rohm and Haas Resin N-17 (a triazone-formaldehyde resin, e.g., dimethylol ethyl triazone), Dextraset 48 (a uron-formaldehyde resin), Eponite 100 (believed to be a butadiene diepoxide). Other polyepoxides can be used including bisphenol-A epichlorhydrin, 1,4-bis (2,3-epoxypropoxy) benzene, 1,3-bis (2,3-epoxypropoxy) octane, ethylene glycol diglycidyl ether as well as any of the other polyepoxides set forth in Schroeder et al. Patent 2,774,691. Other crease-proofing agents such as those set forth in "Textile Industries," October 1959, pages 116-127, can also be used. The fabrics are then treated by either the first or second method described above or by a combination of both. The wrinkle resistant properties are greatly enhanced. This procedure is illustrated in FIGURE 2 and Tables 4, 5, 6 and 7.

TABLE 4

Sample	Time of HCHO Reaction (min.)	After Step I			After Step II		
		Tensile, p.s.i. (filling)	DWR (W and F)	WWR (W and F)	Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)
1-----	1	30	2.8 x 3.18	3.5 x 3.5	28	3.42 x 3.5	3.74 x 3.6
2-----	2	25	2.08 x 3.28	3.6 x 3.4	22	3.7 x 3.89	3.75 x 3.73
3-----	3	24	3.22 x 3.3	3.6 x 3.6	23	3.6 x 3.7	3.71 x 3.67

As shown in FIGURE 2 cotton cloth 11 containing resin or starch is continuously unrolled from roll 12 and passed through aqueous hydrochloric or other acid 15

Table 5 is similar to Table 4 and the procedure is identical except the formaldehyde employed was 5% formaldehyde in anhydrous glacial acetic acid.

TABLE 5

Sample	Time of HCHO Reaction (min.)	After Step I			After Step II		
		Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)	Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)
1-----	1	29	3.3 x 3.2	3.4 x 3.4	32	3.6 x 3.6	3.7 x 3.5
2-----	2	32	3.1 x 3.0	3.5 x 3.3	28	3.8 x 3.7	3.7 x 3.6
3-----	3	31	3.2 x 3.3	3.6 x 3.6	26	3.9 x 3.7	3.8 x 3.7

in tank 13 where the cloth picks up 60-70% by weight of the solution. The cloth then is passed through the formaldehyde reactor 14 containing formaldehyde dissolved in 40-70% aqueous calcium chloride hexahydrate (or dissolved in glacial acetic acid). The cloth is then washed in cold water in washing operation 15 and dried in drier 16 at a temperature not over 150° C. Upon drying a latent catalyst, e.g., magnesium chloride is applied to the surface of the fabric in padder 17. The

In Table 6 the cotton fabric was treated with 1% aqueous hydrochloric acid to a wet pickup of 60% and then treated with 5% formaldehyde in an anhydrous solution of acetic acid containing 10% calcium chloride in step I. Then the fabric was washed for 5 minutes in cold water, dried below 150° C., and padded through an aqueous solution containing 2% magnesium chloride and 2% of B-15 (an acrylic ester copolymer). The fabric was then dried below 150° C. and cured at 350° F.

TABLE 6

Sample	Time of HCHO Reaction (min.)	After Step I			After Step II		
		Tensile, p.s.i. (F)	DWR (F and W)	WWR (F and W)	Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)
1-----	1	37	3.15 x 3.0	3.4 x 3.7	28	3.7 x 3.6	3.6 x 3.7
2-----	2	36	3.2 x 3.2	3.4 x 3.4	29	3.7 x 3.6	3.6 x 3.6
3-----	3	36	3.1 x 3.0	3.3 x 3.3	28	3.6 x 3.7	3.6 x 3.7

fabric is dried in drier 18 at a temperature below 150° C., cured at a temperature of at least 150° C., preferably at least 160° C. in curing oven 19, washed in washing operation 20 and passed through sanforizer 21.

The effects of the two step formaldehyde process on the wrinkle resistance and tensile properties of cotton fabric pretreated with a thermosetting resin are shown in Table 4. The fabric was pretreated with 8% Aerotex 23, then padded with 1% aqueous hydrochloric acid to a 60-70% pickup and reacted with formaldehyde in step I. Then the treated fabrics were washed in cold water for 5 minutes, treated with 2% aqueous magnesium chloride, dried at 300° F. for 1½ minutes and cured at 350° F. for 1½ minutes in step II.

In Table 7 the cotton fabrics were pretreated as indicated with 4 or 8% of Aerotex 23. The dry resin treated fabrics were then padded as indicated with 1, 2 or 3% aqueous hydrochloric acid to a 60% wet pickup prior to formaldehyde reaction. The reaction medium contained 5% aqueous formaldehyde, 1% hydrochloric acid and 70% calcium chloride hexahydrate and the reaction was carried out at 50° C. for 30 seconds in step I.

In step II the treated fabrics were then washed in cold water for 5 minutes, dried below 150° C. and padded through a solution containing 2% magnesium chloride. The fabric was dried for 1½ minutes at 300° F. and cured for 1½ minutes at 350° F.

TABLE 7

Sample	Percent Resin	Percent Initial Acid	After Step I			After Step II		
			Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)	Tensile, p.s.i. (F)	DWR (W and F)	WWR (W and F)
1-----	8	1	33	3.4 x 3.4	3.4 x 3.4	28	3.0 x 3.4	3.5 x 3.4
2-----	4	1	29	2.9 x 2.8	3.5 x 3.4	32	3.4 x 3.3	3.4 x 3.4
3-----	8	2	33	3.2 x 3.3	3.3 x 3.3	31	3.7 x 3.7	3.7 x 3.4
4-----	4	2	30	3.3 x 3.2	3.5 x 3.5	30	3.6 x 3.5	3.7 x 3.5
5-----	8	3	31	3.5 x 3.3	3.5 x 3.4	30	3.6 x 3.5	3.7 x 3.4
6-----	4	3	29	3.3 x 3.2	3.6 x 3.5	27	3.5 x 3.3	3.5 x 3.5

If it is desired to change other chemical and/or physical properties of fabrics containing cellulosic fiber treated by the methods described above, conventional textile finishing chemicals or auxiliaries can be added to the latent catalyst prior to drying and post curing. For example hand builders, softeners, water repellents, water proofing agents, oil repellents, fungicides, mildew resistant chemicals and fire proofing agents can be added.

If a slight amount of tension is applied to either the warp or filling yarns the loss in tensile strength can be further minimized as shown in Table 8.

In Table 8 tension of about 10-25 p.s.i. was applied in the warp direction in runs I and III and in the filling direction in runs II and IV. In runs I and II the cotton fabrics were padded with water to a 60-70% pickup and reacted in an aqueous solution containing 18% formaldehyde, 3% hydrochloric acid and 60% calcium chloride hexahydrate. For sample 1 the reaction time was 1 minute and for sample 2 the reaction time was 5 minutes. For both samples, the reaction temperature was 32° C.

In runs III and IV the cotton fabrics were padded with water to a 60-70% pickup and reacted in an aqueous solution containing 18% formaldehyde, 5% hydrochloric acid and 60% calcium chloride hexahydrate. For sample 3 the reaction time was 2½ minutes, for sample 4 the reaction time was 1 minute and for sample 5 the reaction time was 4 minutes. The reaction temperature for samples 3, 4 and 5 was 50° C.

TABLE 8

Sample	Run	Tensile Strength, p.s.i. W and F	Wet Wrinkle Recovery W and F
1-----	1	46 x 35	3.35 x 3.32
2-----	1	40 x 28	3.55 x 3.42
1-----	2	45 x 38	3.48 x 3.5
2-----	2	38 x 29	3.62 x 3.52
3-----	3	34 x 21	3.47 x 3.42
4-----	3	38 x 27	3.47 x 3.52
5-----	3	36 x 21	3.59 x 3.53
3-----	4	35 x 24	3.53 x 3.6
4-----	4	35 x 29	3.4 x 3.47
5-----	4	32 x 25	3.52 x 3.55

If it is desired to only increase either the wet wrinkle recovery and the dimensional stability or both then the procedure is that described in FIGURE 3 omitting the latent catalyst pad.

If it is desired to pleat or crease fabrics after they have been made up into apparel the procedure is that described in FIGURE 3. Thus the cotton cloth 22 is continuously padded through aqueous acid in tank 23 and then passes into formaldehyde reactor 24, through washing operation 25, drier 26, sanforizer 27 and finally latent catalyst pad 28. The materials employed as well as the proportions and conditions for these operations are those which have been previously set forth for the catalyst padding solution, formaldehyde reactor, latent catalyst, etc. The latent catalyst in the procedure set forth in FIGURE 3 is added to the finished fabric. The fabric is then dried at a low temperature and packaged for shipment.

In methods 1 and 2 if a washing step utilizing hot soapy water is introduced subsequent to the treatment with the latent catalyst but prior to the drying or curing in order to eliminate the secondary reaction, the fabrics are permanently stabilized without seriously affecting the other physical properties of the treated fabrics such as abrasion, tensile strength, hand and appearance. Thus

in the process described in connection with Table 1 the fabric can be treated with hot, 90° C., soapy water after adding the 2% magnesium chloride and prior to the drying step. By this procedure permanent dimensional stability is obtained.

As previously indicated the cellulosic fabric, e.g., the cotton cloth prepared according to the process described in connection with Table 1 is mechanically embossed after the addition of the magnesium chloride latent catalyst and prior to the drying and curing the fabric will be dimensionally stabilized with the embossed print imbedded into the wet fabric.

The embossing process can be employed with any of methods 1, 2 and 3.

We claim:

1. A process for improving the wash and wear properties of a cellulosic fabric comprising treating the fabric with an aqueous medium until the fabric contains 10-100% of its own weight of water; substantially immediately thereafter passing the wet fabric into a dehydrating solution selected from the group consisting of (a) aqueous calcium chloride solution containing at least 3% formaldehyde and (b) anhydrous acetic acid containing at least 3% formaldehyde whereby the formaldehyde reacts with said fabric; washing the thus treated fabric with water to remove free formaldehyde; applying to the fabric from 0.5 to 6% by weight, based on the dry weight of said fabric, of a latent catalyst for curing formaldehyde resins; drying the fabric at a temperature below 150° C. and then curing by heating at a temperature above 150° C.

2. A process according to claim 1 wherein the fabric is a cotton fabric and the catalyst is magnesium chloride.

3. A process according to claim 1 wherein the dehydrating solution is an aqueous solution containing at least 20% calcium chloride.

4. A process according to claim 1 wherein the aqueous medium contains a mineral acid.

5. A process according to claim 1 wherein the aqueous medium contains a wetting agent for said fabric and the dehydrating solution contains a mineral acid.

6. A process according to claim 1 wherein the cellulose fabric employed is one which has been pretreated with a member of the group consisting of cellulose crease-proofing resins and starch.

7. A process according to claim 6 wherein the cellulose fabric is one which has been pretreated with a crease-proofing resin.

8. A process according to claim 1 wherein the fabric is kept taut in the warp direction during the treatment.

9. A process according to claim 1 wherein the fabric is kept taut in the filling direction during the treatment.

10. A cellulosic fabric treated according to claim 1.

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