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[54] **DURABLE PRESS PROCESS FOR TREATING CELLULOSIC MATERIAL WITH METHYLOLAMIDES AND ACETIC ACID OR FORMIC ACID VAPORS**

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[52] **U.S. Cl.** ..... **2/243 R**, 8/115.6, 8/115.7, 8/129, 8/182, 8/183, 8/185, 8/186, 8/187, 8/DIG. 4, 8/DIG. 9, 8/DIG. 10, 8/DIG. 21, 34/37, 38/144, 8/149.1, 8/149.3

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[58] **Field of Search** 8/116.3, 149.1, 149.3, 8/186, 185, 183, 182, 187; 38/144; 2/243

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[57] **ABSTRACT**

The dimensional stability, wrinkle resistance, smooth drying characteristics and total shape retentivity of cellulosic materials such as cotton fabrics are improved by treatment with acetic acid or formic acid vapors after impregnation of the materials with an aqueous solution of a water-soluble crease-proofing agent containing reactive N-methylol groups such as trimethylolmelamine or DHDMEU, whereby the cellulosic fibers become crosslinked.

9 Claims, No Drawings

DURABLE PRESS PROCESS FOR TREATING CELLULOSIC MATERIAL WITH METHYLOLAMIDES AND ACETIC ACID OR FORMIC ACID VAPORS

CROSS-REFERENCE

This application is a continuation-in-part of Ser. No. 762,119, which was filed Sept. 24, 1968 and is now U.S. Pat. No. 3,653,805.

BACKGROUND OF THE INVENTION

In recent years various methods have been devised for treating cellulosic fiber-containing products, such as cloth made of cotton or cotton blends, in order to impart durable crease resistance and smooth drying characteristics thereto. For example, cellulosic materials have been crosslinked with formaldehyde, giving durable crosslinks having good resistance to repeated laundering and also to various acids and alkalis, and chlorine bleaches. These formaldehyde treated cellulosic materials have certain advantageous features. For example, they are resistant to discoloration and yellowing.

However, while formaldehyde has made a significant contribution to the cotton finishing art, the results have been far from perfect. For instance, in some cases the formaldehyde crosslinking treatment has tended to lack reproducibility, since control of the formaldehyde crosslinking reaction heretofore has been difficult. When high curing temperatures were used with an acid or potential acid catalyst, overreaction and degradation of the cotton often happened which considerably impaired its strength. On the other hand, when attempts were made to achieve reproducibility at temperatures of 50°C. or less, much longer reaction or finishing times were usually required, rendering the process economically relatively unattractive. See for example, British Patent 980,980. In other cases, formaldehyde crosslinking has not been able to meet commercial standards with respect to dry wrinkle recovery. For these and similar reasons, efforts have been continuing to develop new and better cellulosic and cotton finishing processes.

The use of an atmosphere containing hydrochloric acid to catalyze crosslinking between a crease-proofing agent and a cellulosic fabric material in which the agent is impregnated has been suggested in the prior art. Control of such a reaction is difficult but important since the strong mineral acid catalyst may degrade the fabric itself. Hydrochloric acid-catalyzed fabric materials also have been found to have low tensile strength properties, particularly if the crosslinked fabric is post-heated.

SUMMARY OF THE INVENTION

Accordingly, a primary object of the present invention is to provide a practical process for treating cellulosic materials with a suitable crease-proofing agent which process substantially prevents or alleviates the problems mentioned above.

A more specific object has been to develop a process for crosslinking cotton with the aid of a water-soluble crease-proofing agent containing reactive N-methylol groups, using an acid catalyst used in the vapor phase, so as to keep fiber injury to a minimum.

Another more specific object is to provide a process for crease-proofing cotton or other cellulosic materials using a water-soluble crease-proofing agent containing reactive N-methylol groups which permits the cure of the treated material to be safely delayed for long or indefinite periods until after completion of desired articles therefrom including, for instance, the cutting, sewing and pressing of garments.

Another specific object is to provide a crease-proofing process for use with cellulosic materials which produces good wrinkle recovery and smooth drying characteristics, keeps loss of tensile strength and abrasion resistance to a minimum, gives good laundering life and chlorine resistance, employs simple reactants and, if desired, can produce a pre-treated fabric which is relatively insensitive to surrounding conditions and has virtually infinite shelf life prior to final cure.

It is further an object of this invention to provide a process for treating cellulosic materials with an acidic catalyst in the vapor phase without the degrading characteristics of strong mineral acids such as hydrochloric acid.

These and other objects, as well as the scope, nature, and utilization of the invention will become more clearly apparent from the following more detailed description. Unless otherwise indicated, all proportions and percentages of materials or compounds are expressed on a weight basis throughout this specification and appended claims.

In accordance with the present invention, a process is provided for improving the dimensional stability, wrinkle resistance, smooth drying characteristics and total shape retentivity of a cellulosic fiber-containing fabric which comprises: (a) applying to the fabric an aqueous solution of a water-soluble crease-proofing agent containing reactive N-methylol groups; and (b) heating the impregnated fabric containing the water-soluble crease-proofing agent containing reactive N-methylol groups in a non-reactive vapor atmosphere containing a catalyst selected from the group consisting of formic acid and acetic acid to a temperature between above 80°C. up to about 160°C. for a time of between about 10 seconds and 2 hours until the cellulose fibers become effectively crosslinked.

The process requires relatively short reaction times and gives high wrinkle recoveries while at the same time producing satisfactory tensile and tear strengths.

The process of the present invention has substantial advantages of use as compared with typical prior art processes such as hydrochloric acid vapor-catalyzed durable press systems. For example, the process of the present invention prevents excessive degradation of cellulosic fibers and does not require neutralization of the fabric after treatment. Also, there is no need for an afterwash of the fiber. Reproducibility of the reaction is substantially improved and special controls and equipment for handling the highly toxic and corrosive hydrochloric acid is not necessary.

DESCRIPTION OF PREFERRED EMBODIMENTS

In the embodiment disclosed and claimed herein, the cotton or cellulose-containing fabric is impregnated with an aqueous solution containing about 1 to about 40 percent, preferably from about 2 to about 20 percent, most preferably from about 5 to 15 percent, of a water-soluble crease-proofing agent containing reac-

tive N-methylol groups to give a wet pick-up of between about 50 and about 100 percent, preferably from about 60 to about 90 percent, most preferably from about 65 to 85 percent, based on dry fabric weight.

The present invention is useful for treating various natural or artificial cellulosic fibers alone or as mixtures with each other in various proportions or as mixtures with other fibers. Such natural cellulosic fibers include cotton, linen and hemp, and regenerated or artificial cellulosic fibers useful herein include, for example, viscose rayon and cuprammonium rayon. Other fibers which may be used in blends with one or more of the above-mentioned cellulosic fibers are, for example, cellulose acetate, polyamides, polyesters, polyacrylonitrite, polyolefins, polyvinyl chloride, polyvinylidine chloride and polyvinyl alcohol fibers. Such blends preferably include at least about 20 percent by weight and most preferably at least about 40 percent by weight, of cotton or other cellulosic fibers.

The fabric may be knit, woven or non-woven, or be any otherwise constructed fabric. The fabric may be flat, creased, pleated, hemmed or sewn or otherwise formed to produce an article such as a garment of any desired shape prior to contact with the acetic acid or formic acid catalyst-containing atmosphere. After processing, the formed crosslinked fabric will maintain substantially the original configuration for the life of the article, that is, a wash-wear or durable press fabric will be produced.

The crease-proofing agents useful herein include particularly the easily hardenable precondensates which are substantially water soluble and are obtained by condensation of formaldehyde with a compound such as a lower alkyl substituted melamine, a urea, or a phenol such as resorcinol. As is well known in the resin treating art, these precondensates are capable of being applied to the cellulosic material from an aqueous solution. Triazines obtained by condensing a lower alkyl substituted melamine and formaldehyde are examples of such precondensates. Good results are obtained, for instance, using precondensates obtained by condensing 1 mole of melamine or an alkyl substituted melamine with 2 to 6 moles of formaldehyde, i.e., using di-, tri- or hexamethylol melamine. Commercially available products of this kind include Aerotex 23, a triazine-formaldehyde precondensate; Aerotex M—3, a melamine-formaldehyde condensate; Aerotex P–225, hexakis-(methoxymethyl) melamine; and Aerotex 19, which is a less completely fractionated modification of Aerotex P–225. These products are supplied in the form of aqueous solutions by American Cyanamid Company.

Other suitable crease-proofing agents include products such as dihydroxydimethylolethyleneurea, DHDMEU, available as Permafresh 183 or in a somewhat modified, less reactive form as Permafresh 113B from Sun Chemical Company, as well as modified propylene urea compounds such as Fixapret PCL, available from Badische Anilin und Soda-Fabrik. Compounds having at least 1½ moles of formaldehyde combined as methylol formaldehyde with a cyclic urea or cyclic propylene urea are suitable and the dimethylol derivatives are preferred. However, it is similarly feasible to use other known crease-proofing agents such as N-methylol carbamates and methylol urea compounds.

Pretreatment of the cloth, prior to the vapor phase catalytic treatment, with polymeric resinous additives that form soft films, such as conventional dispersions or latexes, can result in an unusually great incremental improvement in wrinkle recovery of the treated fabric. Polymer additives can also improve the flex abrasion resistance and tear strength, or alter the ratio of dry wrinkle recovery to wet wrinkle recovery, or in some instances shorten the reaction time needed to produce an acceptable durable press fabric. Polymeric additives suitable for such purposes are, in most cases, available commercially in concentrated aqueous latex form, and it is desirable to dilute these to a concentration of 1 to 10 percent polymer before padding onto the fabric. Suitable polymeric additives include solid resinous or rubbery acrylonitrile-butadiene copolymers and mixtures containing the same with various vinyl resins; polyethylene; deacetylated copolymers of ethylene and vinyl acetate; polyurethanes and various polymers of alkyl acrylates, other polyesters and polyamides.

The impregnated fabric may be dried or conditioned to a moisture content of from about 2 up to about 100, preferably from about 3 to about 65 percent by weight of the dry cellulosic fabric material. The impregnated fabric may thus be catalyzed in a condition ranging from about essentially dry to about essentially wet condition.

The fabric is then passed into a non-reactive, catalyzing atmosphere containing a catalytically effective amount of formic acid or acetic acid which may be obtained from any convenient source. In addition to the catalyst, the treating atmosphere may contain inert gases such as air, nitrogen, carbon dioxide, helium, steam and the like. The treating atmosphere is "non-reactive" in that it contains the gaseous catalyst and an inert gas. Gaseous materials or monomers that could react, condense or polymerize with the fabric or methylolamide crease-proofing agent should not be present in the treating atmosphere.

The non-reactive atmosphere can contain up to about 100, often from about 5 to 90 volume percent acetic acid or formic acid, balance, (if any) inert gas.

Contact of the conditioned fabric with the non-reactive atmosphere is performed at a temperature of from about 80° and 160°C., preferably from about 100°C. to about 140°C. most preferably from about 110°C. to about 125°C., for a time of between about 10 seconds and 2 hours, preferably from about 1 to about 20 minutes, most preferably from about 2 to about 15 minutes.

Any suitable means to contact the fabric with the gaseous acetic acid or formic acid catalyst may be employed. For example, a batch system utilizing a closed vessel or tube containing the gaseous catalyst may be used into which the conditioned, crease-proofing agent-containing fabric may be placed and there exposed to the treating atmosphere for the appropriate time. In the alternative, a dynamic or continuous system can be used such as one wherein a gas stream containing acetic acid or formic acid catalyst, is passed through a closed elongated chamber through which the impregnated fabric or articles are also passed at an appropriate rate, either concurrently or countercurrently relative to the gas. It is also possible to use combinations of the above, that is, such as by passing a stream

of the catalyst-containing atmosphere over a stationary fabric.

The crosslinked fabric is thereafter desirably heated to a temperature above about 100°C., e.g., in the range of from about 100° to 180°C., preferably from about 140°C. to about 160°C., to volatilize and remove water vapor, residual catalyst and any unbound, volatile, crease-proofing agent. In addition, this heating step further cures the crosslinked fabric thus improving its durability to laundering as well as improving the duration press characteristics of the treated fabric. This heating and curing step may also allow a reduction in the time of exposure to the gaseous catalyst-containing atmosphere without sacrificing durable press performance.

Heating the crosslinked fabric may advantageously be performed in any suitable fabric heating chamber.

The temperature of the post-heating step can be reduced or the post-heating step entirely eliminated without impairing wash-wear performance by using crease-proofing agents more reactive than dihydroxydimethylolethyleneurea. These fabrics containing the more reactive crease-proofing agents may be neutralized with a slightly alkaline solution (such as a 1 percent solution of sodium carbonate) and washed to remove all traces of catalyst or unbound crease-proofing agent.

The invention is additionally illustrated in connection with the following examples which are to be considered as illustrative of the present invention. It should be understood, however, that the invention is not limited to the specific details of the Examples.

EXAMPLES

The reactor used in this work was a cylindrical vessel having a capacity of about 71 liters, constructed of ⅛-inch aluminum (42 cm. inside diameter and 57 cm. high). The walls of this reactor are heated with band heaters equipped with a three-way switch which permits operation at 600, 1,200 or 2,400 watts. The reactor wall temperature is controlled by an adjustable bimetallic thermostat, and the reactor is surrounded by an insulating lanket. the gas content of the reactor is recirculated through an external recycle line by an aluminum pressure blower equipped with a heat slinger and high-temperature, lubricated sealed bearings. An adjustable damper in the recycle line permits some control of the pressure within the reactor, but during normal operation nearly atmospheric reactor pressure is preferred.

This reactor was fitted with aluminum tubing through which a solution containing 85 percent by weight of formic acid is poured to fall onto an evaporating dish in the bottom of the reactor. Substantially all of the vapors in the reactor are in each of the following Examples formic acid vapors evaporated from the evaporating dish. Some water vapor is also present. The acetic acid and hydrochloric acid atmospheres in the Examples are provided in the same manner.

EXAMPLE I

Cotton twill fabric samples and trouser cuffs were padded to 70 percent wet pickup with aqueous solutions containing the amounts of crease-proofing agent and polymeric additive shown in Table I. Crease-proofing agents included trimethylolmelamine (Resloom HP, Monsanto Chemical Co.), methylated methylolmelamine (Resloom M-75, Monsanto Chemical Co.), a mixed amide product including a methylolmelamine (Aerotex 23, American Cyanamid Co.) and dimethylol dihydroxyethylene urea (Permafresh 183, Sun Chemical Co.). Polymeric additives included polyethylene (Mykon SF), and an acrylic resin (Rhoplex K-87). After impregnation, fabric samples were dried to moisture content of about 7–10 percent, exposed to formic acid vapor in the reaction chamber described above at about 115°C. for various reaction times, washed, dried, and tested.

The tabulated data show that high levels of wrinkle recovery were achieved in all cases. Generally, shorter reaction times were necessary and higher tensile strength retentions recorded, when the melamine derivatives were used, which are more polymerizable than the dihydroxyethylene urea derivative.

TABLE I-A

Run No.	Pad Bath Composition		HCO_2H Exposure Time (min)	Total Add-On (%)	Wrinkle Recovery Angle (degrees)				Tearing Strength (grams)		Stoll Flex Abrasion, Warp (cycles)
	Methylol Compound	Softener			Warp		Fill				
					Dry	Wet	Dry	Wet	Warp	Fill	
	15%										
1	Resloom M-75	2% Mykon SF	5	2.4%	146	139	117	110	2420	1580	550
2	↓	↓	4	2.7	154	142	120	111	2090	1660	445
3			3	2.8	146	139	126	119	2620	1670	670
4			2	3.0	131	124	124	111	2820	1880	660
	10%										
5	Aerotex 23	3% Rhoplex K-87	4	7.6	149	148	128	136	1740	1020	580
6	↓	↓	3	7.9	148	147	126	132	1810	1100	560
7			2	8.7	148	150	132	136	1740	1080	460
8			1½	8.6	142	142	122	125	2120	1180	520
	9%										
9	Permafresh 183	2% Mykon SF	5	—	146	136	118	129	2860	1660	1550
10	↓	↓	10	—	144	140	114	122	2620	1780	1180
11			12½	—	144	140	119	132	2600	1570	730
12			15	—	148	139	126	128	2440	1620	680
13	n.a.	n.a.	n.a.	n.a.	90	88	84	82	4240	2780	620

n.a. = not applicable.
a. methylated methylolmelamine
b. a misture of dimethylolurea and trimethylolmelamine
c. dihydroxydimethylolethyleneurea

TABLE I-A—Continued

Run No.	Tensile Properties: Work to Rupture (in.-lb)	Warp Extension at Break (%)	Tensile Strength (lb)	Work to Rupture (in.-lb)	Fill Extension at Break (%)	Tensile Strength (lb)	Wash-Wear Rating: Tumble Dried	Line Dried
1	20.0	12.9	141	5.9	15.4	52	3½	3
2	17.0	12.3	126	5.8	14.8	50	4	3
3	20.0	13.0	137	6.3	16.6	51	4	3
4	21.1	13.4	144	6.2	15.8	51	3½	3
5	14.4	11.0	125	4.7	13.8	45	3½	3
6	14.9	11.2	127	5.7	15.2	50	4	3
7	15.8	11.4	130	5.8	15.0	50	4	3
8	17.8	12.4	136	6.6	16.2	51	3½	3
9	13.7	12.4	114	5.1	16.7	44	3½	3
10	13.9	12.7	114	4.6	15.8	42	4	3
11	13.0	12.4	110	4.5	16.8	41	4	3½
12	13.1	12.3	110	4.8	16.0	44	4	4
13	28.3	12.6	174	11.2	19.9	70	—	—

TABLE I-B

Run No	Pad Bath Composition: Methylol Compound	Softener	Exposure Time[a] (min)	Total Add-On (%)	Wrinkle Recovery Angle (degrees): Warp Dry	Warp Wet	Fill Dry	Fill Wet	Tearing Strength (grams): Warp	Tearing Strength (grams): Fill	Stoll Flex Abrasion, Warp (cycles)
1	15%[b] TMM	3%[b] Rhoplex K-87	1	6.3	124	114	112	102	2380	2480	1300
2			2	8.5	152	136	135	118	1850	1670	560
3			4	8.8	158	140	136	126	1710	1440	410
4			5	8.8	158	146	140	130	1620	1390	450
5	9%[b] Permafresh 183		5	7.9	134	140	104	123	1990	1870	700
6			7½	8.6	151	142	134	139	1530	1450	850
7			10	8.3	152	145	124	131	1570	1680	840
8	n.a. (Untreated control)	n.a.	n.a.	n.a.	93	89	85	84	3100	2940	670

n.a. = not applicable
a. Time exposed to formic acid at 120°C.
b. Percentage solids
c. Trimethylolmelamine
d. Dihydroxydimethylolethylene urea

Run No.	Tensile Properties: Work to Rupture (in.-lb)	Warp Extension at Break (%)	Tensile Strength (lb)	Work to Rupture (in.-lb)	Fill Extension at Break (%)	Tensile Strength (lb)	Damage by Retained Chlorine (% loss in tensile strength)
1	26.9	18.8	133	17.5	20.0	90	—
2	19.0	15.2	126	8.7	15.2	65	—
3	16.1	13.8	114	8.4	15.5	59	—
4	15.4	14.9	107	6.9	14.8	55	—
5	19.9	14.6	124	9.0	14.9	64	70
6	14.1	12.4	105	7.6	16.7	56	17
7	14.5	12.6	108	9.2	18.6	60	31
8	29.5	13.7	156	16.1	19.9	86	n.a.

TABLE I-C

Run No.	Pad Bath Composition	Exposure Time[a] (min)	Wrinkle Recovery Angle (degrees): Warp Dry	Warp Wet	Fill Dry	Fill Wet	Tearing Strength (grams): Warp	Tearing Strength (grams): Fill	Stoll Flex Abrasion, Warp (cycles)
1	15% TMM	2	138	134	113	110	2360	2280	1420
2		3	149	138	136	120	2320	1970	2010
3		4	150	145	136	127	1970	1600	740
4		5	152	144	140	124	2080	1660	870
5		2	133	116	94	116	2280	2160	840
6		3	140	120	110	110	2140	2220	1120
7		4	148	130	122	115	1920	1600	1280
8		5	141	130	120	124	2100	1920	680
9	n.a. (Untreated control)	n.a.	93	89	85	84	3100	2940	670

n.a. = Not applicable
a. Time exposed to formic acid at 110°C.
b. Trimethylolmelamine

TABLE I-C—Continued

Run No.	Tensile Properties: Work to Rupture (in.-lb)	Warp Extension at Break (%)	Tensile Strength (lb)	Work to Rupture (in.-lb)	Fill Extension at Break (%)	Tensile Strength (lb)	Wash-Wear Ratings: Tumble Dried Wash-Wear	Tumble Dried Crease Retention	Line Dried Wash-Wear	Line Dried Crease Retention	Number of Wash-Dry Cycles to Holes
	Properties After 1 Washing										
1	21.4	14.8	148	13.2	19.0	88	3½	4½	3½	4	—
2	21.0	14.0	151	10.9	17.1	82	4	5	4	4	—
3	16.2	12.4	135	7.7	16.2	66	4	5	3½	4	—
4	16.5	12.2	136	8.9	16.8	72	4	5	4	4	—
	Properties After 20 Washings										
5	23.7	16.6	141	12.5	18.0	82	3½	3½	3	3	> 20
6	22.1	15.2	138	11.3	16.4	79	3½	4	3½	4	18,20
7	17.5	13.4	128	9.8	16.0	72	4	4	4	4	10,12
8	19.4	13.7	132	7.5	15.4	61	4	4	4	4	11,14
9	29.5	13.7	156	16.1	19.9	86	n.a.	n.a.	n.a.	n.a.	n.a.

EXAMPLE II

Cotton twill fabric samples ("Twist twill", J. P. Stevens & Co.) were padded with 70 percent wet pickup with an aqueous solution containing 10 percent (solids) of various water-soluble crease-proofing agents having reactive N-methylol groups and 2.5 percent (solids) of urethane Latex E–502, (Wyandotte Chemical Co.), and, without prior drying, were exposed to formic acid vapor in the reaction chamber described above for 2 minutes at 115°C., and then heated in air for 5 minutes at 160°C. Fabric samples were then washed, dried and tested. Results are shown in Table II.

The tabulated results show that a high degree of useful reaction could be achieved with all crease-proofing agents used. Similarly, good results are achieved using 10 percent (solids) solutions of hexamethoxymethylmelamine, trimethylolmelamine and trimethylolmelaminedimethylolurea.

TABLE II

Methylolamide	Wrinkle Recovery Angle (degrees) Dry Warp	Dry Fill	Wet Warp	Wet Fill	Tearing Strength (grams) Warp	Tearing Strength (grams) Fill	Stoll Flex Abrasion, Warp (cycles)	Tensile Strength (lb) Warp	Tensile Strength (lb) Fill
				Properties After 1 Washing					
Dimethylol-propyleneurea	154	134	162	139	(a)	1060	550	100	30
Dimethyloluron	161	134	158	144	(a)	890	190	98	27
Dimethylol-Carbamate	131	110	147	130	2390	1520	960	110	46
Trimethylol-Melamine	164	142	154	146	(a)	940	200	105	33
				Properties After 10 Washings					
Dimethylol-propyleneurea	158	130	154	140	2000	1190	480	98	36
Dimethyloluron	160	131	158	144	(a)	930	180	93	30
Dimethylol-carbamate	120	109	141	123	2590	1590	940	124	49
Trimethylol-melamine	155	138	158	133	(a)	970	230	104	30
Untreated (unwashed)	78	71	74	78	3800	2060	640	175	66
Untreated (Washed)	70	68	69	72	2840	1630	670	161	74

n.a. = not applicable
(a) Fabric specimens tore across filling yarns only.

EXAMPLE III

Samples of the same twill fabric as used in Example II were impregnated with an aqueous solution containing 9 percent (solids) of Permafresh 113B (dimethylol dihydroxyethylene urea) and 2.5 percent (solids) urethane Latex E–502 to 50 percent wet pickup, and, without prior drying, were exposed to formic acid or acetic acid for different times, and then post-heated for different times and at different temperatures as shown in Table III. The samples were then washed, dried and tested. Results are shown in Table III.

TABLE III

Gaseous Catalyst	Exposure Time and Temperature (min/°C)	Heating Time and Temperature (min/°C)	Wrinkle Recovery Angle (degrees) Dry Warp	Dry Fill	Wet Warp	Wet Fill	Tearing Strength (grams) Warp	Tearing Strength (grams) Fill	Stoll Flex Abrasion, Warp (cycles)	Tensile Strength (lb) Warp	Tensile Strength (lb) Fill
HCOOH	3/115	5/160	158	136	152	142	1990	1160	690	105	35
do.	2/115	5/160	150	132	151	134	2050	1270	530	110	40
do.	1.5/115	5/160	154	129	148	134	2150	1250	560	109	34
do.	1/115	5/160	154	128	148	136	2140	1340	570	112	39
do.	2/115	5/150	148	128	136	124	1900	1130	400	118	42
do.	2/115	5/140	146	130	131	122	2030	1200	510	119	45
do.	2/115	5/130	130	120	123	118	2280	1440	700	126	51
CH_3COOH	3/115	5/160	131	122	140	130	2440	1430	720	129	44
do.	2/115	5/160	132	124	137	128	2190	1280	670	111	43
do.	1.5/115	5/160	138	122	138	128	2430	1450	660	121	46
do.	1/115	5/160	140	123	138	128	2410	1350	650	127	43
Untreated (unwashed)		—	78	71	74	78	3800	2060	640	175	66
Untreated (washed)		—	70	68	69	72	2840	1630	670	161	74

These tabulated results show that a short exposure to acetic acid, as well as to formic acid, is sufficient to allow a high level of wrinkle recovery to be achieved after a subsequent heat treatment. The balance of wrinkle recovery gained to strength and abrasion resistance lost is about the same for each catalyst, and comparable with a conventional pad/dry/cure system using the same crease-proofing agent.

EXAMPLE IV

The twill samples of Example II are impregnated with an aqueous solution containing 20 percent dimethylolurea (Permafresh 477) and 10 percent urethane Latex (E–502) and dried to various add-ons as shown in Table IV–A. These impregnated twill samples were exposed to formic or hydrochloric acid vapors at temperatures between 60° and 120°C. and either post-heated in air for 5 minutes at 150°C. or neutralized and washed. Conditions and results are shown in Table IV–A.

These results show the advantages of the present invention as compared with hydrochloric acid systems.

Prior to the post-heating step, fabrics treated with the hydrochloric acid system showed good degrees of wrinkle recovery angles, but rather low tensile strength retentions. The post-heating step, however, proved to be highly detrimental to the strength of these HCl-system fabrics. As in the case of the Permafresh 113B-treated fabrics, the acid degradation was such that it was impossible to measure any of their physical properties.

To show that post-heating at lower temperatures could yield fabrics with acceptable degrees of strength retention for formic acid but not hydrochloric acid systems, further runs were conducted in which fabrics impregnated with dimethylolurea (Permafresh 477) and urethane Latex-502 were exposed to formic or hydrochloric acid vapors for 5 min. at 120° or 60°C., respectively, and then post-heated at 100°–140°C. The resulting fabric properties are listed in Table IV–B.

TABLE IV-A

Catalyst	Exposure Temp. (°C)	Postheated at 150°C for 5 min	Add-on (%)	Wrinkle Recovery Angle, W + F (degrees) Dry	Wrinkle Recovery Angle, W + F (degrees) Wet	Tensile Strength (% retention) Warp	Tensile Strength (% retention) Fill	Wash-Wear Ratings
HCOOH	60	No[b]	2.6	146	208	82	97	2.7
do.	80	do.	3.4	150	210	79	98	3.0
do.	100	do.	5.1	223	257	65	77	3.0
do.	120	do.	5.7	286	270	61	69	4.2
do.	60	Yes	5.2	293	292	56	60	4.4
do.	80	do.	5.4	289	295	53	51	4.4
do.	100	do.	5.4	306	307	54	55	4.3
do.	120	do.	5.5	308	306	52	53	3.9
HCl	60	No[b]	—	258	254	51	62	3.0
do.	80	do.	—	282	284	37	63	3.0
do.	100	do.	—	286	290	34	32	3.6
do.	120	do.	—	305	304	27	16	4.0
do.	60	Yes	—	a	a	a	a	a
do.	80	do.	—	a	a	a	a	a
do.	100	do.	—	a	a	a	a	a
do.	120	do.	—	a	a	a	a	a
Untreated Control	—	—	—	152	160	100 (186 lb)	100 (74 lb)	—

[a] Fabrics too weak to test.
[b] Neutralized with a 1 percent sodium carbonate solution and washed

TABLE IV-B

Catalyst	Exposure Time/Temp (min/°C)	Postheating Time/Temp (min/°C)	Wrinkle Recovery Angle W + F (degrees) Dry	Wet	Tensile Strength (% retention) Warp	Fill	Wash-Wear Ratings
HCOOH	5/120	5/100	296	284	66	61	4.2
do.	do.	5/120	288	281	68	60	4.2
do.	do.	5/130	302	297	66	65	4.2
do.	do.	5/140	309	294	66	61	4.2
HCl	5/60	5/100	290	296	35	31	3.8
do.	do.	5/120	275	304	17	4	3.7
do.	do.	5/130	297	309	10	6	4.0
do.	do.	5/140	294	304	10	8	3.5
Untreated Control	—	—	152	160	100 (186 lb)	100 (74 lb)	—

EXAMPLE V

Cotton twill fabric (7.8 oz./sq. yd., J. P. Stevens twist twill having 112/50 threads per inch) was treated with a 20 percent solution of dihydroxydimethylolethyleneurea (Permafresh 113B, Sun Chemicals Corporation) to 65 percent wet pickup. The solution also contained 5 percent (solids) of an acrylic emulsion (Rhoplex K-14, Rohm and Haas Co.). The impregnated fabric samples were dried, exposed to a formic acid or hydrochloric acid atmosphere at varying temperatures and times.

TABLE V-A

Add-on (%)	HCOOH Exposure Time/Temp. (min/°C)	Wrinkle Recovery Angle, W +F, (degrees) Dry	Wet	Tearing Strength (% retention) Warp	Fill	Tensile Strength (% retention) Warp	Fill	Warp Stoll Flex Abrasion(% retention)	Wash-Wear Ratings
				Properties Prior to Post-heating					
2.2	1/120	236(207)[a]	218(201)[a]	155	144	71	82	308	2.0
4.0	5/120	274(224)	264(254)	105	118	68	77	272	2.2
5.0	10/120	276(260)	285(270)	98	91	60	63	306	3.0
5.0	15/120	281(262)	280(272)	96	99	62	66	253	2.8
4.9	20/120	302(271)	284(282)	91	95	63	65	279	2.4
1.6	1/100	190(179)	214(198)	106	114	92	82	185	2.0
2.5	5/100	225(217)	260(255)	80	96	74	83	162	2.6
5.2	10/100	268(260)	286(278)	76	77	68	67	153	3.2
6.2	15/100	274(264)	295(288)	73	79	65	71	151	3.4
6.2	20/100	268(260)	280(278)	73	75	65	65	156	3.3
2.6	1/80	177(179)	202(194)	104	123	90	95	179	2.0
3.4	5/80	199(180)	204(202)	100	113	89	94	169	2.0
5.1	10.80	206(179)	249(219)	89	101	77	91	157	2.4
5.4	15/80	221(196)	243(246)	85	99	82	86	174	2.3
3.7	20/80	226(212)	250(252)	83	94	79	85	188	2.4
2.8	1/60	178(183)	187(184)	110	121	87	100	193	2.0
3.1	5/60	193(178)	200(186)	116	125	96	110	191	2.0
3.7	10/60	211(193)	201(200)	112	125	94	104	180	2.1
3.7	15/60	197(185)	194(200)	120	124	92	103	177	2.0
4.2	20/60	200(189)	207(192)	117	120	92	102	219	2.0
				Properties After Post-Heating					
5.0	1/120	248(212)	250(231)	127	132	72	69	394	3.0
4.8	5/120	286(275)	272(272)	97	93	60	56	312	3.6
5.4	10/120	296(285)	296(282)	80	84	58	56	151	3.8
5.5	15/120	290(282)	279(285)	93	98	66	60	283	4.0
6.0	20/120	310(285)	285(292)	78	80	60	61	220	3.6
5.6	1/100	241(234)	270(267)	76	84	69	72	168	3.2
6.3	5/100	272(263)	267(274)	69	70	65	61	165	3.4
6.4	10/100	296(281)	301(288)	64	62	58	59	144	4.0
6.3	15/100	291(288)	289(287)	66	61	58	58	133	3.8
6.6	20/100	295(288)	296(291)	64	62	56	57	136	3.6
6.5	1/80	274(251)	289(274)	59	68	64	69	153	3.6
6.8	5/80	268(273)	276(272)	60	64	61	65	148	3.6
7.0	10/80	289(276)	289(276)	59	65	61	62	107	3.5
6.8	15/80	289(276)	286(278)	55	69	62	64	105	3.8
6.2	20/80	290(282)	286(280)	57	59	58	63	123	3.8
4.6	1/60	274(238)	246(242)	90	104	81	88	202	3.1
6.6	5/60	270(265)	270(242)	70	84	73	79	180	3.7
6.6	10/60	257(252)	262(255)	66	82	69	72	192	3.8
6.8	15/60	276(268)	277(261)	68	74	72	69	170	3.7
7.0	20/60	284(272)	277(279)	63	73	70	75	208	4.4
Control	—	152	160	100 (3024 g)	100 (1827 g)	100 (186 lb)	100 (74 lb)	100 (602 cycles)	—

a. WRAs determined after 10 launderings

TABLE V-B

Add-on (%)	HCl Exposure Time/Temp. (min/°C)	Wrinkle Recovery Angle, W + F, (degrees) Dry	Wet	Tearing Strength (% retention) Warp	Fill	Tensile Strength (% retention) Warp	Fill	Warp Stoll Flex Abrasion (% retention)	Wash-Wear Ratings
5.5	1/120	309(302)[b]	308(305)[b]	66	74	51	54	89	3.0
4.8	2/120	314(305)	304(303)	44	75	23	17	59	3.4
5.0	3/120	322(a)	320(a)	31	11	24	16	21	4.3
4.8	4/120	312(a)	297(a)	a	31	a	a	a	a
a	5/120	a	a	a	a	a	a	a	a
a	10/120	a	a	a	a	a	a	a	a
6.4	1/100	275(267)	299(285)	77	93	51	53	128	3.5
6.2	2/100	310(284)	312(289)	26	31	45	34	15	3.6
5.9	3/100	310(293)	304(299)	17	18	47	14	12	3.8
—	4/100	312(a)	314(a)	2	13	30	9	3	3.8
a	5/100	a	a	2	a	a	a	a	a
a	10/100	a	a	2	a	a	a	a	a
5.8	1/80	280(266)	295(252)	68	89	52	63	175	3.5
6.1	2/80	286(288)	308(280)	67	82	51	60	158	3.6
5.9	3/80	307(291)	303(290)	32	27	33	37	52	3.8
4.7	4/80	293(290)	316(301)	26	28	27	34	22	3.7
5.2	5/80	304(294)	312(293)	a	23	16	16	12	4.0
a	10/80	a	a	a	a	a	a	a	a
4.8	1/60	286(260)	279(270)	87	94	67	72	166	3.6
5.5	2/60	299(262)	292(282)	53	78	59	55	98	4.3
6.1	3/60	303(291)	304(296)	46	38	40	49	68	4.0
5.9	4/60	302(296)	316(298)	a	31	35	35	50	4.2
5.7	5/60	306(291)	307(301)	a	21	26	29	16	3.6
a	10/60	a	a	a	a	a	a	a	a
Control —	—	152	160	100 (3024 g)	100 (1827 g)	100 (186 lb)	100 (74 lb)	100 (602 cycles)	—

a. Too weak to test
b. WRAs determined after 10 launderings

With respect to the formic acid system, it is evident from these data that the degree of crosslinking of fabrics as measured by the development of WRA's (wrinkle recovery angles) increased as the length of exposure time or reaction temperature increased. Conversely, the strength retention of these fabrics diminished somewhat as the reaction temperature increased. However, strength losses exhibited by the postheated fabrics were considerably smaller than those shown by the control fabrics. Reaction time, on the other hand, had a less pronounced effect on strength retention. Fabrics exposed for 5 to 20 minutes exhibited similar degrees of strength retentions.

Thus, these results indicate that the process of this invention can be operated within a wide range of reaction times without significantly adversely affecting the strength retention of the treated fabrics. The use of temperatures above 80°C. (100° or 120°C.) is preferred in order to obtain high levels of crosslinking when using Permafresh 113B. The use of other crosslinking agents such as methylated methylolmelamine (Resloom M-75, Monsanto), methylolmelamine (Resloom HP, Monsanto), and a triazineformaldehyde condensate (Aerotex special resin 23, American Cyanamid) reduce the reaction time considerably.

As shown in Table V-B, fabrics treated with the Permafresh 113B-hydrochloric acid system developed high levels of WRAs in very short lengths of time. Fabrics treated for 1 or 2 minutes exhibited significant strength losses comparable to those obtained with the conventional pad-dry-cure process particularly at the lowest reaction temperatures. Samples treated for 3 to 5 minutes were extremely weak and those treated for longer than 5 minutes were too weak to be tested.

Due to the extreme acid degradation exhibited by all hydrochloric acid-catalyzed samples after the postheating step, it was impossible to measure any of their physical properties.

From the above observations, it can be concluded that some of the basic differences between the hydrochloric and formic acid or acetic acid catalyzed systems using fabrics impregnated with methylolamides are: (1) the range of reaction times and temperatures uder which both systems operate, (2) the method of removing the volatile residues (i.e., by washing or heat soaking), and (3) the possibility of treating garments rather than flat goods due to the omission of the neutralizing and washing steps in the formic acid- or acetic acid-catalyzed process.

Some of the disadvantages of the hydrochloric acid-catalyzed system are: (1) excessive degradation of the cotton fibers, (2) the need for neutralization of the fabric after treatment, (3) the need for afterwash, (4) lack of reproducibility due to the narrow range of reaction times and temperatures under which the process operates, and (5) the need for special controls and equipment for handling the highly corrosive and toxid hydrochloric acid.

EXAMPLE VI

The twill samples of Example V were treated with an aqueous solution containing 20 percent dimethylolethyleneurea (Rhonite R-1, Rohm and Haas Co.) and 10 percent Rhoplex K-14, dried and exposed to gaseous formic acid for 5 minutes at 120°C. Conditions and results are shown in Table VI.

TABLE VI

Add-on (%)	Postheating Time & Temp (min/°C)	Wrinkle Recovery Angles, W + F, (degrees) Dry	Wet	Tearing Strength (% retention) Warp	Fill	Tensile Strength (% retention) Warp	Fill	Warp Stoll Flex Abrasion (%retention)	Wash-Wear Ratings
6.7	0	302	284	88	92	69	63	262	3.6
7.4	5/130	299	287	72	77	58	56	204	3.7
7.6	5/140	308	294	68	76	56	60	174	3.5
7.4	5/150	313	294	67	70	58	56	168	3.7
	—	152	160	100 (3024 g)	100 (1827 g)	100 (186 lb)	100 (74 lb)	100 (602 cycles)	—

TABLE VII

Additive (% solids)	Acetic Acid Exposure Time[a] (min)	Total Add-On (%)	Wrinkle Recovery Angle (degrees) Warp Dry	Warp Wet	Fill Dry	Fill Wet	Tearing Strength (grams) Warp	Tearing Strength (grams) Fill	*Stoll Flex Abrasion, Warp (cycles)	Tensile Properties Warp Work-to-Rupture (in.-lb)	Warp Extension at Break (%)	Warp Tensile Strength (lb)	Fill Work-to-Rupture (in.-lb)	Fill Extension at Break (%)	Fill Tensile Strength (lb)
Properties After 1 Washing															
2.5% Latex E-502	8	10.1	155	132	143	116	2420	1570	540	17.1	12.2	138	5.8	13.7	53
	7	9.8	157	135	138	120	2300	1620	520	17.3	12.4	138	6.6	15.0	55
	6	8.1	146	126	131	106	2810	1850	830	20.3	14.3	142	7.6	16.0	58
	5	7.2	156	124	138	114	2810	2040	890	21.8	15.0	146	8.6	15.6	64
2.0% HDPE[b]	12½	10.4	156	136	130	95	2540	1660	440	16.3	13.2	116	4.6	12.0	45
	10	10.4	150	135	122	104	2980	1900	841	20.0	14.8	124	5.8	13.8	42
	7½	10.0	150	124	125	115	3020	1870	1050	20.9	14.8	126	6.0	13.2	49
	5	10.2	144	120	115	106	3070	2100	2760	23.4	16.6	128	6.8	14.6	56
3.2% Rhoplex K-87	8	10.0	150	127	146	118	2220	1290	740	16.6	11.6	140	6.9	15.8	54
	7	10.4	156	135	142	122	1980	1330	560	17.7	11.9	145	7.2	14.6	61
	6	10.8	152	130	138	120	2150	1260	690	18.8	12.2	149	7.3	14.8	60
	5	8.8	144	122	130	108	2460	1500	990	22.9	14.6	152	7.9	15.2	62
Properties After 10 Washings															
2.5% Latex E-502	8	8.3	152	130	131	106	2600	1840	900	17.3	13.8	134	7.5	15.9	57
	7	8.0	147	132	129	108	2580	1700	560	16.6	13.4	134	6.7	15.4	52
	6	5.7	133	120	118	106	2960	2060	810	20.4	15.8	140	9.1	16.2	66
	5	5.5	140	121	118	108	2840	2080	710	20.5	16.0	140	8.7	15.6	65
2.0% HDPE[b]	12½	--	152	128	120	109	2450	1910	290	17.1	15.4	112	5.1	13.0	43
	10	--	148	118	118	107	2920	1760	540	21.0	17.6	120	5.6	13.4	46
	7½	--	142	110	116	106	2880	1520	1180	19.9	16.0	118	5.8	13.2	47
	5	--	144	111	115	101	3030	2000	1300	22.6	19.7	119	6.8	14.5	52
n.a.	n.a.	n.a.	90	88	84	82	4240	2780	620	28.3	12.6	174	11.2	19.9	70

n.a. = not applicable.

a. Fabrics exposed at 115°C.
b. High density polyethylene.

These data show that the post-heating temperature can be reduced or the post-heating step entirely eliminated without diminishing the degree of wash-wear performance by using methylolamides that are more reactive than dihydroxydimethylolethyleneurea. The results shown in Table VI indicate that the WRAs and wash-wear ratings of fabrics treated with dimethylolethyleneurea were not affected by reducing the temperature of or omitting the post-heating step.

EXAMPLE VII

Cotton twill fabrics (7.8 oz/sq yd NCC standard twill) were padded to 70 percent wet pickup with an aqueous solution containing 15 percent trimethylolmelamine (Resloom HP, Monsanto) and either 2.5 percent (solids) Urethane Latex E-502 (Wyandotte Chem. Corp.), 2.0 percent (solids) high density polyethylene or 3.2 percent (solids) Rhoplex K-87, dried, and then exposed to acetic acid vapor at 115°C. Conditions and results are shown in Table VII.

It is evident from Table VII that acetic acid is capable of producing samples with wrinkle recovery and tensile strengths retention comparable to those obtained with formic acid vapor.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. The invention which is intended to be protected herein, however, is not to be construed as limited to the particular forms disclosed, since these are to be regarded as illustrative rather than restrictive. Variations and changes may be made by those skilled in the art without departing from the spirit of the invention.

What is claimed:

1. A process for improving the dimensional stability, wrinkle resistance, smooth drying characteristics and total shape retentivity of a cellulose fiber-containing fabric which process consists essentially of:

a. applying to the fabric an aqueous solution of a water-soluble crease-proofing agent containing reactive N-methylol groups;

b. heating the impregnated fabric containing the said crease-proofing agent in a non-reactive vapor atmosphere containing a catalyst selected from the group consisting of formic acid and acetic acid vapor as essentially the only reactive component to a temperature between above 80°C. and up to about 160°C. for a time of between about 1 to about 20 minutes to crosslink the cellulose fibers to a first level of crosslinking; and

c. heating the said crosslinked fabric in an inert atmosphere in the absence of additional catalyst to a temperature of above about 100°C. to further cure the said crosslinked fabric to a second level of cross-linking having increased Wrinkle Recovery Angles and Wash-Wear Ratings while dissipating residual reagents.

2. A process according to claim 1 wherein said aqueous solution contains from about 1 to about 40 percent of the said crease-proofing agent.

3. A process for improving the dimensional stability, crease resistance, smooth drying characteristics and total shape retentivity of cotton-containing fabrics which comprises in sequence the steps of:

a. applying to the fabric an aqueous solution consisting essentially of about 5 to about 15 percent by weight of a water-soluble, crease-proofing agent containing reactive N-methylol groups;

b. conditioning or drying the fabric to give the cotton a moisture content of between about 2 to about 100 percent based on dry weight of the fabric;

c. exposing the conditioned fabric to a non-reactive vapor phase consisting essentially of a catalytically effective amount of formic acid or acetic acid as essentially the only reactive component in a reaction zone maintained at a temperature between about 100°C. and about 140°C. for a time of between about 1 and 20 minutes to crosslink the cotton fibers to a first level of crosslinking;

d. at the end of said crosslinking step (c) heating said fabric in an inert gaseous atmosphere in the absence of additional catalyst at a temperature of from about 100°C. to about 180°C., to further cure the fabric to a second, higher level of crosslinking while dissipating residual reagents thereby directly producing a dry, crosslinked, essentially neutral fabric.

4. A process according to claim 3 wherein said non-reactive vapor phase consists essentially of formic acid.

5. A process according to claim 3 wherein said non-reactive vapor phase consists essentially of acetic acid.

6. A process for improving the dimensional stability, wrinkle resistance, smooth drying characteristics and total shape retentivity of cotton-containing fabrics which consists of the sequential steps of:

a. impregnating the fabric with an aqueous solution containing about 5 to 15 percent trimethylolmelamine or dihydroxydimethylolethyleneurea to give a wet pick-up between about 65 and 85 percent based on dry cotton weight;

b. drying and conditioning the impregnated fabric to a moisture content of between about 3 to about 65 percent;

c. exposing the fabric to a non-reactive gaseous atmosphere consisting of from about 20 to 50 volume percent of a catalytic material taken from the group consisting of formic acid and acetic acid, balance inert gaseous material, at a temperature between 110° and 125°C. for a time of about 2 to about 15 minutes, thereby effecting a first level of crosslinking;

d. removing said fabric from said atmosphere; and

e. postheating the said fabric at a temperature of from about 140°C. to about 160°C. to further cure the fabric to a second level of crosslinking while dissipating residual reagents.

7. A process according to claim 6 wherein the fabric is introduced into the process as a flat fabric, and prior to step (c) is formed into a garment.

8. A process according to claim 6 which process is continuous and in which the fabric being treated is flat fabric.

9. A process according to claim 6 which process is continuous and in which the fabric being treated is a garment.

* * * * *