

- [54] RECURABLE CROSSLINKED CELLULOSE
FABRICS FROM METHYLOL REAGENTS
AND POLYCARBOXYLIC ACIDS AND
METHOD OF MAKING
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[57] ABSTRACT

Cellulosic fabrics are treated with formulations containing methylol crosslinking reagents and polycarboxylic acids having three or more acidic groups per molecule. The treated fabrics are cured in a flat configuration and washed. The fabric is subsequently heated in a folded configuration whereby the folded or creased configuration is permanently imparted to the fabric. A metal salt activating catalyst included in the formulation of the textile treating solution decreases the time required to form sharp, permanent creases in the cured fabrics.

3 Claims, No Drawings

RECURABLE CROSSLINKED CELLULOSE FABRICS FROM METHYLOL REAGENTS AND POLYCARBOXYLIC ACIDS AND METHOD OF MAKING

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout all the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America. This is a continuation-in-part of Ser. No. 248,200, filed Apr. 27, 1972, now U.S. Pat. No. 3,776,692.

This invention relates to chemical treatment of cellulosic textiles. Specifically, this invention relates to imparting durable configurations to cellulosic textile products. More specifically, this invention relates to the chemical treatment of cellulosic textiles with mixtures containing a methylol crosslinking reagent and a polycarboxylic acid to produce a product consisting of a crosslinked cellulose derivative having acidic, catalytic groups covalently bonded to the cellulose. More specifically yet, this invention relates to the production of cellulosic textiles having the properties of wrinkle resistance and smooth drying, but which can be given a heat treatment subsequent to the cure in order to impart a new durable crease or other configuration to the textile product. By the process of the instant invention, cellulosic textiles, garments, and other products may be treated to give them the properties generally known as durable press, except that the textiles, garments, or other products may be given a heat treatment at any time subsequent to the cure, thereby imparting durable creases, pleats, or other desired configurations to the textile products. This invention constitutes a process which is useful in the preparation of improved cellulosic fabrics or improved blended fabrics.

The main object of this invention is to provide treated textiles or textile products which have smooth drying and wrinkle-resistant properties, but which can be given a heat treatment at any time subsequent to the curing step of the finishing operation in order to impart new, permanent creases, pleats, or other desired configurations to the fabric.

Another object of this invention is to provide textile treating compositions, formulations, and methods which can be used in conventional textile treating processes to produce wrinkle-resistant cellulosic textile products which can be permanently creased or pleated at any time subsequent to a conventional precure or postcure step by a further heat treatment.

Another object of this invention is to provide a process whereby sharp, permanent creases may be formed rapidly in wrinkle-resistant cellulosic textiles using conventional equipment and pressing times.

BACKGROUND AND PRIOR ART

It is well known to those versed in the art of textile treatment that wrinkle-resistant and smooth-drying properties are imparted to cellulosic or cellulosic blended fabrics by chemical treatments which establish crosslinks between the molecules of the cellulosic fibers. The crosslinks bind the fibers, and therefore the fabric, in the configuration present at the time the crosslinks are established. The covalent nature of the crosslinks makes it impossible to change the configuration of the treated fabric without a chemical reaction

which involves breaking crosslinks and reforming them in new positions to bind the fibers, and therefore the fabric in the new configuration. Conventional delayed cure processes are useful for imparting creases or other desired configurations to textile products, but do not solve the problem of unalterability of finished cellulosic textile products.

In examining the prior art for solutions to this problem of unalterability of crosslinked cellulosic textile products, we find several approaches to solutions of this problem. One approach is through the use of thermally reversible crosslinks, that is, crosslinks which break and reform in new positions when heated. Examples of such crosslinks are those containing partial chemical structure such as Diels-Alder adducts, aryl biscarbamates, and partial esters of polycarboxylic acids. Fabrics with crosslinks such as these can be given heat treatments to impart new, durable configurations, but long periods of heat at high temperatures are required to impart sharp, durable creases in these fabrics, and the fabrics do not have the high wrinkle resistance and smooth drying properties required of durable-press fabrics.

Another approach to alterable, crosslinked cellulosic fabrics is through internally catalyzed fabrics, that is, fabrics containing catalytic groups covalently bonded to the cellulose of the fibers, along with conventional crosslinks. An example of such a fabric is one prepared by first reacting a cotton fabric with reagents which bond quaternary ammonium hydroxide groups to the cellulose, then reacting the resulting fabric with divinyl sulfone to introduce crosslinks into the cellulose. Such a fabric has high resilience and can be given new, durable configurations by heat treatments, but the manufacture of such a fabric requires a number of steps and unusual reagents, and therefore is not widely accepted by textile manufacturers on the basis of its high cost.

On further examination of the prior art, one finds that polycarboxylic acids are used as crosslinking reagents in processes for producing wrinkle-resistant cotton textiles. In these processes, polycarboxylic acids are used as a sole crosslinking agent and produce a modified textile fabric having partial ester crosslinks, that is, part of the carboxyl groups of the reagents are in the form of ester groups bonding the reagent and the cellulose molecules, and the remainder of the carboxyl groups are in the form of free acidic groups bonded to the cellulose matrix.

In searching the prior art it is also found that numerous carboxylic acids are used as catalysts for crosslinking reactions of methylol reagents with cellulose. These carboxylic acids are used, either alone or in conjunction with other inorganic catalysts, in small, catalytic amounts to promote crosslinking reactions of the methylol reagents, but it is not the practice or intent to carry out the crosslinking reactions in such a manner that large amounts of the carboxylic acids become permanently attached to the cellulose.

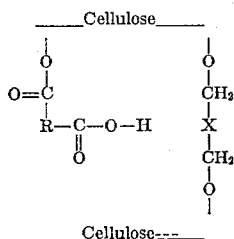
It is also found in the prior art that crosslinked cellulosic fabrics may be given new, durable configurations when a catalyst is applied to the cured fabric and the fabric is given a heat treatment. In these processes of the prior art, the ability to accept a new, permanent configuration is dependent on the added catalyst, which is not bonded to the fabric but may be washed out of the fabric with water. The reagents employed in this type of recurring process are usually strong cata-

lysts, and consequently have deleterious effects on the strength of the fabric and the durable press properties of the treated areas of the fabric.

THE NEW INVENTION

We have now discovered that cellulosic textile products may be impregnated with aqueous solutions of conventional methylol crosslinking reagent and a polycarboxylic acid containing three or more carboxyl groups per molecule, dried, and cured, and that the resulting textile product which has high wrinkle resistance and smooth drying properties and which may or may not be washed to remove excess reagents and which may be given a heat treatment to impart new, permanent creases, pleats, or other desired configurations to the textile product. The essence of this discovery may be stated as follows: Recurable durable-press fabrics may be produced by reacting cellulosic textile products with combinations of methylol reagents and polycarboxylic acids. In this statement the terms recurability and durable press may be defined as follows: Durable press (as applied to cellulosic fabrics) may be defined as having the properties of high wrinkle resistance, good smooth-drying appearance, and excellent retention of creases imparted to the fabric during the cure. Durable press properties are generally imparted to cellulosic fabrics by reactions which form crosslinks in the cellulose. Recurability may be defined as the property of crosslinked cellulosic fabrics being able to accept new, durable configurations when subjected to a heat treatment, by virtue of a chemical reaction which breaks the crosslinks and reforms them in new positions.

In the process of this invention, the polycarboxylic acid serves two essential functions: (a) by virtue of its acidic nature, the polycarboxylic acid serves as the catalyst for the crosslinking reaction of the methylol reagent with the cellulose of the fibers, and (b) the polycarboxylic acid reacts with the cellulose to form partial ester groups which have free carboxylic acid groups which are able to catalyze the breaking and reformation of the crosslinks from the methylol reagent. The structure of the modified cellulose may be depicted as follows:



where the structure represents two cellulose chains joined by a crosslink containing methylol groups and the non-methylol portion of the reagent, represented as X. Attached to one of the cellulose chains, by an ester group, is a polycarboxylic acid, shown as having a free carboxylic acid group, and the remainder of the molecule represented by R which may have more ester or carboxylic acid groups.

In addition, we have discovered that activating catalysts can be added to the textile treating formulations

containing methylol reagents and polycarboxylic acids. These activating catalysts, which may be conventional metal salt catalysts normally used for crosslinking reactions of methylol reagents with fibrous cellulose, have the function of accelerating the recurring reaction and thus reducing the time required to form sharp, durable creases in the cured fabrics of this invention. This acceleration of the recurring action therefore makes it possible to use fully cured durable press fabrics in garment manufacturing operations in which the sewed garments are pressed by conventional methods to form sharp creases and flat seams and do not require a post-cure step to make these configurations permanent.

Since the combination of polycarboxylic acid and an activating catalyst is a very active catalyst system, it is of course necessary to adjust the conditions to the curing step to obtain a full cure (generally defined as a good durable press appearance rating and a conditioned wrinkle recovery angle of 280° (W+F) or greater) without causing excessive degradation of the cellulose and consequent loss of strength in the fabric. Since the activating catalyst does not become covalently bonded to the fabric during the cure step, it is not completely retained in the fabric if the fabric is washed after curing, but the polycarboxylic acid does become bonded to the cellulose during the cure and the washed fabric retains the same degree of recurability as the fabrics of this invention not containing the activating catalysts.

The novelty of this additional discovery is based on the fact that cellulosic fabrics treated with a combination of a methylol crosslinking reagent with a polycarboxylic acid and an activating catalyst are able to accept sharp, durable creases at any time after they are cured if they are pressed under mild conditions of time and temperature. This is in contrast to durable press fabrics cured with conventional catalysts, which are relatively more resistant to recurring, even if the original catalyst is allowed to remain in the cured fabric, than the fabrics of this invention containing the activating catalysts. It is possible that the higher degree of recurability of these fabrics is a result of the presence of relatively large amounts of carboxylic acids which would be efficient "catalysts" for the breaking of the chemical bonds of the crosslinks as well as for the formation of new crosslinking bonds. This catalysis of the recurring reactions may be a result of the formation of methylol carboxylate groups as intermediates in the recurring reactions. These methylol carboxylate groups would be free to move in the cellulose matrix to positions appropriate for the new configuration being formed in the recurring process. Both the formation of the intermediate groups and the reattachment of the methylol groups to the cellulose hydroxyl groups would be catalyzed by the activating catalysts. Cured fabrics containing conventional catalysts or even the newer mixed acid catalysts would not have sufficient amounts of carboxyl groups to catalyze recurring reactions by this mechanism.

In the practice of the invention, substantially any cellulosic textile material may be used, but our preferred materials are textile materials made either entirely of cotton fibers or of cotton fibers blended with other natural or synthetic fibers. The cellulosic textile material is impregnated with an aqueous solution containing from 8 to 40% of a methylol crosslinking reagent and from 3 to 12% of a polycarboxylic acid. The solution

may also contain other useful textile finishing agents, such as wetting agents or polymeric softeners. The preferred concentrations of the methylol reagents in the treating solutions are from 8 to 12%, depending on the weave of the fabric, and the preferred concentration of the polycarboxylic acid is from 25 to 50% of that of the methylol reagent.

The methylol crosslinking reagent may be any of the conventional crosslinking reagents used for finishing cellulosic fabrics. The preferred reagent is dimethyloldihydroxyethyleneurea, but other reagents which also may be used include methylated methylol melamines, methylated ureaformaldehyde reagents, methylolated carbamates, formaldehyde, methylol urons, dimethylolpropyleneurea, methylol triazones, and dimethylolethyleneurea.

The polycarboxylic acid may be an acidic organic compound having three or more carboxylic acid groups per molecule and which is soluble in water to the extent required in a treating solution. The preferred polycarboxylic acids are cyclopentanetetracarboxylic acid and tetrahydrofuran-tetracarboxylic acid. Other carboxylic acids which may be used include mellitic acid, nitrilotriacetic acid, (ethylenedinitrilo)tetraacetic acid, pyromellitic acid, tris(carboxyethyl)isocyanurate, naphthalenetetracarboxylic acid, and benzophenonetetracarboxylic acid.

After the cellulosic textile is impregnated, it may be dried immediately or it may be stored in the wet state or subjected to a fixation process before it is dried. The methylol reagent may also be fixed to the cotton fabric, the fabric washed, and the polycarboxylic acid applied in a second impregnation step. The impregnated and dried textile may be cured immediately or it may be stored or manufactured into garments or other useful articles before it is cured. The curing step consists of a high temperature treatment carried out in an oven or apparatus such as a hot-head press. The curing step may be carried out at any temperature between 130°C and 205°C, and for times varying between 15 seconds and 12 minutes. The preferred curing conditions are eight minutes at 160°C, in either a forced draft oven or a tenter frame. The cured textile may be washed with water containing a nonionic detergent to remove unreacted reagents, but this washing is not essential. The cured textile, prepared according to the preferred conditions, has a conditioned wrinkle recovery angle of 270° to 295° (W+F) if no softener is used in the treating solution, and 290° to 310° (W+F) if a softener is used. Textile fabrics prepared according to the preferred conditions of this invention have strength retentions comparable to conventional durable press fabrics.

The cured fabric of this invention is subjected to a heat treatment during which it is constrained in the new desired configuration. The textile may be constrained by folding it in the desired configuration and applying pressure from a hand iron or other heated object. This may also be accomplished with a stem or electrically heated hot-head press. Pressure may be applied in order to produce sharp creases. The textile may be wet or dry when it is constrained and heated, but of course it becomes dried during the heating. The temperatures of the heat treatment may vary between 130°C and 205°C, and the time of the heat treatment may vary from 15 seconds to 8 minutes. In the preferred process, the textile is wet, folded at the position of the desired new crease, placed on a preheated surface, and cov-

ered with a heated hand iron. The temperature in the textile is maintained at 160°C and the textile is held at this temperature for four to five minutes.

If the cured textile has been washed with an alkaline detergent, it may lose its ability to accept durable creases or other configurations when subjected to a heat treatment. In this case, the recurability of the fabric may be restored by soaking it for a short time in a very dilute solution of an acid, for example a solution of 5% or less of acetic acid in water. After this acid treatment, the fabric may be creased by the usual heat treatment as described above.

Fabrics prepared and given heat treatments according to the process of this invention permanently retain the creases or other configurations imparted by the heat treatments. Thus, textiles prepared by the preferred process and given creases according to the preferred heat treatments retain creases rated at 4.0 or better according to the AATCC crease appearance test after five machine wash and tumble dry cycles.

In addition, if an activating catalyst is to be used in the fabric treatment, substantially any catalyst normally used for the curing of crosslinking reactions of methylol reagents with cellulosic fibers may be added to the treatment solution also containing the polycarboxylic acid and the methylol reagent. Our preferred activating catalysts are magnesium chloride hexahydrate and zinc nitrate hexahydrate, but any metal salt which behaves as a latent acid when heated to curing temperatures may be used in the practice of this invention. Other examples of such activating catalysts include zinc chloride, aluminum chloride, aluminum chlorohydroxide, ammonium chloride, calcium chloride, and magnesium dihydrogen phosphate.

The amount of activating catalyst to be included in the formulation of the fabric treating solution is chosen to give the optimum response to both the curing step and the recuring step. Generally 0.25 to 1.0% of the activating catalyst is used in the treating solution, depending on the nature and construction of the fabric, the other reagents used, the time and temperature of the cure, and the degree of cure and recurability desired in the finished fabric. Larger amounts of activating catalysts generally cause severe strength loss and smaller amounts of activating catalysts require more strenuous curing conditions and result in lower recurability of the finished fabric. It is generally preferable to use smaller amounts of the polycarboxylic acid in the treating solution if an activating catalyst is also used.

Since the combination of the polycarboxylic acid and the activating catalyst constitutes a very active catalyst system, it is possible and preferred to use milder conditions of time and temperature in the curing operation. Thus, there activated fabrics may be cured with lower input of thermal energy and/or with shorter dwell time of fabric in the tenter frame. The optimum curing conditions for each combination of fabric, methylol crosslinking agent, polycarboxylic acid, and activating catalyst must be determined by experiments appropriate to the equipment to be used and the properties desired of the finished fabrics. In general, the addition of 0.5% of an activating catalyst to the treating solution allows a decrease of about 30°C in the curing temperature and a decrease of about half of the curing time to obtain wrinkle recovery and strength retention properties similar to those in corresponding treatments without activating catalysts. The dried fabrics containing the meth-

ylol reagent, the polycarboxylic acid, and the activating catalyst may also be cured by storing them at ambient conditions (20°–30°C) for 30–90 days.

The heat treatments used to form permanent creases or other configurations in the cure fabrics containing the activating catalysts are the same as those used for this purpose with the fabrics of this invention without the activating catalysts, except that shorter times and/or lower temperatures are required to give equivalent creases. Thus, heat treatments of 15 sec. at 135 to 160°C are sufficient to produce creases rated at 5 on the AATCC scale (after 5 laundering cycles) in the fabrics containing the activating catalysts.

SUMMARY

This invention can be summarized as a new process and cellulosic ether derivatives produced by the new process. The cellulosic derivatives being those resulting from reactions involving polycarboxylic acids and di- or poly functional N-methylol agents.

The process being one for imparting to cellulosic textiles high resilience and smooth-drying qualities and capability of qualities to thermal formation and reformation at any time after the cure, the process comprising these steps:

- a. impregnating the cellulosic textile with an aqueous solution containing:
 1. a methylol crosslinking agent selected from the group consisting of
 - formaldehyde
 - dimethylolpropyleneurea
 - bis(methoxymethyl)uron
 - tris(methoxymethyl)urea
 - dimethyloltriazone
 - dimethyloldihydroxyethyleneurea
 - highly methylated, fully-methylolated melamine
 - dimethylolethyleneurea
 - dimethylolmethylcarbamate, and
 - partially-methylated trimethylolmelamine; and
 2. a polycarboxylic acid having 3 or more carboxylic acid groups to the molecule, said polycarboxylic acid selected from the group consisting of:
 - mellitic acid
 - pyromellitic acid
 - nitrilotetracetic acid
 - cyclopentanetetracarboxylic acid
 - (ethylenedinitrilo)tetracetic acid
 - tetrahydrofurantetracarboxylic acid
 - tris(carboxyethyl)isocyanurate
 - naphthalenetetracarboxylic acid, and
 - benzophenonetetracarboxylic acid;
- b. curing the impregnated cellulosic textile for about from 2 to 12.5 minutes at temperatures about from 130° to 205°C,
- c. optionally washing the cured cellulosic textile with a nonionic detergent and drying the washed cellulosic textile, and
- d. optionally subjecting the cellulosic textile to a heat treatment while constrained with or without pressure for about from 0.25 to 8 minutes at a temperature of about from 130° to 205°C. c

Note: There are instances where a drying step would be more suitable prior to the curing step of the process.

This invention also includes a modification of the above process comprising of these steps:

- a. impregnating a cellulosic textile with an aqueous solution containing:

1. a methylol crosslinking agent selected from the same group as above,
2. a polycarboxylic acid selected from the same group as above, and
3. an activating catalyst, which is a metal salt which behaves as a latent acid at elevated temperatures, said activating catalyst selected from the group consisting of
 - magnesium chloride
 - zinc nitrate
 - zinc chloride
 - aluminum chloride
 - aluminum chlorohydroxide
 - ammonium chloride
 - calcium chloride, and
 - magnesium dihydrogen phosphate;

- b. curing the impregnated cellulosic textile as above or under milder conditions of time and/or temperature; and at any time subsequent to the cure,

- c. subjecting the cured cellulosic textile or articles manufactured therefrom to a heat treatment while constrained with or without pressure, said heat treatment being of short duration and/or at mild temperatures to produce sharp, permanent creases or other configurations in the textiles or textile products. s

Percentage composition values as employed herein after refer to percent by weight.

The following list of examples is presented to illustrate this invention and is not meant to limit its scope in any manner whatever.

EXAMPLE 1

Cotton twill fabric (7.6 oz/yd²) was impregnated to 70% wet pick-up with a solution containing 12% of dimethyloldihydroxyethyleneurea (DMDHEU), 6% of cyclopentanetetracarboxylic acid (CPTA), 2% of an emulsified polyethylene softener, and 0.1% of a non-ionic wetting agent. The fiber was dried on a pin frame in a forced draft oven for 8 minutes at 70°C, then cured in the same equipment for 8 minutes at 160°C. After washing in water with a nonionic detergent, the fabric had an add-on of 9.1% and a conditioned wrinkle recovery angle (WRA) (determined by the procedure of ASTM designation B1295-67) of 306° (W+F), a wet WRA of 276° (W+F), a Stroll flex abrasion resistance in the warp direction (determined by the method of ASTM designation D1175-64 T) of 30% of that of the unmodified, laundered fabric, and a tearing strength in the fill direction (measured by the Elmendorf method, as described in ASTM Designation D1424-63) of 50% of that of the unmodified control. These physical properties are similar to those of cotton fabrics treated by conventional durable press processes.

A portion of the fabric was analyzed for nitrogen by the Kjeldahl method and for formaldehyde by the chromotropic acid method. The fabric was found to contain 1.29% N and 1.43% formaldehyde. Another portion of the fabric was analyzed for saponification equivalent by a modified Eberstadt method (as described by Tanghe, et al. in "Methods of Carbohydrate Chemistry," Vol. III, R. L. Whistler, Ed., 1963, pp. 201–203) and free carboxyl groups by a titration (as described by Reinhardt, Fenner, and Reid in Textile Research Journal, Vol. 27, p. 873 (1957)). The fabric was found to contain

0.54 meq/g of saponifiable groups (ester and carboxyl) and 0.33 meq/g of free carboxylic acid groups. These analyses indicate that the textile contained crosslinks from the methylol reagent dimethyloldihydroxyethyleneurea (DMDHEU), chemically known as 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone) and ester and free carboxylic acid groups from the polycarboxylic acid cyclopentanetetracarboxylic acid. The textile therefore consisted of the cellulosic derivative, the 1,3-dimethylene-4,5-dihydroxy-2-imidazolidinone ether of cellulose cyclopentanetetracarboxylate.

EXAMPLE 2

A portion of the textile prepared according to Example 1 was soaked in distilled water, folded so that the warp yarns were bent, and placed on a preheated cloth surface. A thermocouple was placed between the sides of the fabric sample and the assembly was covered with a heated hand iron. The temperature of the iron was controlled by an apparatus attached to the thermocouple. The fabric sample was heated at 160°C for 5 minutes. After the creasing treatment, the fabric sample was rinsed in hot, running water, then stapled to a towel and subjected to five machine washing and tumble drying cycles. After the last drying cycle, the crease remaining in the fabric sample was evaluated by the AATCC method (AATCC Test Method 88 C-1969) modified as described by Hobart in Textile Research Journal, Vol. 37, p. 380 (1967). The crease retained in this fabric after the laundering cycles was rated at 4.3 on the AATCC scale (running from 0 — no crease — to 5 — excellent). This example indicates that good, very durable creases are imparted to fabrics prepared according to Example 1 and treated according to this Example by a heat treatment. The most reasonable explanation for the formation of durable creases in the heat treatment is that a recure (as defined above) occurred during the heat treatment and was catalyzed by the free acid groups in the fabric.

EXAMPLE 3

Cotton twill fabric was treated according to the process of Example 1 except that it was dried at 70°C for 4 minutes in a tenter frame and cured at 160°C for 4 minutes in the tenter frame. This fabric had a conditioned WRA of 292° (W+F). Other physical and chemical tests gave results similar to those in Example 1. This fabric was given a heat treatment according to the process of Example 2. After the five laundering cycles the fabric retained a crease with an AATCC crease rating of 5.0.

EXAMPLE 4

Cotton twill fabrics were treated according to the process of Example 1 except that the curing times were varied from 30 seconds to 6 minutes. The fabric samples were given heat treatments according to the process of Example 2. The conditioned WRA and the AATCC crease ratings after five launderings are reported in Table I.

Table I

Cure Time (min.)	Cond. WRA (°W+F)	AATCC Crease Rating
0.5	260	4.6

Table I-Continued

Cure Time (min.)	Cond. WRA (°W+F)	AATCC Crease Rating
1.0	273	5.0
2.0	280	4.9
3.0	279	5.0
4.0	286	4.9
5.0	278	4.6
6.0	287	4.5

EXAMPLE 5

Cotton twill fabric was heated according to Example 1 except that different concentrations of various polycarboxylic acids were used in the treating solutions. These fabrics were creased according to the procedure of Example 2. The conditioned WRA and AATCC crease ratings after five launderings are given along with the name and concentration of the polycarboxylic acids in Table II.

Table II

Polycarboxylic Acid	Concentration (%)	Cond. WRA (°W+F)	AATCC Crease Rating
Tetrahydrofuran-tetracarboxylic Acid	3	302	4.1
Tetrahydrofuran-tetracarboxylic Acid	6	309	4.0
Tetrahydrofuran-tetracarboxylic Acid	12	300	4.0
Nitrilotriacetic Acid	3	286	0.8
(Ethylenedinitrilo)tetracetic Acid	3	280	1.0

EXAMPLE 6

Cotton printcloth (3.2 oz/yd²) was impregnated with a solution containing 8% of DMDHEU, 6.3% of a polycarboxylic acid, and a trace of a nonionic wetting agent. The impregnated fabric samples were dried and cured according to the procedure of Example 1. The cured fabrics were creased according to the procedure of Example 2. The concentration of DMDHEU, the polycarboxylic acid and its concentration are given along with the conditioned WRA and the AATCC rating of the crease remaining after the five laundering cycles are given in Table III.

Table III

Polycarboxylic Acid	Cond. WRA (°W+F)	AATCC Crease Rating
Mellitic Acid	283	2.8
Tris(carboxyethyl)isocyanurate	258	2.8
Benzophenonetetracarboxylic Acid	286	4.2

EXAMPLE 7

Samples of cotton printcloth were impregnated with solutions containing 8% of a methylol crosslinking reagent, 4% of CPTA, 2% of polyethylene softener, and a trace of a nonionic wetting agent. The fabric samples were dried and cured according to the process of Example 1 and creased according to the process of Example 2. The methylol crosslinking reagents, conditioned

WRA and AATCC crease ratings after five laundering cycles are given in Table IV.

Table IV

Methylol Reagent	Cond. WRA (°W+F)	AATCC Crease Rating
Formaldehyde	309	1.0
Dimethylolpropyleneurea	258	2.3
Bis(methoxymethyl)uron	298	3.5
Tris(methoxymethyl)urea	311	4.0
Dimethyloltriazone	296	3.8
Dimethyloldihydroxyethyleneurea	318	4.0
Highly methylated, fully methylolated melamine	298	3.0
Dimethylolethyleneurea:	230	2.0
Dimethylolmethylcarbamate	261	0.6
Partially methylated trimethylol- melamine	240	2.1

EXAMPLE 8

Cotton twill fabric was impregnated with a solution containing 20% of DMDHEU, 20% of a highly methylated fully methololated melamine, and sufficient hydrochloric acid to lower the pH of the solution to 2.0. The fabric was stored in the wet state for 24 hours, then washed to remove the excess reagents. The fabric was then impregnated with a solution containing 15% of mellitic acid, dried for 8 minutes at 80°C, and cured for 12.5 minutes at 160°C. The cured fabric had a conditioned WRA of 265° (W+F). This fabric was creased according to the process of Example 2. After five laundering cycles it had an AATCC crease rating of 3.3.

EXAMPLE 9

Cotton twill fabric was impregnated and dried according to the process of Example 3. Portions of this fabric were cured by heating the in an electrically heat hot-head press for 2 minutes at various temperatures between 130° and 205°C. These fabric samples all had very good smooth drying appearances and retained creases which were present during the heating process to repeated washing and drying cycles. This demonstrates that at least a fair cure was obtained in all of the samples by heating them in a hot-heat press.

EXAMPLE 10

Portions of the fabric prepared and cured in Example 3 were creased according to the process of Example 2, except that a series of different times and temperature were used for the heat treatments. The times and temperatures of the heat treatments are given along with crease ratings of the fabrics after five washing and drying cycles in Table V.

Table V

Temperature (°C)	Time (min.)	AATCC Crease Rating
130	0.25	1.2
145	0.25	1.3
160	0.25	2.0
180	0.25	2.7
205	2.0	5.0
160	1.0	3.3
160	5.0	4.0
160	8.0	5.0

EXAMPLE 11

A portion of the cotton twill fabric treated according

to the process of Example 3 was creased according to the process of Example 2. After five laundering cycles it had an AATCC crease rating of 4.0. Another portion of the fabric prepared according to Example 3 was given one washing cycle with an alkaline detergent, followed by tumble drying. This washed fabric was creased according to of process of Example 2. After five machine wash and dry cycles this fabric retained a crease with an AATCC crease rating of 1.7. A portion of the fabric washed with the alkaline detergent was soaked in a water solution containing 5% acetic acid for 30 minutes, then rinsed with distilled water. The acidified fabric was creased according to the process of Example 2. After five washing and drying cycles this fabric retained a crease with an AATCC crease rating of 3.7.

EXAMPLE 12

Cotton twill fabric was treated according to the process of Example 1 except that 6% of tetrahydrofuran-tetracarboxylic acid was used in place of the cyclopentanetetracarboxylic acid. This fabric had a conditioned WRA of 309° (W+F). A portion of the fabric was subjected to a heat treatment according to the process of Example 2. After five washing and drying cycles, this portion of the fabric retained a crease rated at 4.0 on the AATCC scale. Portions of the fabric were analyzed for nitrogen, formaldehyde, saponification equivalent, and free carboxyl groups by the methods given in Example 1. The fabric was found to contain 1.14% nitrogen, 1.22% formaldehyde, 0.33 meq/g of saponifiable groups, and 0.21 meq/g of free carboxyl groups. These analyses indicated that the textile contained crosslinks from the methylol reagent dimethyloldihydroxyethyleneurea (DMDHEU, chemically known as 1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone) and ester and free carboxylic acid groups from the polycarboxylic acid tetrahydrofuran-tetracarboxylic acid. The textile therefore consisted of the cellulosic derivative, the 1,3-dimethylene-4,5-dihydroxy-2-imidazolidinone ether of cellulose tetrahydrofuran-tetracarboxylate.

EXAMPLE 13

Cotton twill fabric was treated according to the process of Example 1, except that the impregnating solution contained only 4% of cyclopentanetetracarboxylic acid and in addition contained 0.5% of magnesium chloride hexahydrate. The fabric sample was cured for 4 min, at 130°C instead of for 8 min. at 160°C. The fabric sample was not washed after the cure and had a conditioned wrinkle recovery angle of 298° (W+F). A sample of this fabric was subjected to a heat treatment according to the process of Example 2, except that the folded fabric sample was heated for 15 sec. at 160°C. The fabric sample retained a crease rated at 5 on the AATCC scale after five laundering cycles.

EXAMPLE 14

Cotton twill fabric was treated according to the process of Example 13, except that 0.5% of zinc nitrate hexahydrate was used in place of the magnesium chloride hexahydrate. This fabric had a conditioned wrinkle recovery angle of 303° (W+F) after the cure and retained a crease rated at 3.1 on the AATCC scale after the heat treatment and five laundering cycles.

EXAMPLE 15

Samples of cotton printcloth were impregnated with solutions containing 8% of DMDHEU, 3% of cyclopentanetetracarboxylic acid, 0.5% of an activating catalyst, 2% of emulsified polyethylene softener, and a trace of a nonionic wetting agent. The fabric samples were then dried at 70°C for 8 min. and cured at 130°C for 4 min. Portions of each of the cured fabric samples were subjected to heat treatments according to the process of Example 2, except that the fabric samples were heated for 15 sec. at 160°C. The activating catalyst, the conditioned WRA of the cured samples, and the AATCC crease ratings of the recured fabrics after five laundering cycles are given in Table VI.

Table VI

Activating Catalyst	Cond. WRA (°, W+F)	AATCC Crease Rating
Aluminum Chloride	315	3.0
Calcium Chloride	305	4.1
Magnesium Dihydrogen Phosphate	296	3.5
Ammonium Chloride	302	3.6
Zinc Chloride	291	3.8
Aluminum Chlorohydroxide	312	4.3

EXAMPLE 16

Cotton twill fabric was treated according to the process of Example 1, except that the impregnating solution contained 4% cyclopentanetetracarboxylic acid and in addition contained 1% of magnesium chloride hexahydrate. The fabric sample was not subjected to a high temperature cure, but was stored at ambient temperature for 60 days. After this time the fabric sample had a conditioned wrinkle recovery angle of 280° (W+F). A sample of this fabric was subjected to a heat treatment according to the process of Example 2, except that the folded fabric sample was heated for 15 sec. at 160°C. This fabric sample retained a crease rated at 4.2 on the AATCC scale after five laundering cycles.

EXAMPLE 17

Samples of cotton printcloth were treated according to the process of Example 15, except that magnesium chloride hexahydrate was used as the activating catalyst and the dried fabric samples were cured at different temperatures and for different times. Portions of the cured fabric samples were subjected to heat treatments according to the process of Example 2, except that the fabric samples were heated for 15 sec. at 160°C. The times and temperatures of the cures, the conditioned WRA of the cured fabric samples, and the AATCC crease ratings of the recured fabrics after five laundering cycles are given in Table VII.

Table VII

Cure Time (min)	Cure Temperature (°C.)	Cond. WRA (°, W+F)	AATCC Crease Rating
4	100	271	4.8
4	115	292	3.2
4	130	303	2.4
4	145	309	3.0
4	160	310	2.7
2	130	302	4.7
6	130	309	2.5
8	130	303	2.5

EXAMPLE 18

Samples of cotton printcloth were treated according to the process of Example 15, except that various concentrations of cyclopentanetetracarboxylic acid and magnesium chloride hexahydrate were used in the pad bath. The dried fabric samples were cured at 130°C for 4 min. Portions of the cured fabrics were subjected to heat treatments according to the process of Example 2, except that the fabric samples were heated for 15 sec. at 160°C. The concentrations of cyclopentanetetracarboxylic acid (CPTA) and magnesium chloride hexahydrate in the pad bath, the conditioned WRA of the cured fabric samples, and the AATCC crease ratings of the recured fabrics after five laundering cycles are given in Table VIII.

Table VIII

Concentration of CPTA (%)	Concentration of MgCl ₂ ·6H ₂ O (%)	Cond. WRA (°, W+F)	AATCC Crease Rating
4	0.5	303	3.2
3	0.5	305	3.1
2	0.5	304	3.7
1	0.5	302	3.8
3	0.1	276	2.8
3	0.25	294	4.2
3	1.0	301	4.0
3	2.0	309	4.2

We claim:

1. An improvement in the process of impregnating a cellulosic textile with a solution of a methylolated cellulose crosslinking reagent and a polycarboxylic acid having at least three carboxylic acid groups, curing the textile and thermally reforming the cured textile, the improvement comprising including from about 0.25 to 1.0 weight percent of a latent acid catalyst in said solution.

2. A process for thermally reforming a resilient, smooth-drying crosslinked cellulosic textile subsequent to the crosslinking treatment, which process consists of the following steps:

- impregnating the cellulosic textile with a methylolated crosslinking reagent augmented with from 1-6 weight percent of a polycarboxylic acid having at least three carboxylic acid groups and from 0.25 to 1.0 weight percent of a latent acid catalyst;
- curing the impregnated cellulosic textile at a temperature not exceeding 160°C. to produce a resilient, smooth-drying crosslinked cellulosic textile, and
- at any time subsequent to the cure, thermally reforming, with constraint, the said crosslinked cellulosic textile at a temperature of about 160°C. for a time interval of at least 15 seconds.

3. The initially crosslinked and subsequently thermally reformed cellulosic textile produced according to the process of claim 2.

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