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METHOD OF IMPROVING THE DIMENSIONAL STABILITY AND ELASTIC RECOVERY OF ALL-COTTON STRETCHABLE FABRICS AND PRODUCTS THEREOF

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A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout 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 invention relates to methods for improving the dimensional stability and elastic recovery of all-cotton stretchable fabrics produced by swelling type treatments. Stretch fabrics treated by the methods herein disclosed retain their original dimensions better when subjected to such treatments as commercial and home laundering, and have more rapid and complete recovery from stress or strain during normal use than fabrics without subsequent treatment.

The improvements are obtained by reacting the cotton fibers with polyfunctional reagents to crosslink the cellulose chains within the fiber to dimensionally stabilize the fiber and increase the recovery forces necessary for the fiber to return to its original condition after deformation. This can be done with or without thermoplastic or other softening agents.

It is known that all-cotton stretch fabrics can be produced by shrinking techniques. The extent of the stretch properties imparted are directly related to the extent of change that occurs in the cotton fibers when subjected to a swelling type treatment. The most common swelling type treatment used to impart stretch properties to cotton fabrics is mercerization in 13% to 45% aqueous solution of sodium hydroxide. Solution concentration is largely determined by the temperature of the treating bath. Higher temperatures require higher solution concentrations for similar results. When the cotton fiber is permitted to shrink without restrictive tension in such a bath, the fiber shrinks from about 14% to 19%, depending on the fiber type and morphology. Since the density of the cotton fiber is reduced, the cross sectional area of the cotton fiber must increase slightly more than the amount of longitudinal shrinkage that takes place. When cotton fibers are made into yarns the fibers are held together by lateral twist. When the fibers in cotton yarns are swollen as by mercerization under relaxed conditions, the shrinkage of the fiber and the increase in cross sectional area have an additive effect to further reduce the length of the cotton yarns. This reduction in length of the cotton yarns varies from about 19% to 35% for yarns that do not develop crimp. It is known that cotton yarns spun with sufficiently high twist have a tendency to crimp. For any selected yarn the shrinking treatment causes an increase in the number of twist turns per inch. Consequently, for yarns of higher twist, additional reductions in length may be obtained by the formation of crimp in the yarn. Table I illustrates this effect of twist on the shrinkage of cotton yarns varying in twist multiplier (T.M.) from 2.5 to 5.25:

TABLE I.—EFFECT OF TWIST ON SHRINKAGE OF SLACK MERCERIZED 20/1 YARNS

T.M.:	Percent shrinkage
2.50	32
3.25	41
4.00	53
4.75	62
5.25	67

Equation:

$$\frac{\text{Number of Turns Per Inch}}{\text{Square Root of Yarn Number}} = \text{T.M.}$$

As can be seen from Table I, the length of a yarn can be reduced by more than 60% by the combined effects of fiber shrinkage, increase in cross sectional area of the fibers, and increase in twist due to shrinkage. Tests of higher T.M. were not made but indications are that further increases in T.M. would further increase the overall shrinkage of cotton yarns. This general principle applies to any other cotton fiber swelling type treatment that has essentially the same effects on the cotton fiber.

If the cotton yarns are woven into fabrics the amount of shrinkage, and conversely the amount of stretch, imparted are influenced by the weaving structure. Fabrics of open weave would tend to shrink more because of less restriction of crossing yarns, but be dependent on the yarn twist, and whether the weaving structure promoted or retarded the formation of yarn crimp. Table II illustrates the variation in shrinkage obtained by relaxed mercerization of plain weave fabrics that promotes yarn crimp. Thus the amount of shrinkage in cotton fabrics when subjected to swelling type treatment can be varied over very wide ranges by the well known principles of variations in yarn twist and fabric construction, to produce stretchable cotton fabrics.

TABLE II.—SHRINKAGE OF FABRICS UPON SLACK MERCERIZATION

Fabric Description	Percent Shrinkage	
	Warp	Filling
Plain Weave:		
48 x 44 Sheeting	16	27
64 x 68 Sheeting	11	21
Osnaburg	23	23
Dobby Weave: Waffle	34	44

Regardless of the method of producing stretchable cotton fabrics by swelling type treatments, the permanence of the stretch properties and the quality of dimensional stability are dependent on the permanence of the changes that took place in the cotton fiber. The permanence of the changes in the cotton fiber is related to the rearrangement of hydrogen bonds that hold the cellulose chains together within the cotton fiber. Hydrogen bonds are known to be water sensitive, thus it is easier to restretch a stretchable cotton fabric produced by a swelling type treatment while it is wet or exposed to high humidity than it is when the product is dry or exposed to a relatively low humidity.

To overcome this serious effect of moisture and to increase recovery from deformation and dimensional stability it is necessary to supplement the attractive forces of hydrogen bonding with co-valent cross-links between cellulose chains. We have found that any polyfunctional reagent that reacts with cotton cellulose to form co-valent

cross-links between cellulose chains will reduce the effects of moisture on the stretch properties of these products and also increase the rate and extent of recovery deformation as well as improve dimensional stability for treatment such as laundering and tumble drying. Experiments have not been made to cover all such polyfunctional reagents, but as long as the reagent meets the requirements of being able to form co-valent cross-links between cellulose chains within the stretchable cotton fiber it would have essentially the same effect as the reagents tested. Also variations of cross-linking reagent application such as type of catalyst, treatment conditions, and the use of alkaline crystallized reagents that may be applied as part of the swelling type treatment, would have essentially the same effect on the cotton fibers as more conventional methods of application of the cross-linking reagents.

Although this invention was primarily for the improvement of the dimensional stability and elastic recovery for all-cotton stretch fabrics produced by swelling type treatments, it was found that the crease recovery of these products was improved by the cross-linking treatments. Table III illustrates the improvement in crease recovery of all-cotton stretch fabrics produced by a swelling type treatment.

TABLE III.—EFFECT OF RESIN TREATMENT ON CREASE RECOVERY ANGLE OF SLACK MERCERIZED FABRICS

Fabric Description	Crease Recovery Angles, Degrees	
	(W+F) Dry	(W+F) Wet
Waffle Weave	268	155
Waffle Weave Resin Treated	302	216
Homespun (61-74), brown	208	198
Homespun (61-74), br. resin treated	279	236
Homespun (61-74), red	168	195
Homespun (61-74), red resin treated	259	227
Homespun (61-75), brown	185	206
Homespun (61-75), br. resin treated	246	220
Homespun (61-75), red	189	214
Homespun (61-75), red resin treated	289	240

These results show that easy care properties can be imparted to this type stretch fabrics similar to those imparted to conventional cotton fabrics by cross-linking type treatments.

Example 1

Cotton fabrics of the types used for household, industrial, and wearing apparel uses were swollen without restrictive tensions in a 23% to 25% aqueous solution of sodium hydroxide at 25° C., for about 5 minutes. Time of immersion varied with type of wetting agent used, the condition of the fabric being treated, and the construction of the fabric. The immersion time should be long enough to insure essentially complete fabric shrinkage. The shrunken fabrics were washed in hot water up to 210° F. to facilitate removal of the sodium hydroxide. Highest practical washing temperatures are preferred, but lower temperatures have essentially the same effect. The fabrics were then acid soured for complete removal of the sodium hydroxide from the fabrics and rinsed thoroughly, and dried.

All processing steps were carried out under minimum processing tensions to avoid restretching the fabric which would have the effect of reducing the stretch properties. The fabrics were immersed in a solution of a cross-linking type reagent containing 7% dimethylolethylene urea, 1.5% polyethylene, and 3% magnesium chloride hexahydrate, and for convenience passed through squeeze rolls, to remove excess solution. However, the method of applying the cross-linking reagent to the fabrics is unimportant, as long as it meets the requirements of the cross-linking reagent being in molecular contact with the cotton cellulose and does not remove stretch properties. Techniques such as immersion and centrifugal extraction, fogging, and jet spraying could also satisfy these requirements. The fabrics were dried at 190° F. for 4 minutes, then cured at 320° F. for 3 minutes to effect cross-linking. A processing wash was then given to remove extraneous materials from the treated stretch fabrics, and then dried. Again, minimum tensions are preferred processing conditions. The results of tests on stretch fabrics with and without cross-linking treatments are shown in Tables IV(A) and IV(B).

TABLE IV (A).—PERCENT RECOVERY AFTER 70% OF TOTAL ELONGATION

Sample Tested	Warp Direction			Filling Direction		
	Immediate Recovery	5 Min. Delay	Permanent Set	Immediate Recovery	5 Min. Delay	Permanent Set
80 x 54 Slack Mercerized Sheeting	2.6	48.0	49.4	3.7	40.8	55.5
Resin Treated 80 x 54 Slack Mercerized Sheeting	7.5	78.0	14.5	4.8	78.7	16.5
Osnaburg Slack Mercerized	2.8	32.2	65.0	2.2	32.5	65.3
Resin Treated Osnaburg Slack Mercerized	5.9	69.5	24.6	3.4	78.1	18.5

Definitions: Percent of strain recovered as determined by the point of intersection of a line drawn tangent to the slope of the unload curve with the zero load axis.
5 minute delay is the percentage of the strain recovered after 5 minutes relaxation of the strain on sample.
Permanent set is the percentage of the strain not recovered after the 5 minute delay.

Equation:

$$IR + \text{Delayed Recovery} + PS = 100\% \text{ of Total Strain}$$

TABLE IV (B).—INCREASE IN LENGTH AFTER STRESSING TO ONE THIRD OF BREAKING LOAD

	Actual Percent Growth After 2 Cycles	Actual Percent Growth After 10 Cycles
Warpwise:		
1	19.5	21.5
IR	1.9	2.4
2	15.9	17.8
2R	2.5	3.3
Fillwise:		
1	11.5	12.8
IR	5.2	6.5
2	23.5	25.7
2R	9.4	11.6

NOTE.—The coded samples are the same as those in Table IV (A), where "IR" represents the Slack Mercerized Sheeting which has been Resin Treated, and the "1" is its Control, etc.
Definition: Growth is the percentage increase in the length of he test specimen.

In every case comparing the slack mercerized and resin treated fabrics with the recovery values of the fabric that had been slack mercerized only, there was a significant improvement in the immediate elastic recovery, the recovery after 5 minute relaxation, and a reduction in the permanent set. Growth after cyclic loading to ⅓ the breaking load is considerably less for the slack mercerized and resin treated fabrics in comparison with the fabric that has been slack mercerized only. These results apply to both warp and filling tests.

The *percent permanent set* of slack mercerized-resin treated fabrics was lower at 40% than at 70% elongation, and even lower at 20% elongation. These changes are not linear but rather logarithmic, and the percent difference between the 20%, 40%, and 70% samples, and their

respective controls also varies logarithmically, which simply means that our invention will impart excellent elasticity to a cotton fabric with, of course, better recovery when the treated fabric is not stretched excessively.

Example 2

A roll of fabric containing 100 yards of 80 x 80 cotton printcloth was mercerized by the procedure described in Example 1 and treated with an aqueous dimethylol ethyl carbamate solution. The mercerizing, as well as all other steps were carried out maintaining a minimum of restrictive tension on the cloth. The preparation and application of the resinous dimethylol ethyl carbamate on the cotton fabric were done on standard pilot plant equipment.

Firstly, a 50% solution was prepared employing a 2:1 molar ratio of formaldehyde to ethyl carbamate, respectively. The mixture consisted of 1432 grams of ethyl carbamate, 2940 grams of 36.3% formaldehyde, and 628 grams of water. This 5000 grams of solution was then brought to a pH of 8.5 with 20% NaOH, and allowed to stand overnight, then adjusted to pH 7.0 with dilute HCl.

Secondly, the solution was diluted to 10% total solids by the addition of more water, which contained the 3% catalyst, 1.5% softener, and 0.1% wetting agent. Quantitatively these substances were as follows:

	Grams
Magnesium chloride ($6H_2O$)	750
Polyethylene	1250
Wetting agent	50
Water	17,950

Thirdly, this aqueous resin solution, which is 10 parts solids was then applied to the mercerized fabric, which was passed through squeeze rolls, yielding a fabric with a homogenous 65% to 70% wet pickup. The fabric was dried at 187° F., cured at 320° F., and washed and dried again. The drying and curing steps were carried out at 4 yards per minute, and the last rinse took about 20 minutes. The final weight gain was ca. 5%.

Example 3

An 18 inch wide by 10 yards long sample of 80 x 80 cotton printcloth was slack mercerized in the same manner as the cloth of Examples 1 and 2; then padded with a cross-linking resinous aqueous solution, which was 15 parts by weight tris-aziridinyl phosphine oxide. The fabric was passed through squeeze rolls, and a wet pickup of 70% was obtained. The pilot plant equipment was adjusted in such manner as to maintain a minimum of restrictive tension on the fabric throughout the entire sequence of treatments.

The fabric was then passed through a roller-type, forced draft, gas fired oven to dry at 85° C. for about 4 minutes (actually 4 yards per minute) and cured immediately thereafter, in a tandem operation, at 155° C. for about 4 minutes; washed in hot water for 30 minutes; and then dried on the tenter frame at 85° C. The resin add-on was about 8%.

The polyfunctional aqueous chemical mixture applied to the slack mercerized cloth was computed to obtain a 2000 gram quantity of a 15% tris-aziridinyl phosphine oxide (APO) solution, and was prepared by mixing the following quantities, immediately prior to the use of the solution, and at temperatures of 20° to 25° to avoid prepolymerization:

	Grams
APO, 80% by weight, in ethanol	375.0
Zinc fluoroborate, 40% by weight, in water	52.5
Wetting agent	20.0
Distilled water	1552.5

We claim:

1. A process for the production of a dimensionally stabilized creaseproof, and stretchable cotton fabric comprising

(a) slack mercerizing a cotton fabric with an aqueous solution containing about from 13 to 45 parts by weight of sodium hydroxide to produce an essentially completely-shrunken cotton fabric;

(b) hot water-washing and acid-souring the thus-shrunken cotton fabric to remove all excess sodium hydroxide;

(c) resin-treating the shrunken cotton fabric, under minimum processing tensions to avoid restretching the shrunken cotton fabric and to a wet-pickup of about from 60 to 100 weight percent, with an aqueous solution containing about from 0.7 to 3.0 weight percent of an acid-type catalyst and about from 5 to 15 weight percent of dimethylol ethylene urea; and

(d) while maintaining said minimum processing tensions to avoid restretching the shrunken cotton fabric, heating the resin-treated shrunken fabric at a temperature of about from 25° to 160° C. for about from 15 minutes to 3 minutes, the longer times being employed with the lower temperatures, to dry cure the dimethylol ethylene urea, thereby to produce a dimensionally stabilized, creaseproof, and stretchable cotton fabric.

2. The dimensionally stabilized, creaseproof, and stretchable cotton fabric produced by the process of claim 1.

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