

UNITED STATES PATENT OFFICE

2,436,076

METHOD OF STABILIZING AGAINST
SHRINKAGE TEXTILE MATERIALS OF
REGENERATED CELLULOSEEdward C. Pfeffer, Jr., and Jack Epelberg, Troy,
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Serial No. 699,627

5 Claims. (Cl. 8—116.4)

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This invention pertains to textiles and relates more particularly to a novel method of preparing a material, for example a woven fabric, to make it permanently stable with respect to laundry shrinkage, and resistant to wrinkling, abrasion, crushing and creasing.

This application is a continuation in part of our copending application Serial No. 495,620, filed on July 21, 1943, for an "Improvement in textile material and method of preparing same," and a continuation of our co-pending application S. N. 644,188, filed January 29, 1946, same title, both now abandoned.

The term "textile material" is intended to include filaments and fibers, staple or yarns, whether in the finished stages or at some intermediate stage in the production thereof. The term also includes fabrics, whether knitted, woven or felted, as well as garments or other articles made from such fabrics.

The novel features of the present invention are of particular importance with reference to fabrics made of yarns spun from staple fibers of the regenerated cellulose type, including those which are predominantly of spun viscose rayon or other synthetic yarns characterized by progressive shrinkage in response to repeated launderings, and it is also of value in its application to fabrics predominantly of regenerated cellulose filament rayon.

It has heretofore been proposed to stabilize textile fabrics, especially those made from or predominantly of spun viscose rayon, by impregnating the fabric with a solution or suspension of an intermediate condensation product of a synthetic resin or resin components, with or without a plasticizer, and forming and curing the resin in situ. Various theories have been advanced to account for the observed crease and crush proofing resultant from such a treatment. For example, it has been supposed that the resin components are actually absorbed by the constituent fibers of the fabric and that the resin solidifies within the fibers on baking, thereby imparting to the fabric an increased resistance to creasing or crushing. It has also been suggested that under certain conditions the resin is deposited upon the outer surfaces of the fibers and in solidifying forms a tough resilient outer coating without actually affecting the constitution of the fiber itself.

Whether or not either of the above theories represents the true state of facts, it is well recognized that the potentially resin-forming materials heretofore employed (phenol-formaldehyde, 55

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urea-formaldehyde, and melamine-formaldehyde, etc.) possess many disadvantages which substantially lessen their field of usefulness. Some of them, for example, have or emit during curing an exceedingly disagreeable odor, or irritating or toxic fumes necessitating special and expensive precautions in their use; in some instances the disagreeable odor is persistent in or develops in the fabric after finishing; some of these resinous type materials cause permanent discoloration or browning of the fabric so that they are not applicable to white material; some of them make the fibers tender, that is to say, they embrittle the fibers and fabric and thereby reduce its tensile strength; and some of them are unduly expensive, particularly when employed in amounts sufficient to provide crease-resistance as well as dimensional stability.

An object of the invention is to provide an improved and novel method of treating textile materials that are formed predominantly of regenerated cellulose, to render them permanently stable against substantial progressive, dimensional shrinkage under repeated washings; with which the color of the treated materials will be unchanged; with which the stabilized materials will be free of any disagreeable or other objectionable odors resulting from the treatment, have a soft and pleasing hand or feel, and have substantial crush, crease and abrasion resistance; which may be practiced without special or expensive apparatus; which will not cause the evolution of disagreeable or dangerous fumes or odors; and which is relatively simple, practical and inexpensive, so that the cost of the treated materials is not objectionably increased.

Other and further objects and advantages of the invention will appear from the following more detailed description of the discovery.

As above suggested, the wash stabilization of fabrics, particularly fabrics made from spun viscose rayon yarn, and which shrink progressively when repeatedly washed, has been the subject of much investigation and is of great importance to the textile and allied industries. To a somewhat lesser extent, it is important to make such fabrics resistant to crushing, abrasion creasing and wrinkling. Various reagents have been suggested for use in treating textile materials for this purpose, and among such reagents formaldehyde is probably the most common. While formaldehyde does, to a certain degree, accomplish the desired purpose, it tenders the textile material, making it less resistant to abrasion (wear); it is not as effective in creaseproofing as is desirable, and its

use is attended by the emission of highly irritating and disagreeable fumes, the odor of which tends to persist in the finished fabrics. Urea-formaldehyde and melamine-formaldehyde have been proposed in substitution for formaldehyde, but they also evolve irritating or disagreeable fumes during the curing operation, and these reagents likewise produce fabrics which discolor badly and are tendered when ironed following a normal chlorine bleach as used in washing white fabrics, due to chlorine retention. Such compounds also must be used in substantial amounts (for example, 10% of melamine-formaldehyde, or 25% urea-formaldehyde upon the weight of the goods) in order to obtain a desirable degree of stabilization. This makes the use of such materials unduly expensive.

We have now discovered that highly satisfactory results as respects shrinkage stabilization, accompanied by increased crush resistance and resistance to creasing and wrinkling, may be obtained by use of a dialdehyde so reacted with the cellulose of the textile material as to convert each fiber into a reaction product which is more resistant to moisture and the effects of laundering than the original fiber. While a dialdehyde might be expected to act similarly to formaldehyde in the formation of a long chain polymer, the presence of the two aldehyde groups in primary linkage is believed to cause this dialdehyde to form a cross-linked, long-chain reaction product with the cellulose, thus providing a more permanent effect than by the use of formaldehyde, and a product characterized (as we believe) by less relative slippage of the molecular chains, so that the material is more resistant to crushing and creasing than the untreated material or one which has been treated with formaldehyde or compounds thereof.

We have discovered that the dialdehyde having the structural formula



and known as "glyoxal," oxalic aldehyde, or ethandial, is highly useful for the stabilization of textile materials, formed predominantly of regenerated cellulose, including filaments, fibers, staple or yarns, as well as fabrics, whether knitted, woven, braided or felted, as well as garments or other articles made from such fabrics. This reagent has but little odor in solution of a strength suitable for such treatment (such odor as it has being pleasant) and does not emit disagreeable fumes during curing; it does not tender the textile material or make it brittle; its application as hereinafter described apparently adds to the wear and abrasion-resistance of textile material; it does not discolor or brown the textile material to any harmful degree; and it may readily be applied without necessitating special equipment and is effective in such small quantities as to make it cheaper to use than the other reagents such as urea-formaldehyde or melamine-formaldehyde, which, although initially non-odorous, develop formaldehyde odor on curing.

As noted, glyoxal, which is the simplest dialdehyde, behaves in many respects like formaldehyde; for example, the formation of acetals with alcohols may be expected and condensations of glyoxal may occur upon reacting the material with other compounds containing amino groups.

We find it necessary, in order to hasten the

action and to obtain useful results, to employ an acidic catalyst to facilitate the reaction between the glyoxal and the cellulose, or a catalyst which produces an acid reaction on heating. Since it is not ordinarily advisable to use free mineral acids in the treating of textiles, we prefer to use such acidic reagents as oxalic acid, ammonium chloride, ammonium sulphate, or ammonium nitrate as the catalyst. We have found oxalic acid to be a highly satisfactory catalyst, since its use avoids the development of any substantial color during the heat treatment.

Glyoxal has been available commercially only in aqueous solution (about 30% by weight), and it is decidedly acid with a pH between about 1.00 and 1.30. When a 30% glyoxal solution, with a pH of about 1.12, is diluted with water so as to contain about 120 cc. glyoxal per litre, the pH is approximately 2.05. When 6 grams of oxalic acid are added to this dilute solution, the acidity is increased to provide a treating bath having a pH of about 1.55. The water used for the dilution was approximately neutral, with a pH of 7.2. The pH of a solution of 6 grams of oxalic acid per litre is about 1.65. The relative amounts of glyoxal and acidic catalyst in the solution can be varied within limits, which causes some variation in the acidity of the treating liquid. The particular acidic catalyst used also causes some variation in the acidity of the treating bath.

If the catalyst is a salt which dissociates upon the application of heat to produce an acid, the treating solution containing such salt when formed may have a pH of possibly 2.5, yet when that solution is heated to the curing temperature, which happens when the textile material treated with that solution is cured at a temperature above about 212° F., the catalyst salt will dissociate and liberate an acid that changes the pH of the solution, during the curing, to about 1 to 2. When the catalyst is itself an acid, such as oxalic acid, the treating liquid as made up has a pH preferably between about 1.0 and 2.0 for the best results. Summarizing, the treating bath or liquid should be strongly acid and have a pH between about 1.0 and 2.5 preferably between about 1.0 and 2.0 inclusive. Inasmuch as those acids which are substantially volatile at drying temperatures while in solution, are normally lost with the moisture to a considerable extent during the drying to approximate dryness and early part of the curing period, such volatile acidic components will not normally be available in sufficient concentration and acidity in the early part of the curing period to cause the reaction between the regenerated cellulose and the glyoxal to occur. Since it is difficult, under plant production conditions, to prevent such loss of a volatile acid, it is preferable to employ an acidic catalyst with an acidic component that increases in acidity and is not eliminated under drying and early curing conditions. As illustrative without limitation of the scope of the invention, the following examples of reagent strengths and conditions of treatment are cited:

1. Amount of glyoxal: 30 to 200 cubic cms. of 30% by weight glyoxal aqueous solution per liter of treating bath, or approximately 1.12% to 7.5% glyoxal by weight in the aqueous treating bath.

2. Type of catalyst: Acidic or acid-reacting, such as organic acids, or salts of inorganic acids or organic acids which produce an acid effect.

3. Amount of catalyst: 1 to 20 gms. per liter of treating bath, or approximately 0.1% to 2% by weight of treating bath.

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4. Baking temperature: Above about 212° F. and preferably from about 212° F. to 400° F.

5. Baking time: Until stabilization has been substantially effected and for the preferred temperature range, between about 30 minutes and ½ minute.

6. The pH of the treating liquid is between approximately 1.0 and 2.5.

Obviously the baking temperature and the baking time are inversely related.

The following specific examples will serve to illustrate and explain our invention:

EXAMPLE #1

A plain weave, 100% spun viscose rayon chalis fabric in the greige, made of 28/1 warp and 14/1 filling yarns, was desized, boiled off, and dried on a tenter frame. The white, pure finished fabric had a count of 66 x 41 and a weight of four ounces per yard. This fabric was then passed through an aqueous impregnating solution containing per liter, 120 cubic centimeters of glyoxal solution (of 30% glyoxal content by weight) and 15 grams of oxalic acid, with a pH of about 1.25. After the fabric was passed through this solution and was well wetted out (requiring about 10 seconds immersion) it was squeezed to remove solution in excess of 130 percent pick-up and was then dried on a pin-tenter frame in air at around 250° F. to the dimensions that the fabric possessed before impregnating. The dried, tentered fabric was then cured in circulating air at 300° F. for 5 minutes. The fabric, after curing was removed from the pin-frame and subjected to five standard (CCC-T-191a) cotton wash tests for shrinkage. In the above procedure, no shrinkage is permitted during the process so that the residual shrinkage in the wash tests is a measure of the effectiveness of the process. A comparison of the shrinkage of the untreated and of the treated fabric is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

	1st Wash	2nd Wash	3rd Wash	4th Wash	5th Wash
Untreated.....	5.5	6.0	6.4	6.8	7.5
Treated.....	1.2	1.1	1.2	1.4	1.4

In commercial practice, the fabric is washed and slack dried after curing to permit shrinkage resulting in a residual shrinkage or less than one percent in the finished fabric.

EXAMPLE #2

The fabric described in Example #1 was immersed for ten seconds in an aqueous impregnating solution containing per liter, 180 c. c. of 30% glyoxal solution, 6 grams of oxalic acid and 3 grams of boric acid, with a pH of about 1.45. After the fabric was well wetted out, it was squeezed to remove solution in excess of 130% pick-up, and was then dried on a pin-tenter frame in air at around 250° F. to the dimensions that the fabric possessed prior to impregnating. The dried, tentered fabric was then cured in circulating air at 280° F. for five minutes. The fabric, after curing, was removed from the pin-

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frame and subjected to five standard (CCC-T-191a) cotton wash tests for shrinkage. In the above procedure, no shrinkage is permitted during the process so that the residual shrinkage in the wash test is a measure of the effectiveness of the process. A comparison of the shrinkage of the untreated and of the treated fabric is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

	1st Wash	2nd Wash	3rd Wash	4th Wash	5th Wash
Untreated.....	5.5	6.0	6.4	6.8	7.5
Treated.....	1.1	1.3	1.4	1.5	1.4

In commercial practice, the fabric is washed and slack dried after curing to permit shrinkage resulting in a residual shrinkage of less than one percent in the finished fabric.

EXAMPLE #3

A 100% viscose, spun rayon 2 x 1 left handed twill fabric in the greige made of 30/1 warp and filling yarn was desized, boiled off and dried on a tenter frame. The white, pure finished fabric had a count of 124 x 60 and a weight of five ounces per yard. This fabric was then passed through an aqueous impregnating solution containing per liter, 120 c. c. of 30% glyoxal solution and 3 grams of ammonium chloride, with a pH of about 2.1 as made up. After the fabric was well wetted out it was squeezed to remove solution in excess of 130% pick-up, and was then dried on a pin tenter frame in air at around 250° F. to the dimensions that the fabric possessed prior to impregnating. The dried, tentered fabric was then cured in circulating air at 280° F. for five minutes. The fabric, after curing, was removed from the pin-frame and subjected to five standard (CCC-T-191a) cotton wash tests for shrinkage. In the above procedure, no shrinkage is permitted during the process so that the residual shrinkage in the wash tests is a measure of the effective of the process. A comparison of the shrinkage of the untreated and of the treated fabric is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

	1st Wash	2nd Wash	3rd Wash	4th Wash	5th Wash
Untreated.....	3.9	4.4	4.6	4.9	4.8
Treated.....	1.3	1.3	1.4	1.4	1.4

In commercial practice, the fabric is washed and slack dried after curing to permit shrinkage resulting in a residual shrinkage of less than one percent in the finished fabric.

EXAMPLE #4

A 100% viscose Shantung type greige fabric with a filament warp and spun filling, was desized, boiled off and dried on a tenter frame. The fabric

was then vat dyed blue by the usual method. The blue, pure finish fabric had a count of 100 x 72 and a weight of 3.3 ounces per yard. 3000 yards of this fabric was then treated by impregnating it with an aqueous solution containing per 100 gallons: 12 gallons of 30% glyoxal solution and 5 pounds of oxalic acid, with a pH of about 1.55. The fabric was run through a padder and squeezed to remove solution in excess of 100 percent pick-up. The fabric was then dried on a covered clip tenter running at 20 yards per minute at a temperature of 245° F. The fabric was then cured for 5 minutes at 260° F. on a loop dryer. The fabric, after curing, was washed in a dyebeck with soap and soda and then slack dried and finally framed to width and decatized. A comparison of the shrinkage of the fabric before and after treatment is given below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

	1st Wash		2nd Wash		3rd Wash		4th Wash		5th Wash	
	W	F	W	F	W	F	W	F	W	F
Untreated.....	3.8	1.7	4.1	1.9	4.3	1.9	4.6	2.0	4.8	2.1
Treated.....	1.7	0	1.5	0	1.3	0	1.2	0	1.3	0

* Denotes a gain.

EXAMPLE #5

A linen type 100% spun viscose rayon fabric in the greige, made of 14/1 warp and filling yarns was desized, boiled off and dried on a tenter frame. The white, pure finished fabric had a count of 38 x 42 and a weight of 3.75 yards per pound. This fabric was then passed through an aqueous impregnating solution containing per liter, 150 c. c. of 30% glyoxal solution and 15 grams of oxalic acid, with a pH of about 1.29. After the fabric was passed through this solution and was well wetted out (requiring about 10 seconds immersion), it was squeezed to remove solution in excess of 130 percent pick-up and was then dried on a pin-tenter frame in air at around 250° F. to the dimensions that the fabric possessed before impregnating. The dried, tentered fabric was then cured in circulating air at 300° F. for 5 minutes. The fabric after curing was removed from the pin-frame and subjected to five standard (CCC-T-191a) cotton wash tests for shrinkage. In the above procedure, no shrinkage is permitted during the process so that the residual shrinkage in the wash tests is a measure of the effectiveness of the process. A comparison of the shrinkage of the untreated and of the treated fabric is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

	1st Wash	2nd Wash	3rd Wash	4th Wash	5th Wash
Untreated.....	2.7	4.0	4.2	4.5	4.6
Treated.....	.6	.8	.5	.8	.8

In commercial practice, the fabric is washed and slack dried after curing to permit shrinkage resulting in a residual shrinkage of less than one percent in the finished fabric.

EXAMPLE #6

A 2 x 1 twill 80% spun viscose rayon and 20% spun acetate rayon fabric in the greige, made of blended 14/1 warp and filling yarns was desized and boiled off and dried on a tenter frame.

The fabric was then vat dyed blue by the usual methods. The blue, pure finished fabric had a count of 106 x 60 and weighed 6.5 ounces per yard. This fabric was then passed through an aqueous impregnation solution containing per liter, 90 c. c. of 30% glyoxal solution and 10 grams of oxalic acid, with a pH of about 1.42. After the fabric was passed through this solution and was well wetted out (requiring about 10 seconds immersion), it was squeezed to remove solution in excess of 130 percent pick-up and was then dried on a pin-tenter frame in air at around 250° F. to the dimensions that the fabric possessed before impregnating. The dried, tentered fabric was then cured in circulating air at 300° F. for 5 minutes. The fabric, after curing, was removed from the pin-frame and subjected to five standard (CCC-T-191a) cotton wash tests for shrinkage. In the above procedure, no shrinkage is permitted during the process so that the residual shrinkage in the wash tests is a measure of the effectiveness of the process. A comparison of the shrinkage of the untreated and of the treated fabric is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing—Standard (CCC-T-191a) cotton wash test

[Inches per yard]

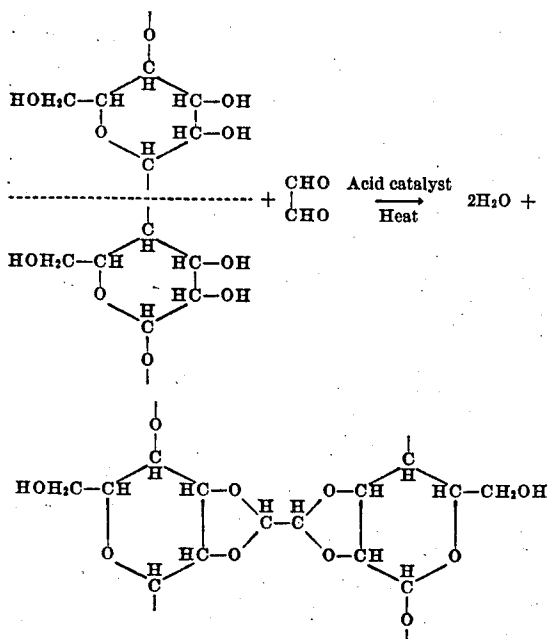
	1st Wash	2nd Wash	3rd Wash	4th Wash	5th Wash
Untreated.....	2.3	2.6	2.7	2.9	2.7
Treated.....	.9	1.1	.9	.8	.9

In commercial practice, the fabric is washed and slack dried after curing to permit shrinkage resulting in a residual shrinkage of less than one percent in the finished fabric.

Apparently substantially all of the glyoxal absorbed by the fibers during the initial wetting operation, reacts with the cellulose of the fibers, and only about a 1.00% to 7.5% by weight, solution of glyoxal is necessary to accomplish the desired result. Since so little of this reagent is necessary, and since the cost of the catalyst is almost negligible, the total cost of this treatment is very considerably less than that of treating fabrics with urea-formaldehyde or melamine-formaldehyde, for the latter reagents must be employed in much greater percentage than the glyoxal in order to obtain any useful results.

While we do not definitely know the exact action which occurs when cellulose in association with glyoxal is heated, we believe that a reaction takes place in consequence of which the cellulose of the individual fibers of the fabric is at least partially converted into a reaction product which may be termed a "partial acetal" or "cellulose glyoxal," as may be preferred, such product being of the long-chain, high molecular weight type, but with cross linkages making it more stable than

the formaldehyde resins. The structural formula indicating our theory of this reaction is as follows:



The effects produced on the physical properties of a cellulosic textile fiber by chemical reaction with glyoxal are probably due to two primary factors. Cellulosic fibers, and in particular regenerated cellulose fibers, have an affinity for water because of the presence of the hydrophilic hydroxyl groups in the cellulose molecular units. The reaction of glyoxal with cellulose as previously postulated results in the removal of hydroxyl groups and the substitution for them of hydrophobic groups insensitive to water through the formation of oxyacetylene bridges. The partial solvation and consequent swelling with water of normal cellulose fibers, which causes yarn and fabric shrinkage, is reduced by the formation of the reaction product of cellulose and glyoxal, and shrinkage is thereby decreased.

It is believed that the reaction between glyoxal and cellulose takes place throughout the entire cellulosic fiber. This is indicated by the fact that the reacted fiber is insoluble in the usual cellulosic solvents. Moreover, while treated fiber dyes uniformly throughout the fiber, it swells much less in water than the untreated fiber. By actual test, treated fibers swelled in water to give an increase in diameter of the fiber of only 10%, while the untreated fibers swelled in water to give an increase in diameter of 45%. The treatment by the present process is uniform because the fibers swell uniformly with the treating solution.

It is important that certain practical principles be applied in the practice of this process. An acid condition is necessary during the reaction in order to obtain the desired degree of reaction within a practicable time, but acids are harmful to cellulose, particularly at elevated temperatures, so that the minimum amount of acid or acid-producing catalyst required to produce the desired results should be used. Also, for some reason not clearly understood, an excess of glyoxal is harmful to the cellulose, so that the minimum quantity of this reagent required to produce the desired result should also be used. The use of quantities of glyoxal and catalyst in excess of the amounts actually required is, there-

fore, not only economically unsound but may be harmful to the fabric.

The process can be performed on textile material before or after bleaching in the case of materials which are to be bleached. If the process is performed before bleaching, the material is then bleached in a normal manner, using established procedures, without harmful effect on the improved resistance to shrinkage produced by the process. If desired, a fabric may be treated with this process before dyeing or printing, although in general it will be more satisfactory to perform the process after dyeing.

After the treatment of the cellulosic material with glyoxal in accordance with our process, the only change in the physical properties of the cellulosic material which we have been able to discover, in addition to its improved crease and crush resistance, is its reduced swelling with water and consequent reduced shrinkage. We have been unable to note any reduction in the softening point of the cellulosic material under heat treatment as a result of the reaction with the glyoxal.

From the above, it will be apparent, therefore, that we have formed in this reaction between cellulose and glyoxal, a modified cellulose which may be described as a partial "acetal." The degree of modification is relatively small from a weight percentage viewpoint, but we believe that this modification or conversion of the cellulose is uniform throughout the diameter of the fiber because the cellulose fibers swell uniformly with the treating solution.

While certain examples have hereinabove been given as illustrative of the utility of this invention, we consider it to be applicable to a wide variety of textile materials, including fibers, yarns and fabric composed of:

- (1) Regenerated cellulose
 - a—Viscose
 - b—Cuprammonium
 - c—Saponified acetate
- (2) Mixtures—Major part of regenerated cellulose
- (3) Spun and filament yarns

It is to be understood that the above are merely by way of example and not by way of limitation, and that the invention is inclusive of all modifications and equivalents falling within the terms of the appended claims.

In the practice of the invention, the aqueous wetting liquid or solution containing the glyoxal and other treating materials may be applied to the textile material in any desired manner, such as by spraying the textile material, while it is traveling with the treating solution in just the right amount, relatively to the rate of travel of the textile material, to give the desired liquid pickup, or even an excess of liquid, or the textile material may be dipped in, or otherwise impregnated or saturated with, the treating solution.

All excess treating solution should be removed from the textile material, before curing the material and this may be accomplished in any suitable manner, such as by centrifugal force, draining, or squeezing. The term wetting, as used in the specification and claims to refer to the application of the treating solution to the textile materials, is intended to include all means and methods for applying the treating solution to the textile materials.

The wetted textile materials are preferably dried, before curing. The wetted fabrics will

not have a temperature exceeding about 212° F., even when the drying temperature is above 212° F., but as soon as the wetted fabric dries, it will at once begin to cure if the temperature then is above 212° F. Therefore it is safer to dry at a temperature at or below 212° F., and then cure the dried fabric at the desired curing temperature. This makes it possible to more accurately control the curing.

We claim as our invention:

1. The method of stabilizing, against progressive, dimensional shrinkage under repeated washings, a textile material predominantly of regenerated cellulose, which comprises wetting the fibers of said material with an aqueous liquid having a pH between approximately 1.0 and 2.5 and containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, and an acidic catalyst the acidic component of which increases in acidity and is not eliminated when concentrated to approximate dryness and subjected to temperatures just about about 212° F., removing excess wetting liquid, then drying the textile material so wetted, after said removal of excess liquid, and heating the dried material to a temperature above about 212° F. for a time interval inversely related to the temperature, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

2. The method of stabilizing, against progressive, dimensional shrinkage under repeated washings, a textile material predominantly of regenerated cellulose, which comprises wetting the fibers of said material with an aqueous liquid having a pH between approximately 1.0 and 2.0 and containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, and oxalic acid, removing excess wetting liquid, then drying the textile material so wetted, after said removal of excess liquid, and heating the dried material to a temperature above about 212° F. for a time interval inversely related to the temperature, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

3. The method of stabilizing, against progressive, dimensional shrinkage under repeated washings, a textile material predominantly of regenerated cellulose, which comprises wetting the fibers of said material with an aqueous liquid having a pH between approximately 1.0 and 2.0 and containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, and oxalic acid in approximately 0.1% to 2% by weight in the treating liquid, removing excess wetting liquid, then drying the textile material so wetted, after said removal of excess liquid, and

heating the dried material to a temperature between 212° F. and 400° F. for a time interval inversely related to the temperature, between approximately 30 minutes and ½ minute, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

4. The method of stabilizing, against progressive, dimensional shrinkage under repeated washings, a textile material predominantly of regenerated cellulose, which comprises wetting the fibers of said material with an aqueous liquid having a pH between approximately 1.0 and 2.0 and containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, and oxalic acid in approximately 0.1% to 2% by weight in the treating liquid, removing excess wetting liquid, then drying the textile material so wetted, after said removal of excess liquid, and heating the dried material to a temperature above about 212° F. for a time interval inversely related to the temperature, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

5. The method of stabilizing, against progressive, dimensional shrinkage under repeated washings, a textile material predominantly of regenerated cellulose, which comprises wetting the fibers of said material with an aqueous liquid containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, and an acidic catalyst the acidic component of which increases in acidity and is not eliminated when concentrated to dryness and subjected to temperatures just about above 212° F., said wetting liquid having a pH between about 1 and 2 when the catalyst is an acid, and between about 1 and 2.5 when the catalyst is a salt, removing excess wetting liquid, then drying the textile material so wetted, after said removal of excess liquid, and heating the dried material to a temperature above about 212° F. for a time interval inversely related to the temperature, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

EDWARD C. PFEFFER, Jr.
JACK EPELBERG.

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The following references are of record in the file of this patent:

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Certificate of Correction

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Patent No. 2,436,076.

February 17, 1948.

EDWARD C. PFEFFER, JR., ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows: Column 11, line 22, claim 1, for the word "about", first occurrence, read *above*; column 12, line 35, claim 5, for "about above" read *above about*; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 18th day of May, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.