Nov. 14, 1950 E. C. PFEFFER, JR., ET AL 2,530,175

STABILIZATION OF REGENERATED CELLULOSE

Filed Sept. 27, 1946 2 Sheets-Sheet 1

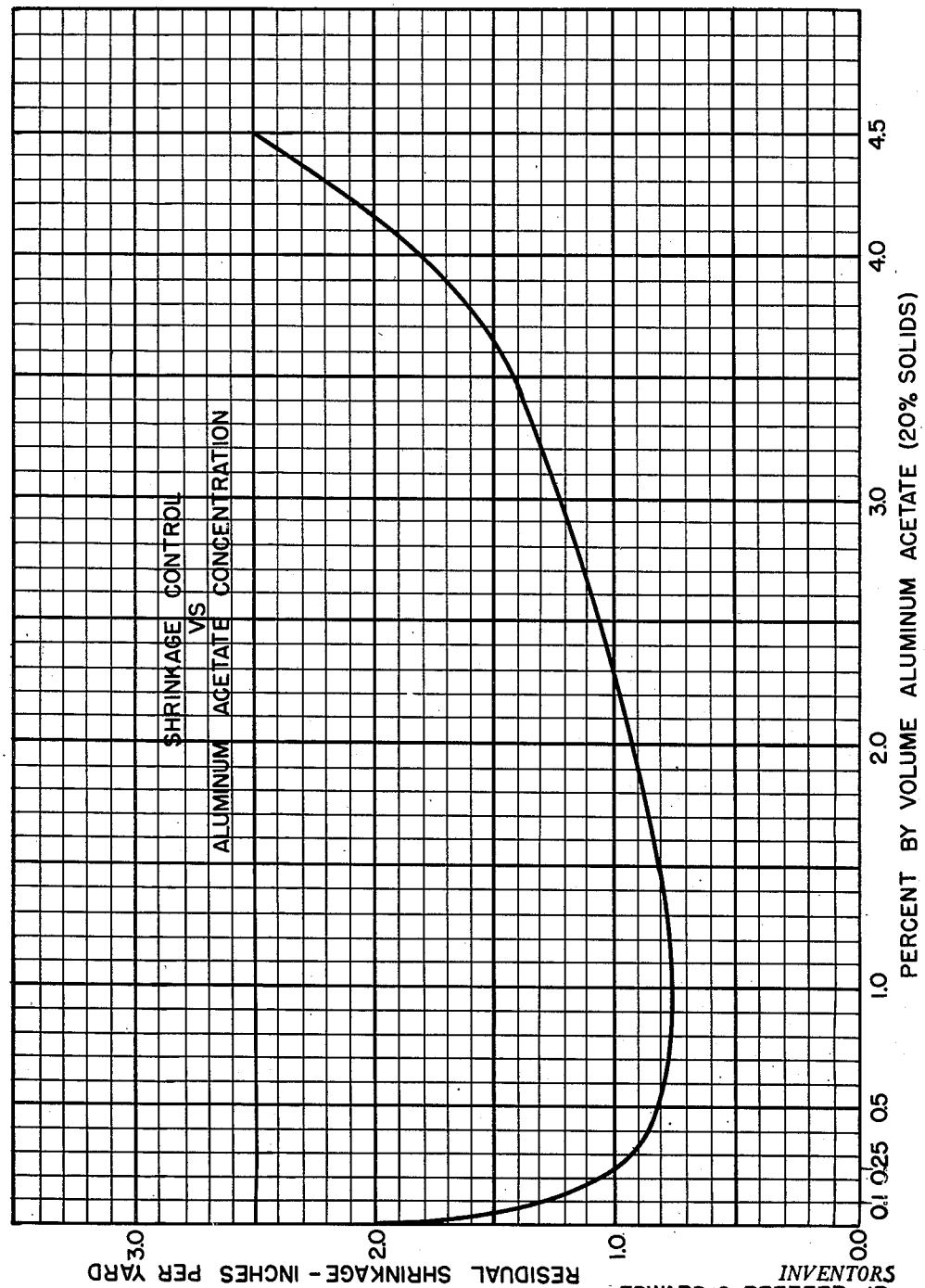


FIG. 1

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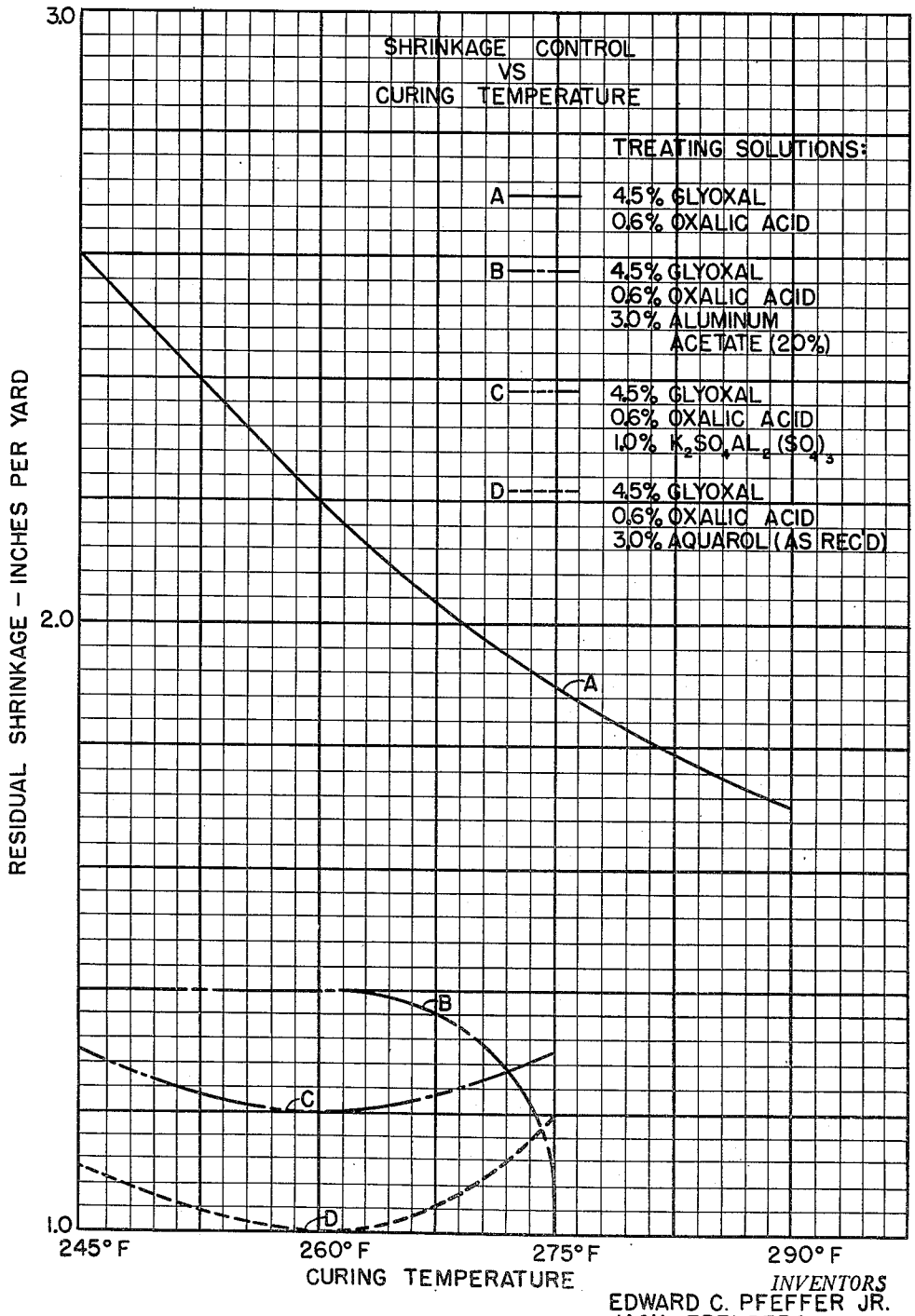


FIG. 2

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UNITED STATES PATENT OFFICE

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STABILIZATION OF REGENERATED CELLULOSE

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Application September 27, 1946, Serial No. 699,626

9 Claims. (Cl. 8—116.4)

1

This invention relates to textiles, and more particularly to the novel method of treating textiles formed predominantly of regenerated cellulose, so as to render them substantially stable with respect to laundry shrinkage and also resistant to crushing and creasing. This application is a continuation in part of our co-pending application S. N. 576,755 filed February 8, 1945, now abandoned, and entitled "Stabilized Textiles." The present invention is in the nature of an improvement over that described and claimed in our application S. N. 644,188 filed January 29, 1946 for "Textile Materials and Method of Preparing the Same" and an earlier application S. N. 495,620 filed July 21, 1943 of which the application S. N. 644,188 was a continuation in part, both now abandoned.

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

The aforesaid applications upon which the present invention is an improvement, disclose the employment of a dialdehyde, more particularly glyoxal, in substitution for the formaldehyde previously employed for the purpose, and points out that highly satisfactory results, as respects shrinkage stabilization, accompanied by increased crush resistance and resistance to creasing and wrinkling, may be obtained by the use of a dialdehyde so reacted, in the presence of an acid catalyst, with the regenerated cellulose of the textile material, as to convert or at least partially to convert each fiber into a reaction product which is more resistant to moisture and the effects of laundering than the original fiber. It was further pointed out that while a dialdehyde may be expected to act in a generally similar manner to formaldehyde in the formation of a long-chain polymer, the presence of the two aldehyde groups in primary linkage may be expected to cause the dialdehyde to form a cross linked long-chain reaction product with the cellulose, thus producing a more permanent effect than formaldehyde, and resulting in a product characterized, it appears, 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. It was further noted that the dialdehyde known as "glyoxal" is highly useful for the stabilization of textile materials formed predominantly of regenerated cellulose, including filaments, fibers, staple or yarns, and fabrics whether knitted, woven, braided or felted, as well as garments or other articles made from such fabrics. Glyoxal has but little odor in solution of a strength suitable for such treatment (such odor as it has being pleasant), it does not emit disagreeable or toxic fumes during curing, it does not tender the textile material nor make it brittle, it does not discolor nor brown the material to any harmful degree, and it may readily be applied without necessitating special equipment, and is effective in smaller quantities than the reagents previously employed for the purpose.

2

Glyoxal is available in substantial quantities only in a commercial form as an impure aqueous solution. This commercial form is a pale straw colored solution containing approximately 30% by weight of glyoxal in water, and it is highly acid with a pH of between about 1.00 and 1.30. It has a specific gravity at 20/20° C. of 1.24 to 1.28.

When a 30% by weight glyoxal solution having a pH of about 1.12 is diluted with water so as to contain about 120 cc. glyoxal per litre, the pH of the solution is then approximately 2.05. The water used for such dilution was approximately neutral with a pH of 7.2.

The principal object of the present invention is to provide a novel method whereby the treatment with glyoxal is greatly accelerated and the time and temperature required for curing the treated materials is reduced, and improved shrinkage control is obtained. Other and further objects and advantages of the invention will be pointed out in the following more detailed description and by reference to the accompanying drawings, wherein

Fig. 1 is a graph illustrating the effects upon shrinkage control of variations in the concentration of the promoter employer; and

Fig. 2 is a graph illustrating the effect upon shrinkage control of variations in the curing temperature.

The present invention is based upon the discovery that the reaction between glyoxal and regenerated cellulose in the presence of an acid catalyst, is greatly accelerated by the addition of small amounts of those aluminum salts which are either soluble in water or are readily dispersible in water. This results in improved shrinkage control and permits lower curing temperatures and/or decreased curing time. The milder curing conditions result in the elimination of possible damage to the fabric which might

come from high baking temperatures and long baking time, the stabilizing process being made commercially more feasible, because of these less severe conditions required for curing.

This use of aluminum salts to accelerate the treatment with glyoxal appears to be wholly novel and the results attained are such as could not be predicated upon the known properties of aluminum salts, since the result of the addition of the aluminum salts to the treating solution is synergic, that is to say, the effect is greater than additive. Aluminum salts alone, unless highly acid by disassociation, do not catalyze the reaction between glyoxal and cellulose. The presence of acid is required for effective reaction between glyoxal and cellulose, and the aluminum salt added to this solution constitutes a promoter for the reaction. A "promoter" has been defined as a substance which increases the catalytic activity to an extent exceeding the additive effect.

Only a very low concentration of reagents is required in obtaining the desired results, and in fact harmful effects may be experienced with larger concentrations of reagents. 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 of commercial glyoxal solution per liter of treating bath, or 1.12% to 7.5% glyoxal by weight in the aqueous treating bath.

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

3. Amount of acid catalyst from 1 to 20 grams per liter, approximately 0.1% to 2% by weight of the treating bath.

4. Amount of aluminum salt from 0.2 to 10 grams per liter (solid basis).

5. Baking or curing temperature: Above 212° F.

6. Baking time: Inversely related to the baking temperature and continued until stabilization is substantially completed.

7. The pH of the treating bath is between approximately 1.0 and 2.5.

As pointed out in said aforesaid copending application, S. N. 644,188, it is not ordinarily advisable to use free mineral acids as catalysts in the treatment of textiles, and we prefer to employ as the catalyst such acidic reagents as oxalic acid, ammonium chloride, ammonium sulfate or ammonium nitrate. Oxalic acid has proven to be very satisfactory.

The graph of Fig. 2 illustrates the effects of the addition of aluminum salts to the glyoxal treating solution containing acid catalyst. The data for this graph was obtained by treating an all spun viscose rayon challis type fabric with the treating solutions shown on the graph. The 100% spun viscose rayon fabric was obtained in the greige, was desized and boiled off to remove size, and was then dried on a tenter frame. The white, pure finish fabric had a residual shrinkage in one CCC—T—191—A cotton wash of 5.5 inches per yard. In each of the series of tests upon which the respective graph is based, the pure finish fabric was immersed in the selected impregnating solution in a padder box for twelve seconds and was then run between rubber squeeze rolls to remove excess treating solution. The liquid pick-up in each case was 130% based on the dry weight of the fabric. The impregnated fabric was then dried on a pin-tenter to the original dimensions before impregnating, using circulating hot air at 250° F. and removing from the drying oven when first free from moisture. The dried fabric was then baked on the pin-frame for each test at the temperature indicated on the graph for eight minutes. In each test the cured fabric was then removed from the pin-frame after curing and subjected to one CCC—T—191—A cotton wash test for shrinkage. The residual shinkage (from the original pure finish dimensions) was then determined as a measure of the shrinkage control of each treating solution at the different curing temperatures. In commercial practice a process loss, or shrinkage, can be taken by permitting the fabric to relax in a slack drying operation, but in the above experimental technique no process shrinkage is permitted prior to the test wash. Thus comparative data on shrinkage control can be accurately obtained.

In the tests made to obtain data for the graph of Fig. 2 the base treating solution, the effects of which on fabric are illustrated by curve A, contained 4.5% glyoxal by weight and 0.6% by weight oxalic acid, the balance being water. The three other treating solutions whose effects are indicated by curves B, C and D, respectively, had additions, respectively, of 3% by volume aluminum acetate solution (20% solids), 1% by weight potassium aluminum sulfate, and 3% by weight "Aquarol" as received. Aquarol is a proprietary water-repellent compound of non-permanent type containing 6% aluminum acetate in addition to a stable emulsion of hydrocarbon waxes. The data and curves derived therefrom show that the addition of the aluminum compounds greatly improved shrinkage control and permit a decrease in baking temperature without any appreciable decrease in shrinkage control. Note that even at a temperature of 290° F. which approaches the danger point as respects fabric damage, the shrinkage reduction produced by the base treating solution was not as great as that produced by the other solution at a temperature of 275° F. or less. The lower temperature bake which can be satisfactorily used with the aluminum compound added is a practical advantage in commercial practice and the improved shrinkage control makes the commercial use of the process more feasible and reduces yardage loss in processing.

The fact that the aluminum salt alone is not a catalyst for the glyoxal process is shown by the following shrinkage data which was developed in the same manner as the data used in the graph of Fig. 2.

Fabric residual shrinkage

Treating Formula	Inches per Yard
Not Treated	5.5
4.5% (by weight) glyoxal 0.6% (by weight) oxalic Balance water	2.1
4.5% (by weight) glyoxal 3.0% (by volume) aluminum acetate solution (20% solids) Balance water	4.0
4.5% (by weight) glyoxal 0.6% (by weight) oxalic acid 3.0 % (by volume) aluminum acetate solution (20% solids) Balance water	0.9

The curing temperature and time was 280° F. for eight minutes.

It can be seen from the above table that the treatment with glyoxal having aluminum acetate added, but without acid catalyst present, pro-

duces no effective shrinkage control but that the treatment with glyoxal with both acid catalyst and aluminum acetate added produces a result superior to that obtained with acid catalyst alone.

We find that the aluminum salts that are suitable for this purpose are all of the aluminum salts which are either soluble in water or readily dispersible in water. A few examples of such suitable aluminum salts are aluminum formate, aluminum acetate, aluminum salts of fatty acids or soaps such as aluminum stearate, and with each of these aluminum salts we find it necessary to employ an acid catalyst. Salts of strong mineral acids, such as aluminum chloride and sulfate, are effective without added acid catalyst because such salts are highly acid by dissociation in solution, but their use is likely to result in an undesirable degree of damage to fabric tensile strength and abrasion resistance.

Mixed salts such as potassium-aluminum sulfate are effective, with the addition of small amounts of an acidic catalyst. Where an aluminum salt that is used as the promoter, is one that does not hydrolyze to give a strongly acid solution with a pH under 2, it is necessary to use an added acid catalyst.

The behavior of aluminum acetate as a promoter is very interesting since in small amounts it aids shrinkage control whereas in larger amounts it acts as a buffer to the acid catalyst and can even harm the degree of shrinkage control. The graph of Fig. 1 illustrates this effect. The data was obtained by the same methods and procedure as that for the graph of Fig. 2. In this case, for each test a different quantity of aluminum acetate solution (20% solids) was added to the base treating solution of 4.5% glyoxal and 0.6% oxalic acid. The curing schedule was at 280° F. for eight minutes. It will be seen that the maximum effect is produced by the use of approximately 1% by volume of the aluminum acetate solution.

Proprietary water-repellent compounds of the non-permanent type containing emulsified aluminum formate or acetate, and emulsified fatty matter and hydrocarbon waxes are also very effective as promoters of the shrinkage control reaction of glyoxal with cellulose in the presence of acid catalyst. Such compounds include "Aquarol" (Arkansas Co.), "Textarid" (Sonneborn Co.), "Aridex" (E. I. du Pont de Nemours & Co.), and "Drax" (Johnson Co.). "Aquarol" is a one bath, water-repellent finish for hosiery and piece goods, and contains a stable emulsion of hydrocarbon waxes and aluminum salts. "Textarid" is a stable wax emulsion used as a one bath water-repellent for rayon, silk and cotton. "Aridex" is a water-repellent solvent paste containing wax and an aluminum salt compound. These products are identified under these trade names in the 1945 year book, page 471, of the American Association of Textile Chemists and Colorists.

The following specific examples are given as illustrative of the application of the present novel process as a practical matter to materials of different types:

EXAMPLE #1

A plain weave, 100% spun viscose rayon challis fabric in the greige 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), 6 grams of oxalic acid, and 5 cc. of a 20% aluminum acetate solution. 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 before impregnating. The dried, tentered fabric was then cured in circulating air at 260° F. for five minutes. The fabric after curing was removed from the pin-frame and subjected to two CCC—T—191—A 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 CCC—T—191—A wash test

	Inches Per Yard	
	1st Wash	2d Wash
Untreated Control	5.4	6.0
Treated	1.3	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 #2

The fabric described in Example #1 was immersed for ten seconds in an aqueous impregnating solution containing per liter, 120 cc. of 30% by weight glyoxal solution, 6 grams of oxalic acid, and 30 cc. of a 20% aluminum acetate solution. 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 before impregnating. The dried, tentered fabric was then cured in circulating air at 260° F. for five minutes. The fabric after curing was removed from the pin-frame and subjected to two CCC—T—191—A 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 fabrics is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing CCC—T—191—A wash test

	Inches Per Yard	
	1st Wash	2d Wash
Untreated Control	5.4	6.0
Treated	1.3	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

The fabric of the type used in the previous examples was immersed for ten seconds in an aqueous impregnating solution containing per liter, 120 cc. of 30 percent by weight of glyoxal solution, and 30 grams of aluminum sulfate. Aluminum sulfate is a strong acid salt by itself so that it did not require the addition of any oxalic acid catalyst. After the fabric was well wetted out, 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 before impregnating. The dried, tentered fabric was then cured in circulating air at 260° F. for five minutes. The fabric after curing was removed from the pin-frame and subjected to two CCC—T—191—A 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 fabrics is shown below. The tensile strength and the abrasion resistance of the fabric was somewhat lowered by this treatment.

Warp shrinkage on washing CCC—T—191—A wash test

	Inches Per Yard	
	1st Wash	2d Wash
Untreated Control	5.4	6.0
Treated	.5	.6

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

The fabric used in Example #1 was immersed for ten seconds in an aqueous impregnating solution containing per liter, 120 cc. of 30% by weight glyoxal solution, 1 gram oxalic acid, and 10 grams of potassium aluminum sulfate. 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 before impregnating. The dried, tentered fabric was then cured in circulating air at 260° F. for five minutes. The fabric after curing was removed from the pin-frame and subjected to two CCC—T—191—A 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 CCC—T—191—A wash test

	Inches Per Yard	
	1st Wash	2d Wash
Untreated Control	5.4	6.0
Treated	1.1	1.2

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 #5

The fabric used in the previous examples was immersed for ten seconds in an aqueous impregnating solution containing per liter 120 cc. of 30% glyoxal solution, 6 grams of oxalic acid, and 30 grams of a proprietary impermanent type of water repellent (wax-aluminum acetate emulsion) such as "Aquarol" (supplied by Arkansas Company). After the fabric was passed through this solution and 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 before impregnating. The dried, tentered fabric was then cured in circulating air at 260° F. for five minutes. The fabric after curing was removed from the pin-frame and subjected to two CCC—T—191—A 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 fabrics is shown below. The tensile strength and the abrasion resistance of the fabric were not appreciably affected by the process.

Warp shrinkage on washing CCC—T—191—A wash test

	Inches Per Yard	
	1st Wash	2d Wash
Untreated Control	5.4	6.0
Treated	1.0	1.0

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.

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 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. The improvement in resistance to creasing which is conferred on cellulose fabrics by reaction with glyoxal is, we believe, due to the cross-linking of molecular chains which occurs in this reaction with consequent reduction in the relative slippage of the molecular chains during transverse deformation.

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 de-

sired result 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 therefore not only economically unsound but is harmful to the fabric.

The acidity of the commercially available glyoxal solution (it usually has a pH of between 1.00 and 1.30) is not alone sufficient to cause a reaction with the regenerated cellulose. When such glyoxal is diluted with water in the preparation of the treating bath, the acidity decreases. For example, if a 30% by weight commercial glyoxal solution with a pH of about 1.12 is diluted with water having a pH of about 7.2 so as to contain about 120 cc. of such glyoxal per liter, 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 pH of a solution of 6 grams of oxalic acid per liter of water is about 1.65. The relative amounts of such glyoxal and acid catalyst in the solution can be varied within limits, which causes some variations in the acidity of the treating bath or liquid. The particular acid catalyst used also causes some variation in the acidity of the treating bath.

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.

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.

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 and to creasing and crushing produced by the process. Under certain circumstances a fabric may be treated with this process before dyeing or printing, although in general it will be satisfactory to perform the process after dyeing.

After the treatment of the regenerated 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.

It has been found that fabric treated in accordance with this novel method increases in weight by an amount practically equal to the weight of glyoxal applied. Thus a treatment with a solution containing 4.5% glyoxal, (120 cc. per liter of 30% solution), with a liquid pick-up by the fabric of 130% of its weigth, would result in a weight increase in the treated fabric of 5.85% of its original weight. If the glyoxal (solid base) used in the treating solution be from 1.1% to 7.5%, the fabric weight increase limits (with from 80% to 150% possible liquid pick-up) would be from 0.88% to 11.25%.

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

1. Regenerated cellulose: (*a*) Viscose; (*b*) Cuprammonium; (*c*) Saponified acetate.

2. Mixtures: Major part regenerated cellulose.

In the practice of the invention, the 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, relative to the rate of travel of the textile material, to give the desired liquid pick-up, 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 may be removed from the textile material, before the material is cured, 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, an aluminum salt which is soluble or readily dispersible in water, and an acid catalyst, the acidic component of which increases in acidity and is not eliminated when concentrated to dryness and subjected to temperatures just above

about 212° F., removing excess wetting liquid, then heating the textile material so wetted, after said removal of excess liquid, 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, an aluminum salt which is soluble or readily dispersible in water, and oxalic acid, removing the excess wetting liquid, then heating the textile material so wetted, after said removal of excess liquid, 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 2.5 and containing a mixture of glyoxal in approximately 1.12% to 7.5% by weight in the treating liquid, an aluminum salt which is soluble or readily dispersible in water, 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 above about 212° F., and said catalyst comprising approximately 0.1% to 2% by weight in the treating liquid, removing excess wetting liquid, then heating the textile material so wetted, after said removal of excess liquid 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.

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, a small amount of an aluminum salt which is soluble or readily dispersible in water, and oxalic acid in approximately 0.1% to 2% by weight in the treating liquid, removing excess treating liquid, and then heating the textile material so wetted, after said removal of excess liquid, 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 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, from 0.2 to 10 grams per litre of said liquid, of an aluminum salt which is soluble or dispersible in water, and oxalic acid in approximately 0.1% to 2% by weight in the treating liquid, removing excess wetting liquid, drying the treated fabric that is free of excess liquid, and then heating the textile material so wetted, after said removal of excess liquid, 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.

6. 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, less than about 10 grams (solid basis) per litre of said liquid of an aluminum salt which is soluble or dispersible in water, 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 above about 212° F., and said catalyst comprising approximately 0.1% to 2% by weight in the treating liquid, removing the excess wetting liquid, then heating the textile material so wetted, after said removal of excess liquid, to a temperature inversely related to the temperature, until a substantial reaction product of cellulose and glyoxal is formed in situ in the fibers of said material.

7. The method of stabilizing, against laundry shrinkage, textile materials formed predominantly of regenerated cellulose, which comprises wetting said materials with an aqueous solution having a pH between about 1.0 and 2.5 and containing glyoxal in approximately 1.12% to 7.5% by weight in said solution, an aluminum salt which is soluble or dispersible in water and becomes acid by dissociation in water, and sufficient added acidic catalyst to bring the pH of the solution to about 2.5 or less, removing the excess wetting solution, and heating the textile material so wetted, after said removal of excess solution, to a temperature above 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 materials.

8. The method of stabilizing against laundry shrinkage, textile materials formed predominantly of regenerated cellulose which comprises wetting said materials with an aqueous solution having a pH between about 1.0 and 2.5 and containing glyoxal in approximately 1.12% to 7.5% by weight in said solution, less than about 3% by volume of aluminum acetate solution containing 20% solids, and sufficient added acidic catalyst, the acidic component of which increases in acidity and is not eliminated when concentrated to dryness and subjected to temperatures just above about 212° F., to bring the pH of the solution below 2.5, removing excess wetting solution, and heating the textile material so wetted, after said removal of excess solution to a temperature above 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 materials.

9. The method of stabilizing against laundry shrinkage, textile materials formed predominantly of regenerated cellulose, which comprises wetting said materials with an aqueous solution having a pH between about 1.0 and 2.0 and containing glyoxal in approximately 1.12% to 7.5%

by weight in said solution, oxalic acid in approximately 0.1% to 2% by weight of said solution, and less than about 3% by volume of aluminum acetate solution containing 20% solids, removing excess wetting solution, and heating the textile material so wetted, after said removal of excess solution, to a temperature above 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 materials.

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