

UNITED STATES PATENT OFFICE

2,484,545

SHRINKAGE CONTROL OF CELLULOSIC FIBERS

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No Drawing. Application January 18, 1947,
Serial No. 722,955

11 Claims. (Cl. 8—116.4)

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This invention relates to the treatment of textile material of natural or regenerated cellulose for the purpose of eliminating their tendency to shrink upon washing in aqueous soap solutions at elevated temperatures.

Fabrics or fibers of regenerated and/or natural cellulose display little or no tendency to shrink upon washing after treatment according to the present invention. The method herein disclosed can also be successfully applied to mixtures of natural and regenerated cellulose or mixtures containing either regenerated cellulose or natural cellulose with cellulose acetate, provided that the fabric does not contain more than 50% cellulose acetate. The cellulose acetate may be replaced by other cellulose esters of organic acids, such as the propionate. By the terms regenerated cellulose I mean viscose or cuprammonium rayon. By the term natural cellulose I mean such fibers as cotton, linen, hemp or jute. The following treatment of this invention, and which is described below, may be employed on fabrics containing any percentage of cotton since the treatment has no deleterious effect on natural cellulose fiber. This process is thus an extremely important improvement over the nonaldehyde processes for shrinkproofing fibers of vegetable origin.

The treatment may be applied at any stage of the fabric manufacture, namely upon the raw stock, skein or in the woven or the knitted piece. But all traces of starches, gums, glue, natural resins and other sizing agents should be removed in order to permit the aqueous solution of the treating agent to properly penetrate the fibrous material and enter the heart of the fibers.

The normal fabrics made from the aforesaid fibers and mixtures containing the same, i. e. without treatment, have a marked yet normal tendency after successive washing and cleaning to shrink to different degrees; this affects the wearability of the fabric.

Many attempts have been made to develop and perfect processes which control the shrinkage of fabrics with and without the use of resins. Fabrics have been treated with formaldehyde, or compounds which split off formaldehyde, but always in the presence of strong acids, or in the presence of a salt which is acid-reacting per se or becomes acidic during processing. But I have observed that strong acids tender the fabric to the degree that such a process is impractical. These treatments cannot, moreover, be applied to cotton fabrics as the resultant damage renders cotton fabric totally unusable.

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By a more recent development cellulosic fibers and fabrics made therefrom have been treated by a process characterized by the employment of glyoxal, and wherein oxalic acid is the catalyst, to confer stability against laundry shrinkage. But whereas rayon fabrics are made shrinkproof to a great degree they display a loss of 10 to 20% in tensile strength.

According to my invention, by which the aforesaid disadvantages are eliminated, textile materials of the natural or vegetative origin or regenerated cellulosic type are impregnated with a dilute aqueous solution of glyoxal (also known as oxaldehyde), whose formula is $\text{CHO} \cdot \text{CHO}$, in the presence of a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric acid, chloric acid and perchloric acid, squeezed allowing a pick-up of a definite percentage on the dry basis of the goods, dried without tension and afterwards cured without tension by means of dry heating. The drying and curing operations can be carried out as a single step, if the necessary equipment is available. After curing, the fabrics are soaped, rinsed, hydroextracted and dried without tension before making the physical tests thereon and before putting into industrial channels of trade. The curing operation is preferably carried out for a period of 2–5 minutes at $130\text{--}150^\circ \text{C}$. ($266\text{--}302^\circ \text{F}$.), the shorter time for the higher temperature and vice versa. It is preferred to employ the sodium or potassium salt.

As mentioned in the preceding paragraph the oxidizing acids of the alkali metal salts which are suitable are nitric (whose formula is HNO_3), chloric (whose formula is HClO_3) and perchloric (whose formula is HClO_4). By the method of this invention no free oxidizing acids are found in the impregnating bath or formed during the drying or curing of the treated fabrics. Commercially available glyoxal may be satisfactorily employed and has the advantage of being less expensive than the purer grades. Such salts of persulfuric acid are not to be recommended, in as much as free sulfuric acid will be formed during the process, which acid would attack the vegetable fibers. Inherently the oxidation potential of each of these acids in solution of unit activity, referred to the normal hydrogen electrode at 25°C ., is algebraically less than substantially -0.9 volt. For nitric acid this is -0.94 or -0.95 , for perchloric acid -1.35 , and for chloric acid -1.45 (page 843 of the "Handbook of Chemistry and Physics," 19th ed., by Charles D. Hodgman,

published by Chemical Rubber Publishers Co. of Cleveland, Ohio.

The step of impregnating the fibers with the aqueous solution of gloxyl may take place at any time subsequent to the desizing of the fabric which is to be treated.

If desired the "hand" or "body" of the goods treated can be modified in the direction of either softness or a stiffer finish at will by the introduction to the impregnating bath of suitable agents, such as cation softeners for the former effect, or such vegetable or animal colloids as starches, gums, glues, gelatins and modified starches for the latter effect. But the process of this invention is carried out in the absence of any phenolic or amidic compounds capable of forming resinous bodies with aldehydes under the conditions. Therefore, fabrics treated by my method show no tendency toward chlorine retention.

Fabrics of the natural cellulosic type or of the regenerated type treated by my invention herein are stabilized against shrinkage upon washing in aqueous solutions at elevated temperatures as pointed out supra. The superior nature of this process can be appreciated when, moreover, it is realized that this obtained effect is a permanent one, and even successive washings at the boil do not affect the results. It might in addition be noted that this effect of shrinkage control is not accompanied by any increase in the crease resistance of the material. Fabrics of viscose or cuprammonium yarns so treated are further improved by the fact that they show less tendency to fuzz during washing, as compared to an untreated material similarly washed. The loss in tensile strength after this treatment is negligible, and no diminution of abrasion resistance occurs. Provided that the dyes used on the fabrics are fast to repeated boiling in aqueous soap solutions, the treated materials can be considered boil-fast with respect to shrinkage control and wearing properties.

The following specific examples serve to illustrate the results obtained by my process:

EXAMPLE 1

Viscose treated

The goods were a viscose fabric.

This fabric was impregnated on a padder with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% available glyoxal, 5 grams of potassium chlorate, and water to make one liter. It was then squeezed, allowing a wet pick-up of approximately 100% on the dry weight of the goods; then it was dried without tension at approximately 80° C. and cured for 5 minutes at 130° C. After curing, the fabric was soaped, rinsed, hydroextracted and dried without tension.

Wash test

The wash tests were carried out as follows:

The fabric (weighed out to 3 lb. load) is placed in the wheel which is kept running during the entire 60 minute cycle of operations as follows:

- (1) The wheel is started and the time noted.
- (2) The wheel is filled halfway with water (18-20 gals.) having a temperature not exceeding 100° F. (38° C.) and the soap (50 to 70 grams dissolved in a liter of hot water) is added.
- (3) The steam is turned on until the temperature reaches 212° F. (about 20 minutes total time at this point).
- (4) The steam is then turned off and the wheel

is caused to revolve until the total elapsed time is 40 minutes.

(5) Thereupon the soap solution is drained off and the wheel is refilled (without stopping its turning) to the proper level (halfway) with water.

(6) The temperature of the water is raised to 140° F. (60° C.).

(7) At 45 minutes elapsed time the water is drawn off.

(8) The wheel is again filled to the halfway mark with water.

(9) The temperature of this water is raised to 140° F. (60° C.).

(10) After 55 minutes elapsed time the water is drawn off and the machine is allowed to run without further additions of any aqueous fluids to complete the full 60 minute cycle of operation.

The switches were allowed to come to standard conditions, after which they were measured. The results were as follows:

TABLE I

Shrinkage after washing (warp direction)

	1st Wash	2d Wash	3rd Wash	4th Wash
Original (untreated goods)---	9.7	10.2	10.6	10.8
Treated goods-----	+0.1	+0.1	0	+0.1

TABLE II

Tensile strength

	Warp, lbs.	Filling, lbs.
Original (untreated goods)-----	54	60
Treated goods-----	53	59.5

TABLE III

Abrasion resistance

	Cycles
Original (untreated goods)-----	125
Treated goods-----	130

The abrasion figures were obtained on the Taber machine as is likewise true for the values in all examples herein.

From Table I supra it can be seen that the viscose fabric treated by the method set out in Example 1, and subjected to the wash test described below said example, exhibited a tendency to shrink which was almost nil after the first wash test and no increased tendency to shrink on successive washings at the boil.

From Table II it can be seen that the loss of tensile strength was negligible.

In Table III the figures bear out that there was not only no decrease in abrasion but a small increase.

EXAMPLE 2

Viscose treated

A viscose fabric was impregnated on a padder with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% available glyoxal, 5 grams of sodium nitrate and water to make 1 liter. The swatches were then squeezed, allowing a wet pick-up of the fabric of approximately 100%, based on the dry weight of the goods. The fabric was then dried without tension at approximately 80° C. and cured for 5 minutes at 130° C. After curing, the fabric was soaped, rinsed, hydroextracted and dried without

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tension. The wash tests carried out were the same as those described in the ten steps supra.

The swatches were conditioned under standard conditions of humidity and temperature, after which they were measured and physically tested. The results were as follows:

TABLE IV

Shrinkage after washing (warp direction)

	1st Wash	2nd Wash	3rd Wash	4th Wash
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Original (untreated goods)---	9.7	10.2	10.6	10.8
Treated goods-----	0	0	-0.1	0

TABLE V

Tensile strength

	Warp, lbs.	Filling, lbs.
Original (untreated goods)-----	54	60
Treated goods-----	52.8	59

EXAMPLE 3

Viscose treated

A viscose fabric was impregnated on a padder with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% available glyoxal, 4 grams of potassium perchlorate and water to make 1 liter. The swatches were then squeezed, allowing a wet pick-up of the fabric of approximately 100%, based on the dry weight of the goods. The fabric was then dried without tension at approximately 80° C. and cured for 5 minutes at 130° C. After curing, the fabric was soaped, rinsed, hydroextracted and dried without tension. The wash tests were carried out as described by the procedure in Example 1.

The swatches were conditioned under standard conditions of humidity and temperature, after which they were measured and physically tested. The results were as follows:

TABLE VI

Shrinkage after washing (warp direction)

	1st Wash	2nd Wash	3rd Wash	4th Wash
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Original (untreated goods)---	9.7	10.2	10.6	10.8
Treated Goods-----	+0.2	+0.2	+0.1	+0.1

Table VII

Tensile strength

	Warp, lbs.	Filling, lbs.
Original (untreated goods)-----	54	60
Treated goods-----	52	58

Observations on Examples 1, 2 and 3

From the results depicted in Examples 1, 2 and 3 it will be seen that as compared with the untreated goods: (1) there was either no measurable shrinkage, or practically none, of the unmixed viscose fabric which underwent the impregnation by aqueous solutions of either glyoxal and potassium chlorate, glyoxal and sodium ni-

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trate, glyoxal and potassium perchlorate; (2) this fabric in each of the respective treatments no longer showed any tendency to shrink on successive washings at the boil; (3) there was only a slight decrease in the tensile strength with both the warp and filling. It is significant that there was no more shrinkage after the fourth wash than after the initial wash. Whereas only in Example 1 was the abrasion resistance measured, the fabric so treated had a somewhat greater resistance than the untreated viscose.

EXAMPLE 4

70% viscose yarn, 30% cotton yarn

A fabric containing 70% viscose and 30% cotton yarn was impregnated on a padder with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% glyoxal, 5 grams of potassium chlorate and water to make one liter. The swatches were then squeezed, allowing a wet pick-up of the fabric of approximately 100%, based on the dry weight of the goods. The subsequent steps of drying and curing were the same as in Example 1, as well as the wash tests and conditioning steps set out in that example.

The swatches were then measured and physically tested. The results were as follows:

TABLE VIII

Shrinkage after washing (warp direction)

	1st Wash	2nd Wash	3rd Wash	4th Wash
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Original (untreated goods)---	6.3	7.0	7.5	7.8
Treated goods-----	1.4	1.2	1.3	1.4

TABLE IX

Tensile strength

	Warp, lbs.	Filling, lbs.
Original (untreated goods)-----	43.8	37.8
Treated goods-----	41.8	36.9

EXAMPLE 5

70% viscose yarn, 30% cotton yarn

A fabric containing 70% viscose yarn and 30% cotton yarn was impregnated on a padder with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% available glyoxal, 5 grams of sodium nitrate and water to make 1 liter. The rest of the steps of the treatment were the same as described in Example 1, as well as the wash tests and conditioning steps set out in that example.

The swatches were then measured and physically tested. The results were as follows:

TABLE X

Shrinkage after washing (warp direction)

	1st Wash	2nd Wash	3rd Wash	4th Wash
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Original (untreated goods)---	6.3	7.0	7.5	7.8
Treated goods-----	1.2	1.2	1.5	1.2

TABLE XI
Tensile strength

	Warp, lbs.	Filling, lbs.
Original (untreated goods).....	43.8	37.8
Treated goods.....	40.5	35.8

EXAMPLE 6

80% viscose yarn, 20% cellulose acetate

A fabric containing 80% viscose yarn and 20% cellulose acetate yarn was impregnated on a paddler with a solution containing 40 c. c. of commercially available glyoxal containing approximately 30% available glyoxal, 5 grams of potassium chlorate and water to make 1 liter. The swatches were then squeezed, allowing a wet pick-up of the fabric of approximately 100% based on the dry weight of the goods. The subsequent steps of drying and curing were the same as in Example 1, as well as the wash tests and conditioning steps set out in that example.

The swatches were then measured. The results were as follows:

Table XII

Shrinkage after washing (warp direction)

	1st Wash	2nd Wash	3rd Wash	4th Wash
Original (untreated goods).....	Per cent 9.5	Per cent 10.0	Per cent 10.5	Per cent 11.0
Treated goods.....	0.9	0.8	0.9	1.0

Observations on Examples 4, 5 and 6

Examples 4, 5 and 6 embraced treatments of fabrics made of mixed yarns, whereas the other three previous examples were on unmixed viscose fabrics. In Examples 4 and 5 the mixture was 70% viscose yarn and 30% cotton yarn; and in Example 6 it was 80% viscose and 20% cellulose acetate.

From the results set out in those examples it will be seen that as compared with the untreated goods: (1) in the 1st wash the shrinkage was small on the viscose-cotton mixture fabrics which underwent the impregnation by aqueous solutions of either glyoxal with potassium chlorate, or glyoxal with sodium nitrate, and on the viscose-cellulose acetate mixture fabric subjected to the glyoxal, potassium chlorate aqueous solution; (2) the fabric in each of the respective treatments no longer showed any tendency to shrink on successive washings at the boil; (3) there was only a slight decrease in the tensile strength with both the warp and filling in the case of the former two (no measurement on the last). It is indeed significant that with respect to the mixed yarns, wherein cotton and a cellulose ester were components respectively with the viscose yarn, here too there was no more tendency to shrink after the 4th wash than after the initial wash.

While this invention has been described with reference to particular embodiments and specific examples, I do not intend that my invention shall be limited to such embodiments and examples except as hereinafter described in the appended claims. It will be realized by those skilled in the art that changes may be made in the process hereinbefore described without departing from the scope of the claims. In the claims the term "textile material," unless otherwise qualified, 75

means at any stage of fabric manufacture embracing raw stock, skein or in the woven or the knitted piece, etc.

I claim:

1. In the process of shrinkage control of textile materials, the steps of impregnating textile materials of the group consisting of natural cellulose, regenerated cellulose and mixtures with each other and up to substantially 50% of cellulose esters of organic acids, which textile materials are substantially free from starches, gums, and glues, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

2. In the process of shrinkage control of textile materials, the steps of impregnating textile materials of the group consisting of natural cellulose, regenerated cellulose and mixtures with each other and up to substantially 50% of cellulose esters of organic acids, which textile materials are substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a water-soluble alkali metal salt of chloric acid, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

3. In the process of shrinkage control of textile materials, the steps of impregnating textile materials of the group consisting of natural cellulose, regenerated cellulose and mixtures with each other and up to substantially 50% of cellulose esters of organic acids, which textile materials are substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a water-soluble alkali metal salt of nitric acid, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

4. In the process of shrinkage control of textile materials, the steps of impregnating textile materials of the group consisting of natural cellulose, regenerated cellulose and mixtures with each other and up to substantially 50% of cellulose esters of organic acids, which textile materials are substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a water-soluble alkali metal salt of perchloric acid, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

5. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and a natural cellulose which mixture is substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from textile material, drying without tension until most of the water has been removed and curing at a temperature above the

drying temperature but not above substantially 150° C.

6. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and a cellulose ester of an organic acid which mixture is substantially free from starches, gums and glues, wherein the amount of cellulose ester does not comprise more than 50% of the mixture, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

7. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and a cellulose acetate which mixture is substantially free from starches, gums and glues, wherein the amount of cellulose acetate does not comprise more than 50% of the mixture, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

8. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and cotton which mixture is substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

9. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and cotton which is substantially free from starches, gums and glues with a dilute aqueous solution

containing glyoxal and an alkali metal chlorate, removing the surplus liquid from the textile materials, drying without tension until most of the water has been removed and curing at a temperature above substantially 150° C.

10. In the process of shrinkage control of textile materials, the steps of impregnating a textile material mixture of regenerated cellulose and cotton which is substantially free from starches, gums and glues with a dilute aqueous solution containing glyoxal and an alkali metal nitrate, removing the surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

11. In the process of shrinkage control of textile materials, the steps of impregnating viscose which is substantially free from starches, gums and glues, with a dilute aqueous solution containing glyoxal and a substantially neutral, water-soluble alkali metal salt of an oxidizing acid from the group consisting of nitric, chloric and perchloric acids, removing surplus liquid from the textile material, drying without tension until most of the water has been removed and curing at a temperature above the drying temperature but not above substantially 150° C.

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