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3,472,606

TWO-COMPONENT WET FIXATION PROCESS FOR IMPARTING DURABLE PRESS TO CELLULOSE-CONTAINING MATERIALS

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ABSTRACT OF THE DISCLOSURE

Good wrinkle recovery is imparted to cellulose containing textile materials with a minimum sacrifice in tensile strength and wear resistance by depositing in the material a substantial amount of a polymer builder from an aqueous medium, wet fixing the polymer builder in the material while maintaining the moisture content of the latter at more than 20%, also applying to the material a more active cellulose cross-linking agent, and finally dry curing said material.

This invention relates to an improvement in cellulose-containing textile materials and more particularly to a process for finishing such textile materials to impart to them good wrinkle recovery with a minimum sacrifice in tensile strength and wear resistance.

In the cotton garment industry it is well known to treat cotton-containing textile materials with a cross-linking agent such as an aminoplast to improve the shape holding properties of such materials, i.e., their ability to retain pressed-in creases as well as their resistance to wrinkling when dry or wet. Particularly good shape holding properties have been obtained when the cure of such resin treated fabrics was delayed until after the treated fabric was cut and sewn to produce the desired finished garment and after such garment was given the desired shape by pressing. However, the tensile and tear strength and the abrasion resistance of resin-treated fabrics has heretofore usually been reduced approximately in proportion to the improvements of the appearance. Garments made from such treated cotton fabrics therefore have a somewhat shorter wear life than similar garments made from untreated fabrics. This disadvantage has been particularly noticeable in the case of garments employing the delayed cure technique because the high degree of permanence of creases in such garments tends to concentrate abrasion of the garment at such vulnerable areas.

It has been previously proposed to alleviate this problem by various process modifications. For instance, it has been proposed to fix the cross-linking agent, such as a hardenable aminoplast, in the textile fibers while the latter were in a wet, swollen state, to dry the fabric, and only then to subject the fabric to the proper cure. See, for instance, U.S. Patents 3,138,802 (Getchell) and 3,177,093 (Van Loo et al.). However, even these modified processes resulted in a substantial reduction in the original tensile strength of the material when it was desired to obtain a high degree of wrinkle recovery. On the other hand, when process conditions were chosen to minimize strength loss the resulting improvement in wrinkle recovery was considerably less than optimum.

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It is an object of this invention to provide resilient, cellulose-containing textile materials and finished articles such as garments made therefrom having good crease recovery as well as good tensile strength, and abrasion resistance. A more specific object is to provide a process for cross-linking cellulosic materials to impart to them superior wrinkle resistance with a minimum impairment of their natural tensile strength and abrasion resistance. A still more specific object is to provide a process for the production of improved easy-care cellulosic materials such as cotton-containing fabrics which process includes preconditioning such materials by wet fixing in the cellulosic fibers a melamine-containing resin before effecting final cross-linking by the dry cure in the fibers of another agent which is a potent cross-linker but a relatively poor polymer builder, e.g., cyclic urea-formaldehyde resin. Still other objects of the invention, as well as its nature, scope, various modes of practice and its various advantages will become apparent from the following description. It will be understood, of course, that the invention is not limited to the particular embodiments described and that these are set forth herein primarily for purposes of illustration rather than limitation.

The present invention is based on the discovery that a greatly improved combination of textile material properties can be achieved by treating the material with a plurality of agents of two substantially different types. More specifically, it has been discovered that unexpectedly good results are obtained when one of the agents used is a relatively slow acting aminoplast precondensate which is easy to affix to the material at high add-ons, e.g., a melamine-formaldehyde precondensate, and the other is a cross-linking agent which is highly reactive as a cellulose cross-linker but difficult to apply at high add-ons, e.g., dihydroxy ethylene ureas, cyclic ethylene urea-formaldehyde precondensates, etc.

The essential characteristic of the first agent or polymer builder is that it can be applied to the textile material from aqueous solution and wet fixed in the swollen material at relatively high dry add-ons. Such agents, even when cured, do not by themselves improve the wrinkle recovery of the material as much as the trade increasingly demands. However, they have been found to assure a high order of mobility of the cellulose molecules or fibrils in the finished material and thereby result in a treated material having substantially better tensile strength, softness and abrasion resistance than materials treated with more potent cross-linkers.

The essential characteristic of the second agent is that it is one of the more highly reactive cellulose cross-linking agents such as a formaldehyde-cyclic ethylene urea precondensate, an N-methylol carbamate, bis(hydroxy ethyl) sulfone, etc. Such agents are well known to impart excellent wrinkle recovery to cellulosic materials upon high temperature curing but are very difficult to wet fix in the material at high add-ons. When used by themselves, they therefore tend to result either in inadequate wrinkle recovery or in excessive strength loss, or both. Moreover, because of the difficulty of wet fixing them in the fibers at high add-ons, these agents have not readily lent themselves for use in the delayed cure technique wherein preferred practice generally requires scouring the material after the wet fixing of the resin therein and prior to final cure.

It has now been found that by using these two types of reactants in combination or sequence a far better

balance of fabric properties is obtained than what one would have expected from results obtained when either reactant is used by itself. To put it differently, it has been found that use of both types of reactants in a single process results in a textile product which has a substantially better combination of strength and recovery characteristics than the sum of effects one would expect to obtain by treating the same fabric with an equal or larger total quantity of either reactant used individually. More particularly, it has been found that cellulosic materials which have a fiber conditioner such as a melamine resin wet fixed therein while the fibers are in a swollen state and which are then scoured, dried and finally cross-linked with a good cross-linking agent such as a formaldehyde condensate of cyclic ethylene urea, have a far better balance of tensile strength and wrinkle recovery than similar materials which are treated with the melamine resin alone or with a highly reactive cross-linking agent alone. Fabrics which have been treated with a combination of agents in accordance with the present invention possess similar appearance characteristics and less strength loss at lower concentrations of cross-linking agent than fabrics treated with one such agent without the other. Conversely, at the same add-on of cross-linking agent in the fabric, fabrics treated by the present process have serviceability similar to and much better appearance than fabrics treated with such cross-linking agent alone. Moreover, whereas the more reactive cross-linking agents have heretofore been rather difficult to use because of the hazard of causing an overcure, the present invention substantially eliminates this hazard.

The improvement, while useful in finishing fabrics flat before tailoring, has been found to be particularly beneficial in conjunction with the so-called delayed cure or "permanent-press" type process wherein the resin treated fabric is cured only after the garment is finished and all creases, cuffs, pockets, etc. are fully pressed. In this type of garment sharp creases in slacks and sharp edges of cuffs, collar, waistband and pockets remain in essentially the same place in the fabric throughout the life of the garment rather than being reformed in slightly different fabric areas after each laundering as is the case in untreated garments or in ordinary flat-cured "wash-and-wear" garments. This characteristic of the "permanent-press" type garments tends to accelerate their wearing through at exposed areas of stress such as creases and cuff edges. Since resin treatment has heretofore generally also resulted in a substantial reduction of the natural strength of the cellulose fibers, "permanent-press" type garments have tended to wear out faster than garments made from untreated cotton or from flat-cured cotton fabrics.

In accordance with the present invention, the aforementioned disadvantages are minimized and an improved cellulosic material is obtained by a combination of steps which comprises: impregnating the material with a hardenable polymer builder or aminoplast such as trimethylol melamine; insolubilizing the polymer builder in the material by wet fixation to provide a dry resin add-on of at least 8%; also impregnating the material with an active cross-linking agent such as dihydroxy dimethylethylene urea; and thereafter dry curing the material to provide the desired wrinkle resistance. The material may be converted into a garment either before or after the dry curing step. In practicing such process it is possible to apply both the polymer builder and the active cross-linking agent in an initial impregnation or padding step, prior to the wet fixation step, and then to apply a curing catalyst after the wet fixation step and to dry cure the applied resin in the material during the final curing step. Alternatively, in some cases it may be preferred to apply only the polymer builder in the initial padding bath, and to apply the active cross-linking agent and appropriate curing catalyst to the textile material only after the initially applied aminoplast has been wet fixed therein and the material containing the

wet fixed resin has been scoured to remove excess polymer builder and dried.

The process is applicable to a wide variety of cellulosic fibrous materials containing cotton or viscose fibers, e.g., fibers, filaments, yarns, threads, and particularly woven and non-woven fabrics. It is especially useful in the manufacture of permanent-press garments, but offers important advantages in the manufacture of other types of cellulosic textile articles as well, whenever good shape retention, abrasion resistance and strength are desired, e.g., in the manufacture of tufted cotton carpets, molded cotton batting and so forth. The invention is particularly effective with natural cellulose materials such as cotton and linen, but is also applicable to regenerated cellulose such as viscose and high wet modulus rayon. The invention is also important for fabric blends containing at least about 15% cellulosic fiber, e.g., blends of cotton and polyester (such as polyethylene terephthalate), cotton-and-nylon, etc., wherein the inclusion of cotton to improve desirable properties such as moisture regain has heretofore concomitantly resulted in the impairment of other qualities, such as abrasion resistance.

The polymer builders useful herein in pretreating or conditioning the material prior to dry curing the cross-linking agent therein include particularly the easily hardenable precondensates which are substantially water soluble and are obtained by condensation of formaldehyde with a compound such as 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 to deposit therein more than 8% and up to about 20% precondensate based on dry weight of the material, and they are capable of being insolubilized in the material by wet fixing, as described, for instance in U.S. Patent 3,138,802. 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 one mole of melamine or an alkyl substituted melamine with two or three moles of formaldehyde, i.e., using dimethylol melamine or trimethylol melamine. A readily available commercial product useful as a polymer builder herein is a mixture of hexamethyl methylol melamine and triazone ("Aerotex 23"). When this product is used by itself in the present invention the methylol melamine acts as the polymer builder while the triazone is capable of acting as the cross-linker. In many cases it may be advantageous to fortify the cross-linking action of this commercial product by including with it an additional cross-linker such as dihydroxy dimethylol ethylene urea ("DHDMEU").

To be applied by padding, the polymer builder is dissolved in water to form a solution containing from about 15 to 40%, e.g., 25% of the hardenable precondensate. To facilitate its wet fixation in the fabric in the desired amount it is necessary to add to the padding solution a conventional acidic catalyst such as hydrogen peroxide, formic acid, maleic anhydride, hydrochloric or sulfuric acid or an acid acting salt such as zinc nitrate, magnesium chloride, ammonium chloride, aluminum chloride, etc. Such catalyst may be added to the padding bath in an amount equal to about 1 to 10%, e.g., about 5%, based on the weight of the precondensate. It is desirable to allow the bath to age before padding in order to raise the molecular weight of the precondensate and thereby facilitate its add-on at high concentrations. Formation of the insoluble condensate in the fiber is aided by heat and acidity. Thus, when operating with the less reactive polymer builders such as hexamethyl methylol melamine it is desirable to adjust the pH of the padding bath to between 1 and 4.

The active cross-linking agent used to bring about the desired cross-linking of the material may be selected from

a wide variety of compounds which are well known in the art for this general purpose. The highly reactive condensates of formaldehyde and a 5-membered cyclic ethylene urea of the kind shown in U.S. Patent 3,177,093, and especially the products such as dimethylol ethylene urea, dihydroxy dimethylol ethylene urea, etc. have been found particularly outstanding in the present invention. Condensates having at least 1.5 moles of formaldehyde combined as methylol formaldehyde with a cyclic urea are suitable and the dimethylol derivatives are preferred. However, other agents such as the rapidly acting triazones, N-methylol carbamates, formaldehyde itself, tris (1-aziridinyl) phosphine oxide, divinyl sulfone, as well as epoxy resins, etc. can be used likewise. Unlike the polymer builder which is used herein to condition or swell the cellulosic structure of the material, for which purpose the polymer builder must be capable of building up a solid resin add-on of at least 8% in the cellulosic material by wet fixing, it is sufficient for the active cross-linking agent to be deposited in the material at a relatively low add-on, e.g., 1 to 3% based on dry material. Of course, to bring about a proper cure of such cross-linking agent an appropriate catalyst should also be present in the material during the final curing step. In the case of the amine type cross-linking agents, such as the cyclic ethylene ureas or triazones, one of the acid reacting catalyst described earlier herein such as zinc nitrate or magnesium chloride or aluminum chloride may be used in accordance with otherwise well known practice. On the other hand, when a base catalyzed cross-linking agent such as bis(hydroxyethyl) sulfone is used an alkaline catalyst such as sodium carbonate or hydroxide is employed.

Impregnation of the cellulosic material with the polymer builder or curing agent can be done by conventional padding using customary equipment, or by spraying and other processes well known in the art.

Wet fixing of the deposited resin in the fibrous material can be effected in a known manner, for instance, as described in U.S. Patent 3,138,802. Thus, after impregnating the fibrous material at about 10° to 30° C. on a padding mangle, the impregnated material is first dried to a moisture content of between about 20 and about 100%, preferably 40 to 60% (based on dry weight) by passage through a tenter frame or the like and the partially dried material is then heated to between about 80° and 120° C. for about 2 to 15 minutes while enclosed in a wet state, e.g., by treatment with saturated steam (at about 100° C.) in a Mather-Platt high speed steamer or similar equipment. In this manner the moisture content of the material is maintained within the aforementioned limits while the resin is wet fixed and thus made water insoluble therein. Alternatively, satisfactory wet fixation of readily polymerizable polymer builders can be obtained by appropriate treatment of the partially dried impregnated fabric at room temperature, e.g., by rolling the partially dried fabric, wrapping the roll air-tight in a polyethylene or similar thermoplastic film and then storing the moist fabric at 20° to 30° C. for several days until the desired degree of resin insolubilization is reached.

An essential characteristic of a cotton-containing material in which a polymer builder has been properly wet fixed in accordance with this invention is that the resin can no longer be removed from the material by ordinary laundering but that the cotton remains dyeable by direct cotton dyes, e.g., by Direct Blue 14. In other words, proper wet fixing leaves the reactive hydroxyl groups of the cotton available for direct dyeing. In contrast, in cotton cross-linked by a dry cure the reactive groups are taken up by reaction with the cross-linking agent and such cross-linked cotton therefore cannot normally be dyed with a direct cotton dye. The use of a direct dye thus affords a convenient test for determining that proper wet fixation has been obtained. Of course, the

fact that the material having the polymer builder wet fixed therein is dyeable with direct cotton dyes, and in many cases also with dyes of the type ordinarily used on wool, e.g., acid dyes, is in itself an important advantage.

When the resin has been properly insolubilized by wet fixing as desired, the material is preferably scoured to remove residual catalyst and other water soluble compounds and subsequently dried. The removal of the water soluble compounds at this stage facilitates more exact control of the final cure while drying of course facilitates imbibition of liquid in any subsequent padding stage.

The dried material containing the polymer builder wet fixed therein is subsequently padded through an aqueous solution of a cross-linking agent such as dihydroxy dimethylol ethylene urea containing a catalytic amount of zinc nitrate or other appropriate catalyst. The inclusion of a conventional wetting agent in such a solution often is helpful. Other conventional additives such as textile lubricants, softeners, compatible water repellent and stain resistant finishing agents, and the like may also be included. Thereupon the padded material is again dried and finally cured. Curing can be effected either directly in the flat state or after a garment has been completed from the treated material. The final dry curing step is generally carried out at temperatures above about 100° C. and below charring temperature of the material, e.g., between about 120° and 180° C. For instance, residence of the finished garment in a forced air oven at 150° C. for about 2 to 5 minutes usually gives satisfactory results. Somewhat longer residence times may be necessary at lower curing temperatures and shorter times may be preferred at higher curing temperatures, as can be readily determined by any person skilled in the art.

According to an alternative embodiment, both the polymer builder and the strong cross-linker such as formaldehyde or DHDMEU may be included in a single, initial treating bath. After padding the fabric in such a bath, the polymer builder and the cross-linker are wet fixed in the fabric under substantially the same conditions as described before. In this case, however, the washed and dried fabric containing the wet fixed reagents is then treated in a second bath which, in addition to any conventional processing aids, softeners, etc., includes a catalyst to facilitate the final dry cure of the previously wet fixed cross-linker.

The following examples are illustrative of the process of the invention and of the results obtained thereby. It should be understood, however, that these examples are not intended to be limiting and that many variations and modifications of this invention not specifically described herein can be made by persons skilled in the art without departing from the scope and spirit of this invention. Unless otherwise indicated, all percentages and ratios of materials are expressed on a weight basis herein.

Example 1

A 6 ounce/square yard, combed, bleached, mercerized cotton twill was padded through a solution containing 16.2% trimethylolmelamine (Arigal C, Ciba Chemical & Dye Company), and 1% hydrogen peroxide (35% active). The padding speed was 20 yards/minute, the bath temperature 24° C., and the pick-up 68%. The fabric was rolled-up, sealed in polyethylene film, and allowed to cure at room temperature (20°-25° C.) for 4 days. It was then scoured with a water solution of soda ash and soap, and dried. The fabric pH was then neutral, and the add-on of trimethylolmelamine ("TMM"), as measured by nitrogen determination, was about 11%.

Samples of the thus pre-treated fabric were then padded through aqueous solutions calculated to give add-ons of dihydroxy-dimethylol ethylene urea ("DHDMEU," Permafresh 183, Sun Chemical Corp.) of 3, 4.5 and 6% (dry basis), i.e., the solutions contained approximately 10, 15 and 20% dihydroxy-dimethylol ethylene urea and

6.5, 7.5 and 8.5% of zinc nitrate catalyst. The catalyst of course serves to catalyze the eventual cure of both the DHDMEU and the TMM applied in the pre-treatment. For purposes of comparison, the same fabric, but without the TMM pre-treatment, was padded with similar solutions containing 15% to 20% DHDMEU, respectively. In these runs, however, only 3% zinc nitrate was included in the 15% DHDMEU bath, and only 3.7% zinc nitrate for 20% DHDMEU bath, since DHDMEU was the only resin in the fabric to be cured. All fabrics were dried at 65° C. Part of each fabric was made up into simulated garments, pressed on a tailor's press, and cured at 160°

were pressed so that the cuffs had sharply bent edges and there were two creases in each simulated garment, at right angles to the cuffs. They were then cured in an oven set to 160° C. for 6 minutes. Wetting was in a home washing machine, set for a 2-minute laundering cycle, and otherwise standard rinse and spin cycles, without use of soap (soap acts as a lubricant and causes less wear than wetting only). Following this, the samples were tumbled dried. The holes formed in the cuffs and creases of the simulated garments were counted after repeated wetting and tumble drying cycles.

The results are summarized in Table I below.

TABLE I.—CURED FABRICS SEQUENTIALLY TREATED WITH MELAMINE AND ETHYLENE UREA RESINS

	Sample No.						
	Untreated Control	1	2	3	4	5	6
Treatment:							
TMM,* percent add-on.....	0	0	0	11	11	11	11
DHDMEU,** percent add-on.....	0	6	4.5	0	3	4.5	6
ZnNO ₃ , percent add-on.....	0	0.8	0.5	1.0	1.4	1.5	1.8
Serviceability Characteristics, Wet. Tumb. Dr. Test, Hole Counts, Percent: ¹							
Cuffs, 10 cycles.....	100	80	75	130	100	160	
Cuffs, 15 cycles.....	100	75	65	90	55	100	
Creases, 10 cycles.....	100	³ (0)	³ (15)	³ (70)	³ (45)	³ (170)	
Creases, 15 cycles.....	100	10	5	5	25	130	
Taber abraser cycles, percent ²	100	36	50	100	71	50	32
Breaking strength, warp, percent ²	100	56	56	100	95	81	84
Breaking strength, filling, percent ²	100	40	46	74	64	52	50
Tear strength, warp, percent ²	100	39	47	72	60	49	47
Tear strength, filling, percent ²	100	44	50	72	57	50	44
Appearance Characteristics (degrees):							
Monsanto Cr. Rec., warp, front.....	93	136	128	123	134	148	140
Monsanto Cr. Rec., warp, back.....	102	161	146	117	145	149	156
Monsanto Cr. Rec., filling, front.....	95	133	127	118	137	143	142
Monsanto Cr. Rec., filling, back.....	97	131	123	119	129	139	145
Av. front plus back, warp plus filling.....	194	280	262	238	272	290	292
Wash-Wear Rating:							
After tumble drying, 15th cycle.....	4.9	4.75	2.75	5.0	5.1	5.3	
After air drying, 16th cycle.....	4.5	4.25	3.25	4.4	5.0	5.3	
Crease Retention, after tumble drying, 15th cycle.....	5.0	5.0	4.75	5.0	5.0	5.0	

¹ Percent of 6% DHDMEU Control which had the following properties:

Hole count: 10 cycles, 6/cuff, 1.7/crease.

Hole count: 15 cycles, 12.5/cuff, 10/crease.

² Percent of Untreated Control.

³ Results are only qualitatively significant because of low numbers of holes involved (1 hole/crease=60%).

*Trimethylolmelamine.

**Dihydroxydimethylethylene urea.

C. for 6 minutes; other parts, to be used in strength, abrasion and crease recovery tests, were cured in the flat state under the same conditions.

The appearance characteristics of the fabric were evaluated as follows:

(a) The appearance of the fabric, in flat or garment form, was evaluated subjectively after laundering and spin or tumble drying on a scale where "6" indicated a perfectly smooth fabric and lower ratings indicated progressively less smoothness, a rating of "1" being given to very wrinkled fabrics.

(b) The retention of the crease inserted in a garment before curing during repeated laundering and tumble drying cycles was rated subjectively on a scale of 5-perfect to 1-essentially no crease.

(c) The recovery of the fabric from creasing was measured objectively, using ASTM Method D 1295 (Monsanto Wrinkle Recovery Test).

The serviceability characteristics of the fabrics were evaluated as follows:

(a) The breaking strength was measured by the raveled strip method, ASTM D 1682.

(b) The tear strength was measured on the Elmendorf (falling pendulum) apparatus, ASTM D 1424.

(c) The abrasion resistance was determined by the Rotary Platform, Double Head (Taber Abraser) method, ASTM D 1175-D.

(d) Serviceability was also evaluated by repeated wetting and tumble drying of simulated garments. The garments were in the shape of short trouser legs, with cuffs on both ends. These were sewn from the fabric treated with cross-linking resin and dried out before curing. They

In general, equally good or better appearance characteristics and importantly better serviceability characteristics were attained in the samples pre-treated with TMM and given a 4.5% add-on of DHDMEU than in the samples conventionally treated with 6% add-on of DHDMEU, without pre-treatment. Thus, the crease recovery of the TMM-DHDMEU combination samples was 290° (sum of warp and filling), i.e., better than that of the 6% DHDMEU sample (no pre-treat) which had a crease recovery of 280°. Likewise the wash-wear rating of the TMM-4.5% DHDMEU samples was about 5 for both tumble and spin drying, as compared with a rating of 5 for the 6% DHDMEU sample (no pre-treat) for tumble and 4.5 for spin drying. The crease retention of the simulated garments after 15 wetting and tumble drying cycles was rated 5 in both cases. Importantly, the TMM-4.5% DHDMEU combination samples had 45% higher tensile strength in the warp and 30% higher tensile strength in the filling than the comparison samples treated with 6% DHDMEU only; the corresponding figures for the tear strength were 25% and 15% better for the TMM-4.5% DHDMEU combination samples than for the 6% DHDMEU samples. Moreover, the resistance to abrasion, measured on the Taber Abraser, was 40% greater for the TMM-4.5% DHDMEU combination samples than for the 6% DHDMEU samples, while the number of holes in simulated garments which had been wetted out and tumble dried through 15 cycles was reduced by 45% in the cuffs and 75% in the crease.

The samples treated with only 4.5% add-on DHDMEU (without pre-treatment) had somewhat lower tensile

strength than, and similar tear strength, Taber abrasion resistance, and hole counts as the samples pre-treated with TMM and then treated with a 4.5% add-on of DHDMEU. However, these reference samples had considerably less crease recovery and poorer appearance after repeated wetting out and tumble drying cycles than the combination samples and also less than the standard reference samples containing 6% DHDMEU only.

The 4.5% DHDMEU reference samples had slightly better tensile strength and serviceability characteristics than the 6% DHDMEU controls but their appearance characteristics were noticeably poorer.

The 11% TMM only samples had very good tensile strength and other serviceability characteristics but very much poorer appearance characteristics than the 6% DHDMEU only samples.

The TMM-3% DHDMEU combination samples had slightly poorer appearance characteristics and somewhat better serviceability characteristics than the TMM-4.5% DHDMEU combination samples, and like the latter, represented an important improvement over samples treated either with TMM only or with DHDMEU only.

The TMM-6% DHDMEU combination samples, while having very good appearance characteristics, had less good serviceability characteristics, thereby illustrating the well known fact that excessive add-on of cross-linking resin impairs abrasion resistance. Optimum proportions of resin add-on are readily determined by conducting preliminary tests for each specific case.

Example 2

In this example the feasibility of applying both the polymer builder and the cross-linker initially and simultaneously from a single treating bath is illustrated. Except in a control run wherein DHDMEU (Permafresh 183) alone was used, this treating bath consisted of 20% solids consisting essentially of a mixture of hexamethyl methylolmelamine and triazone (Aerotex 23) and 20% solids consisting essentially of DHDMEU (Permafresh 183) in water adjusted to pH of 2.0 with hydrochloric acid (HCl). This bath was padded onto a standard twill cloth at 100% wet pick-up, sealed in envelopes made of polyethylene terephthalate film and heated at 82° C. for 15 minutes. The envelopes were opened and the fabric rinsed in 2% Na₂CO₃, laundered, tumble dried, conditioned and weighed for add-on. After this, a bath of ½% Zn(NO₃)₂·6H₂O, with or without softener (1% aqueous polyethylene dispersion, "Mykon") as indicated in Table II below, was padded on at 100% wet pick-up and dried at 42° C. for 20 minutes. Samples were pressed on Hoffman Press for 1 minute at 100° C. or for 30 seconds on a Hot Head press at 160° C. Curing was then carried out in an air oven for 5 minutes at 150° C. or 3 minutes at 150°-160° C. With pressing (for 30 seconds) at 160° C., curing for 3 minutes at 150° C. was found satisfactory. The various properties of the samples were then evaluated by the test procedures described in Example 1. The results obtained are summarized in Tables II and III.

TABLE II.—CURED TWILL FABRICS TREATED WITH MIXTURE OF POLYMER BUILDER AND CROSS-LINKER

	Sample No.					
	Untreated Control	7	8	9	10	11
Polymer System ¹		PC	PC	AP	AP	AP
Add-On, percent		6	6	11.2	11.1	11.1
Softener		No	No	No	No	Yes
Cure, time/temp		None	² 6'/160° C.	(A)	5'/150° C.(B)	5'/150° C.(B)
Breaking Strength, percent:						
Warp	100	95	55	82	67	63
Filling	100	90	40	96	59	53
Tearing Strength, percent:						
Warp	100		44	83	62	89
Filling	100		41	79	58	83
Bending Length, cm.:						
Warp	6.8	6.2	5.8	7.2	5.0	4.5
Filling	3.8	3.6	3.5	4.4	3.2	2.9
Crease Recovery, W+F:						
Face	143	157	267	163	267	294
Back	154	172	263	171	270	292

¹ "PC" refers to DHDMEU-containing control (Permafresh 183), equivalent to Sample No. 1, Table I.

"AP" refers to mixed bath containing "Aerotex 23" (melamine precondensate plus triazone) plus "Permafresh 183" (DHDMEU).

² Pad and dry cure, conventional.

(A) Wet fixed only.

(B) Wet fixed, then dry cured.

TABLE III.—ABRASION BEHAVIOR OF POLYMER IMPREGNATED TWILL

	Sample No.		
	8	12	13
Polymer System ¹	PC	AP	AP
Add-On, percent	6	11.0	9.1
Cure	² 6'/160° C.	3'/160° C.(B)	3'/150° C.(B)
Crease Retention, After Tumble Dry, 1st cycle	5	5-	5-
Wash-Wear Index:			
After Tumble Dry, 1st cycle	5-	5	4+
After Spin Dry, 2nd cycle	5-	4+	5-
After Tumble Dry, 10th cycle	5-	5+	5+
Hole Count:			
After 5th wash and tumble dry	0	0	0
After 10th wash and tumble dry	5	0	0
After 15th wash and tumble dry	9	0	0
After 20th wash and tumble dry	10	1	0

¹ "PC" and "AP" have same meaning as in Table II.

² Pad and dry cure (without wet fixation).

(B) Wet fixed, then dry cured.

Tables II and III show that cotton cloth treated in accordance with the present invention (Sample Nos. 10, 11, 12 and 13) has appearance characteristics which are substantially as good as or better than conventionally resin treated cloth (Sample No. 8). At the same time, the performance characteristics, notably breaking strength, tearing strength, bending length (i.e., softness) and abrasion resistance of the cloth treated in accordance with this invention were quite significantly better than the conventionally treated cloth.

Example 3

This example serves as another illustration of the important advantages obtained when a polymer builder is wet fixed at a high add-on on a cotton fabric before the latter is finally dry cured and its shape set by cross-linking with an active cross-linker. A standard cotton print cloth was used as the material being treated.

The strength and crease recovery of this material, untreated, are compared in Table IV with the corresponding properties obtained when the same material was treated either with the "Permafresh 183" cross-linker alone ("PC," Sample No. 15), or with the commercially available "Aerotex 23" mixture which contains both a polymer builder and a cross-linker ("AC," Sample No. 16), or with the made-up blend containing the "Aerotex 23" mixture further reinforced with "Permafresh 183" as a supplemental cross-linker ("AP," Sample No. 18). Sample No. 17 further shows the properties of the material treated with the same "AP" resin system as Sample No. 18, but wherein the resins were only wet fixed in the fabric, without any final cure.

TABLE IV.—CURED PRINT CLOTH TREATED WITH INDIVIDUAL RESINS AND WITH MIXTURES THEREOF

	Sample Number				
	14	15	16	17	18
Polymer System ¹	(?)	PC	AC	AP	AP
Add-On, Percent.....		5.6	10.5	14.4	11.9
Cure, time/temp.....	3'/150° C. (B)	3'/160° C. (B)	(A)		3'/160° C. (B)
Breaking Strength, percent:					
Warp.....	100			77	51
Filling.....	100	37	44	69	61
Crease Recovery (W plus F):					
Wet.....	186	274	257	256	276
Dry.....	192	296	285	207	282

¹ "PC" and "AP" have the same meaning as in Table II.

"AC" refers to a control test wherein a bath containing "Aerotex 23" (melamine pre-condensate plus triazone), without any DHDMEU, was used.

² Untreated Control.

(A) Wet fixed only.

(B) Wet fixed, then dry cured.

As can be seen from Table IV, the cross-linker alone (Sample No. 15) gave excellent crease recovery but very poor breaking strength. The commercial mixture of polymer builder plus cross-linker (Sample No. 16) gave excellent crease recovery and substantially improved breaking strength in comparison with Sample No. 15. Sample No. 17, which was treated with the blend of the two commercial treating agents, but was wet fixed only, without any dry cure, again illustrates that resin which is only wet fixed impairs fabric strength to only a relatively small degree but fails to result in any worthwhile improvement in dry crease recovery. On the other hand, Sample 18, which was properly treated with the same resin combination as Sample 17 and was dry cured, produced excellent crease recovery as well as a breaking strength which was almost 70% better than that of Sample 15.

In sum, it is apparent that a proper application of a polymer builder and an active cross-linker, wherein a high add-on of the polymer builder is wet fixed on the material prior to final cure, produces a significantly better combination of fabric appearance and serviceability characteristics than can be obtained using either a polymer builder alone or a cross-linker alone. The preliminary wet fixing of the polymer builder in the fabric appears to protect it against the debilitating effect of the subsequent cross-linking reaction without appreciably reducing the effectiveness of the latter as far as improvement in shape holding characteristics is concerned.

It will be understood, of course, that the invention can be practiced in a variety of different ways. For instance, in the examples set forth above both the polymer builder and the cross-linker were applied to woven fabric. In some instances, however, it may be advantageous to apply one or both of the reactants to fibers or to yarns, before a fabric is woven therefrom. Such a procedure may be particularly advantageous in the case of regenerated cellulose material such as rayon. More particularly, in applying the invention to viscose rayon, it can be advantageous to apply the polymer builder to the rayon during its process of manufacture.

For example, the required polymer builder may be included in the viscose dope or applied to freshly extruded filaments of regenerated cellulose during one of the after treatment steps while the filaments or fibers contain sufficient moisture, such as in the customary bleaching, sulphur removal or washing steps. After such application the polymer builder is wet fixed within the fibers or filaments and finally the cross linker is applied to such fibers, filaments or yarns at an appropriate later stage, before or after the treated fibers, filaments or yarns are woven into a fabric. In this manner, for instance, the initial steps of the process constituting the present invention can be carried out by the rayon manufacturer and the remaining steps by subsequent processors. More specifically, the rayon manufacturer can produce viscose fibers containing the required amount of polymer builder wet fixed therein, and these fibers can thereafter be woven and dyed as desired by subsequent processors who can then apply the required cross-linkers to such fibers or fabric and finally dry cure the material or the eventual

finished garment to impart to it the desired shape retentive properties.

Based on the foregoing general description and illustrative embodiments of this invention its subject matter is particularly pointed out and claimed in the appended claims.

What is claimed is:

1. A process of making shape retentive textile articles from a cellulose-containing fibrous material by use of a cellulose cross-linking agent, which comprises

applying an aqueous liquid mixture containing a water soluble polymer builder selected from the group consisting of melamine-formaldehyde and phenol-formaldehyde precondensates to said material in an amount sufficient to deposit thereon more than 8% of said builder based on the weight of dry material, wet fixing said builder in said fibrous material while maintaining the moisture content of the material at more than 20% based on the weight of dry material, whereby an add-on of at least 8% of polymer is formed in said material,

thereafter applying to said material a polyfunctional cellulose cross-linking agent which is different from and more cellulose reactive than said polymer builder in an amount sufficient to make the material shape retentive upon curing, and dry curing said material.

2. A process according to claim 1 wherein the fibrous material is dyed subsequent to having the polymer builder wet fixed therein and prior to the dry curing step.

3. A process according to claim 1 wherein the material is dyed with a direct cotton dye subsequent to having the polymer builder wet fixed therein and prior to the dry curing step.

4. A process according to claim 1 wherein said cross-linking agent comprises at least one member of the class consisting of formaldehyde, hydroxy N-methylol ethylene ureas, N-methylol cyclic ethylene ureas, triazones, N-methylol carbamates, and divinyl sulfone.

5. The process of making shape retentive textile articles from a cellulose-containing fibrous material by use of a cellulose cross-linking agent, which comprises

applying an aqueous liquid mixture containing a water soluble polymer builder selected from the class consisting of melamine-formaldehyde and phenol-formaldehyde precondensates as well as a polyfunctional cellulose cross-linking agent which is different from and more cellulose reactive than said polymer builder to said material in an amount sufficient to deposit thereon more than 8% of said builder based on the weight of a dry material,

wet fixing said builder and cross-linking agent in said fibrous material while maintaining the moisture content of the material at more than 20% based on the weight of dry material, whereby an add-on of at least 8% of polymer is formed in said material, and dry curing said material.

6. A process according to claim 5 wherein said liquid mixture has a pH adjusted to a value between 1 and 4 prior to being applied to said fibrous material, and wherein the material is washed after having said polymer builder wet fixed therein and has a latent curing catalyst applied thereto after having been washed and prior to being dry cured.

7. A process according to claim 5 wherein the material is dyed after having the polymer builder wet fixed therein and prior to the dry curing step.

8. A process according to claim 5 wherein the material is dyed with a direct cotton dye subsequent to having the polymer builder wet fixed therein and prior to the dry curing step.

9. A process according to claim 5 wherein said cross-linking agent comprises at least one member of the class

consisting of formaldehyde, hydroxy N-methylol ethylene ureas, N-methylol cyclic ethylene ureas, triazones, N-methylol carbamates and divinyl sulfone.

10. A process for making shape-retentive textile articles which comprises applying a cyclic-ethylene urea-formaldehyde precondensate as an aqueous solution to a fabric which contains at least 15% cotton fiber and has at least 8% of a melamine-formaldehyde precondensate wet fixed therein, and curing the resulting fabric at a temperature between about 120° and 180° C. in the presence of an acidic curing catalyst.

11. A process for making shape-retentive textile articles which comprises:

applying at least 8% dry add-on of a melamine-formaldehyde precondensate to a cotton fabric by impregnating said fabric with an aqueous solution of said precondensate and heating said precondensate in the fabric in the presence of an acidic curing catalyst at a temperature between about 80° and 120° C. while maintaining a moisture content between about 20%–60% in the fabric, thereby wet fixing said melamine precondensate therein,

scouring water soluble compounds from the fabric, drying the scoured fabric,

reimpregnating the dry fabric with an aqueous solution of an ethylene urea-formaldehyde precondensate and a catalytic amount of an acid catalyst,

drying the reimpregnated fabric,

finishing said fabric into a garment,

and dry curing said garment at a temperature between about 120° and 180° C.

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