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STABILIZING CELLULOSIC TEXTILE MATERIALS AGAINST SHRINKAGE EMPLOYING GLYOXAL AND A METAL SILICOFLUORIDE AS A CATALYST

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

It also relates to the treatment of such designated textile materials to secure excellent stability against laundry shrinkage without incurring any appreciable loss in tensile strength or abrasion resistance.

The normal fabrics made from these 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 by conventionally employed processes in the industry 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, such as baking at elevated temperatures. This results in deterioration in tensile strength and abrasion which is especially serious in the case of cotton.

By a more recent development, cellulosic fibers and fabrics 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 and the shrinkage tendency significantly curbed in the case of cotton fabrics, the former displays a loss in the range of 20% in tensile strength, and the latter the range of 50%.

In the inventor's copending U. S. patent application Serial Number 722,955, filed January 18, 1947, which has become Patent 2,484,545, with issue date of October 11, 1949, this disadvantage is overcome by employing a substantially neutral water-soluble alkali metal salt of an acid whose oxidation potential in solution of unit activity referred to the normal hydrogen electrode at 25° C. is greater than -0.9 volt, such as the chlorate, nitrate of perchlorate, instead of oxalic acid. In his copending U. S. patent application, Serial

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Number 750,159, filed May 23, 1947, the use of an alkali metal sulfate to modify the catalytic action of the oxalic acid is described.

Broadly, it is an object of the present invention to secure the advantage of employing a solution of glyoxal to render textile materials, composed of natural cellulosic material or regenerated cellulose, stable against shrinkage yet mitigating the attendant disadvantages in loss of tensile strength and abrasion resistance in most presently employed commercial processes.

It is the object of the present invention to treat textile materials that are formed predominantly of natural cellulosic materials or regenerated cellulose with dilute aqueous solutions of glyoxal in the presence of a soluble inorganic salt of silicofluoric acid to stabilize them against shrinkage, but with no appreciable loss in tensile strength or abrasion resistance.

It is a more specific object of the present invention to secure stabilization of the aforesaid types of textile materials against shrinkage but without significantly impairing their tensile strength, wherein the fibers are wetted by a dilute solution of glyoxal and subsequently baked at 100° C. or higher until the desired shrinkage control has been secured i. e. a substantial reaction between the cellulose and glyoxal has taken place.

Other objects and features of the invention will be apparent from the following description:

Broadly speaking, my invention consists in employing certain inorganic salts of silicofluoric acid in catalyzing the glyoxal-cellulose reaction which must take place within the fibers of natural or regenerated cellulose if shrinkage resistance is to be attained when using glyoxal. In my invention the acidity of the impregnated goods decreases during baking of the goods at temperatures of 100° C. and above. In terms of pH values this means an increase of the pH, contrary to known methods where the pH decreases during concentration and baking. Also whereas the presence of oxalic acid increases the acidity of the aqueous impregnating glyoxal solution, the presence of magnesium silicofluoride decreases the acidity of the aqueous glyoxal impregnating solution, because an aqueous solution of this salt is not as acidic as the glyoxal solution. Furthermore as explained below, magnesium silicofluoride decomposes during the baking step to yield

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a more basic reacting component and a volatile acid component. The basic component which is formed on the cloth protects it, which would not be true in the case of a fixed acid component.

By the present invention, any form of textile material of the types described *infra* is thoroughly wetted with the aqueous solution of glyoxal in the presence of the silicofluoride, the excess liquid removed mechanically, the textile material then dried, and "cured" or baked at an elevated temperature until a substantial shrinkage reduction has been achieved. This shrinkage reduction may be explained as due to a reaction which is believed to have taken place in the fibers of the textile material, i. e. the glyoxal-cellulose reaction. The goods are then scoured, rinsed, hydroextracted and dried without tension. Finally the fabrics are steamed and framed to predetermined finished dimensions (as indicated by a laundering test). It will be understood, however, that these steps subsequent to the baking do not form part of the present invention.

As has been pointed out *supra* cellulosic textile materials treated by the present invention are characterized by permanent stability against shrinkage. Glyoxal (also known as oxaldehyde or ethandial, and whose structural formula is $\text{CHO}\cdot\text{CHO}$) is the agent which reacts with the cellulose and is responsible for conferring these properties. The inorganic salts of silicofluoric acid act as the catalyst to promote the reaction. Under the condition described herein glyoxal without the catalyst will not confer these properties.

While it appears that all metal salts of silicofluoric acid are suitable for use as catalysts, the water-solubility and hydrolysis rate impose some limitations on the selection of the salts of this group from an operating standpoint. Since it is generally desired that the color of the treated material should remain unchanged this makes certain of these salts undesirable.

The sodium-, and potassium-, and ammonium silicofluorides have each proven satisfactory but are difficult to handle because of their low solubility in water and aqueous solutions. The ammonium salts furthermore tend to yellow the fabric on curing.

Zinc-, magnesium-, and cadmium salts are suitable, and because they are highly water-soluble and do not have the secondary characteristic of discoloring the cellulosic fabrics, either natural or regenerated, they are the choice. In general, I prefer to use magnesium silicofluoride, commercially available as $\text{MgSiF}_6\cdot 6\text{H}_2\text{O}$, because of its ready solubility and its stability at moderate temperatures. That last expression will be understood to embrace the ranges up through 150°C . and somewhat above under the conditions of operation herein.

Moreover, I should like to point out that other metal salts of silicofluoric acid, such as nickel-, cobalt-, iron-, manganese-, or mercury are highly water-soluble and could be used if discoloration caused by the metallic ion is not objectionable for the ultimate purpose. In fact, it is possible by the use of these latter compounds to obtain simultaneously shrinkage control and mildew-resistance or rotproofing, and in some cases even water repellency, or flameproofing; this can be effected by precipitating the metallic salt by a suitable after-treatment, i. e. after baking, using alkali, soap, alkali phosphates or other basic chemical agents.

A possible explanation of the action of these

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compounds on curing, which is the stage of the process when the glyoxal-cellulose reaction takes place, is the decomposition of the silicofluoride as follows:



The volatile silicon fluoride acts as the reaction catalyst while the somewhat alkaline magnesium fluoride, which is formed directly on the cloth, acts as a buffer or protective agent for the cloth. It is thought that this is what transpires that makes it possible to carry out the reaction without loss in tensile strength or abrasion resistance.

In the aqueous wetting solution the suggested range for concentration of glyoxal is 1% to 10% inclusive of 100% glyoxal, preferably 1% to 5% inclusive, based upon the weight of the treating solution. When the quantity is less the goods treated by this process lacks significant shrinkage resistance. When the quantity exceeds 10% there is the risk of damage to the fabric, depending somewhat on the baking temperature and time. Technical glyoxal is sold as 30% by weight glyoxal, so the amount on the 100% basis will have to be computed. As to the catalyst, the amount of about 0.3% to 3.0% by weight of the aqueous impregnating solution, but preferably 0.5% to 2.0% inclusive, in terms of $\text{MgSiF}_6\cdot 6\text{H}_2\text{O}$, is the suggested range. The above percentages of concentration of glyoxal and the silicofluoride catalyst are each based upon a 100% pick up of liquid in reference to the weight of the goods.

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 moreover be successfully applied to mixtures of natural and regenerated cellulose as well as to either alone, or to mixtures containing either regenerated cellulose or natural cellulose with cellulose acetate, provided the fabric does not contain more than 50% cellulose acetate. The last may be replaced by other cellulose esters or organic acids, such as the propionate. By the term "regenerated cellulose" I mean viscose or cuprammonium rayon or saponified cellulose acetate. By the term "natural cellulose" I means such fibers as cotton, linen, hemp and jute, more particularly cotton. The textile materials coming within the preview of this invention are those composed of or predominantly of cellulose fibers of natural vegetative origin or of regenerated cellulose.

The treatment by this invention, and which is described in more detail 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 known aldehyde processes for shrinkproofing fibers of vegetable origin.

The regenerated and/or natural cellulose may be treated in any form, by which is meant filaments, fibers, staple or yarn; woven, knitted, braided or pretreated fabrics as well as clothing or other finished goods. And the term "textile material" unless otherwise qualified includes these.

The step of impregnating the fibers or filaments with the aqueous solution of glyoxal and silicofluoride may take place at any time subsequent to any desizing of the fabric which is to be treated. But all traces of starch, gums, glue or natural resin and other sizing agents should be removed for optimum results in order to per-

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mit the aqueous solution to penetrate the fibrous or filament material and enter the heart of the fibers.

The impregnation or wetting of the textile material with the aqueous liquid or solution can be accomplished in any desired manner, such as by immersion, spraying or coating by other modes. Usually this is done in a continuous manner, the amount applied being governed by the rate of travel of the textile material. The excess liquid should be removed before the drying step. This may be achieved by various mechanical means such as squeeze rolls, centrifugal devices or vacuum extractors. This allows a pick-up of a predetermined percentage, such as 100% liquid retention on the dry basis of the goods.

The drying and curing can, alternatively, be carried out as a single operation. But it is preferred to make two steps of this, and the description will be explained more fully as to that mode. The drying is carried out at low temperatures such as 70-100° C. and preferably at 100° C. although it could be at even lower temperatures, and until the moisture contact has been reduced to about 10%; this moisture limit is not exactly critical but the fabric should not be over-dry. For woven fabrics, this step is accomplished on a tenter frame.

The cellulosic textile material thus treated is then baked or "cured"—usually in a loop dryer without tension. While temperatures of 100° C. or just slightly above can be used, because of the element of time, a range of 130° C. to 150° C. with an inverse time interval of 6 to 2 minutes is preferred. It is of course essential that the time interval in this baking step be of sufficient duration that the treated textile material when subjected to the Federal CCC-T-191A test exhibits a substantial reduction in shrinkage in comparison to the untreated sample of the same material. Those temperature-time conditions giving the optimum stability against shrinkage will normally be selected. Selection and choice for optimum results is not confined to this step but is equally applicable to the conditions in each of the steps and the process as a whole however.

After the curing or baking step the textile material is washed without tension, dried, and finally framed to the dimensions indicated in a preliminary wash test. In some cases, overfeed devices in the final tentering operation are employed, but in other cases, it is necessary to apply some warpwise batching tension to counteract supercontraction in the previous drying operation. However the steps outlined in this paragraph are not part of the present invention, although they are supplemental operations before the textile material is put into industrial channels or trade.

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 impregnation 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 employed. Therefore, fabrics treated by my method show no tendency toward chlorine retention.

Fabrics of the natural cellulosic type or of the

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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. Fabrics of viscose or cuprammonium yarns so processed are further improved as borne out 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.

This invention will be more clearly understood by reference to the following examples. It is to be understood, however, that these examples are merely illustrative of the process, and that the invention is not limited thereto but rather is defined in the appended claims. In the examples the term "check" has the meaning of untreated or original. The term "total shrinkage" signifies the entire shrinkage occurring to the material (in either warp or filling direction) due to complete sequence of processing and wash testing, or wash testing alone in the case of untreated or check sample. The term "compression shrinkage" signifies the total shrinkage of an untreated or unprocessed material after the scouring and wash testing. The term "gain over compression shrinkage" signifies the advantage in length (or width) gained by use of the described process over that of a swatch which has not been subjected to the process, i. e. after both have been scoured and wash tested.

EXAMPLE 1

100% spun viscose rayon fabric treated

The impregnating solutions had the following compositions:

Components	Solutions	
	No. A	No. B
Glyoxal, 30 per cent technical.....grams.....	70	70
MgSiF ₆ ·H ₂ O.....do.....	15	20
Water.....liters.....	1	1

The magnesium silicofluoride was dissolved in water at about 38° C. (higher temperatures might result in some hydrolysis). A wetting agent may advantageously be added to these respective baths to reduce the time necessary for complete saturation, as was done in this example.

Two samples of the above fabric were impregnated on a padder with the above solutions No. A and No. B respectively. Each of them was then squeezed to a liquor retention of 100%, based on the weight of dry goods, and then dried without tension at about 100° C. Care was exercised to avoid over-drying (8% to 10% moisture should remain in the goods at this point).

After drying, the samples were each divided into two parts (A-1, A-2 and B-1, B-2) and cured as follows:

A-1 and B-1.....6 minutes at 138° C.
A-2 and B-2.....6 minutes at 127° C.

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The samples were thereupon washed, rinsed and dried. They were then laundered together with the check sample by the accelerated 1-hour wash test described in Federal Specification CCC-T-191A. The following shrinkages were observed based upon the measurements:

Warp shrinkage (in percentages)

Sample Identification	Treated and Scoured	1-hour wash ¹	Total Shrinkage ²	Gain over Compression Shrinkage
Check.....	-7.5	-1.5	-9.0	-----
A-1.....	-4.9	+0.8	-4.1	4.9
B-1.....	-3.9	+0.7	-3.2	5.8
A-2.....	-5.0	+1.6	-3.4	5.6
B-2.....	-4.6	+2.1	-2.5	6.5

¹ Measured from scoured dimensions.

² Measured from original dimensions.

The samples were subjected to tensile strength measurements, the values of which were:

Tensile strength (lbs. grab-test)

	Dry	Wet
Check.....	40	15
A-1.....	43	15
B-1.....	43	16
A-2.....	46	15
B-2.....	43	15

Conclusions

A considerable degree of permanent stabilization against shrinkage was obtained (see "gain over compressive shrinkage" column) without any loss in tensile strength.

EXAMPLE 2

100% spun rayon fabric treated

The impregnating solutions had the following compositions:

Components	No. 1	No. 2
Glyoxal, 30% tech.....grams..	70	70
MgSiF ₆ ·6H ₂ O.....do.....	15	20
Water.....liters..	1	1

The two solutions were made up, the samples of the fabric (designated No. 1 and No. 2 respectively) wetted with the above solutions respectively, squeezed to 100% retention and dried at about 100° C. as in Example 1. They were then cured for 3½ minutes at 150 C. They were then rinsed, scoured and dried and tested as in Example 1. In this case, laundering shrinkage was measured from the scoured dimensions.

Warp shrinkage (in percentage)

Sample Identification	Treated and Scoured	Successive 1 hr. washes ¹			Total Shrinkage ²	Gain Over Compression Shrinkage
		1st	2nd	3rd		
Check.....	-7.5	-1.4	-2.2	-4.2	-11.7	-----
No. 1.....	-3.9	-0.7	-0.6	0	-3.9	7.8
No. 2.....	-3.3	+0.6	-0.6	0	-3.3	8.4

¹ Measured from scoured dimensions.

² Measured from original dimensions.

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Warp tensile strength, pounds

Check.....	54
#1 (after 3rd wash).....	59
#2 (after 3rd wash).....	53

Conclusion

Again, excellent permanency against shrinkage was obtained, with no appreciable loss in tensile strength.

EXAMPLE 3

Samples of mercerized cotton fabric

The impregnating solutions had the following compositions in grams by weight:

Components	No. 1	No. 2
Glyoxal, 30% tech.....grams..	70	70
MgSiF ₆ ·6H ₂ O.....do.....	5	10
Water.....liters..	1	1

The two solutions were made up, the samples of the fabric immersed therein, squeezed to 100% retention and dried at about 100° C., similar to Example 1. They were then baked for 2½ minutes at 150° C., the same temperature as in Example 2. They were then washed and dried as in Example 1.

Warp shrinkage, per cent

Sample Identification	Treated and Scoured	Successive 1-hour washes ¹		Total Shrinkage ²	Gain Over Compression Shrinkage
		1st	2nd		
Check.....	-5.1	-1.3	-1.3	-6.4	-----
No. 1.....	-3.2	-0.6	-0.8	-4.0	2.4
No. 2.....	-3.3	-0.6	-0.8	-4.0	2.4

¹ Measured from scoured dimensions.

² Measured from original dimensions.

The samples were then subjected to tensile strength measurements.

Tensile strength (lbs., grab-test)

Check.....	54
#1.....	49
#2.....	44

Conclusions

Cotton was also permanently stabilized considerably, using a silicofluoride catalyst, with only slight loss of strength. This is in marked contrast with losses of about 50% when oxalic is used as in the prior art under the same conditions as herein.

EXAMPLE 4

Spun viscose rayon fabric treated

The wetting solution had the following composition: 70 gms. of glyoxal (30% tech.), 15 gms. magnesium silicofluoride (MgSiF₆·6H₂O) and 0.2 gm. "Igepal CTA extra" (a commercial polyethylene condensation product manufactured by General Dyestuff Corporation of New York city) per liter of water.

Three different types of spun viscose rayon fabrics designated Quality A, Quality B and Quality C, were impregnated with this solution, squeezed to 100% pick-up of solution and dried as in Example 1. They were then baked for 3 minutes at 150° C.

The samples were then washed, rinsed, scoured and dried as in Example 2.

Warp shrinkage, per cent

Sample Identification	Treated and Scoured	Successive 1 hr. washes ¹			Total Shrinkage ²	Gain Over Compression Shrinkage
		1st	2nd	3rd		
Quality A, check					-11.4	
Quality A, treated	-3.1	0	+0.5	0	-3.1	8.3
Quality B, check					-12.2	
Quality B, treated	-6.4	+0.6	+0.7	+0.7	-5.7	6.5
Quality C, check					-6.2	
Quality C, treated	-0.1	+0.3	+0.4	+0.4	-0.6	5.6

¹ Measured from scoured dimensions.

² Measured from original dimensions.

Qualities A and C were then subjected to both tensile strength and abrasion resistance measurements, the value of which were:

	Tensile Strength (Warp, lbs. Grab Test)	Abrasion Resistance (Taber Cycle)	
Quality A, check	71	275	300
Quality A, treated	71	275	300
Quality C, check	62	125	130
Quality C, treated	63	125	130

Conclusions

It is quite apparent that the spun viscose rayon fabrics have been quite satisfactorily rendered permanently stable against progressive shrinkage, while the tensile strength and abrasion resistance has not been lessened.

EXAMPLE 5

Spun rayon fabric treated

The impregnating solution had the following composition: 70 gms. of 30% tech. glyoxal, 10 gms. of sodium silicofluoride per liter of water.

A sample of the above fabric was impregnated with this solution at 40° C., squeezed to 100% pick-up of solution and dried as in Example 1. It was then baked at 300° C. for 3 minutes.

It was then washed, rinsed, scoured and dried as in the previous Examples 1 to 4, its tensile strength measured as in those examples or in its abrasion resistance as in Example 4.

EXAMPLE 6

100% spun rayon fabric treated

The impregnating solutions had the following compositions:

Components	Quantities	Quantities
Glyoxal, 30% tech.	grams	70
MgSiF ₆ ·6H ₂ O	do	15
ZnSiF ₆ ·6H ₂ O	do	17
"Icepal CTA"	do	0.5
Water	liters	1

The samples of the above fabric (designated #1 and #2 respectively) were impregnated with the above solutions respectively which had been made up as in Ex. 1. They were then squeezed and dried as in Ex. 1. They were then cured at 150° C. for 3½ minutes. This was followed by the rinsing, scouring and washing steps as previously

mentioned. In this case laundry shrinkage was measured from treated dimensions.

Warp shrinkage, per cent

Sample Identification	Successive 1-hr. washes ¹					Total ² Shrinkage	Gain Over Compression Shrinkage
	1st	2d	3d	4th	5th		
Check #1	-5.8	-5.8	-7.3	-7.4	-8.0	-8.0	
#1	-0.4	-0.1		-0.6	-0.6	-0.6	7.4
#2	-1.5			-0.6	-1.1	-1.1	6.9

¹ Measured from scoured dimensions.

² Measured from scoured dimensions.

From the above examples, it will be seen that by employing the silicofluoride catalysts which I have described, I have succeeded in obtaining rayon and cotton fabrics stabilized against laundry shrinkage, without appreciable diminution in the tensile strength or abrasion resistance of the fabric. On the other hand, baking such fabrics which have been impregnated with an aqueous solution of oxalic acid and glyoxal of 1.0-2.5 pH and containing the corresponding quantity of glyoxal per volume, followed by squeezing and drying wherein the treating conditions correspond in each, result in severe damage to cotton such as a loss of 30-60% in tensile strength or even more; and it frequently reduces the tensile strength of rayon by as much as 10 to 25%. This deleterious effect is described further in my U. S. Patent #2,484,545 of October 11, 1949, and my copending U. S. Patent application Ser. No. 750,159, filed May 23, 1947.

Because high temperatures in forming the solutions and in the wetting step may cause partial hydrolysis of the metallic silicofluoride such temperatures should be avoided. Because an excess of glyoxal and also of the silicofluoride are harmful to cellulosic fibers, the minimum quantity of each which will produce the desired shrinkage reduction without decrease in tensile strength should be used, taking into account the time and temperature.

In the claims the term "short chain aliphatic acid" embraces those not above four carbon atoms.

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.

Having described my invention, what I claim and desire to secure by Letters Patent protection is:

1. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 a short chain aliphatic organic acid, with an aqueous liquid containing substantially 1.0 to 10.0% glyoxal and a water-soluble metallic silicofluoride in an amount of at least substantially 0.3%, each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature above substantially 100° C. for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the un-treated textile material.

2. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 a short chain aliphatic organic acid, with an aqueous liquid containing substantially 1.0 to 10.0% glyoxal and a highly water-soluble metallic silicofluoride in amount of substantially 0.3-3.0%, each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

3. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 acetate, with an aqueous solution containing substantially 1.0% to 10.0% glyoxal and 0.3% to 3.0% of magnesium silicofluoride each by weight, on the basis of the treating solution, and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

4. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 acetate, with an aqueous solution containing substantially 1.0% to 3.0% of glyoxal and 0.5% to 1.5% of magnesium silicofluoride each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid then drying the textile material after said liquid removal, and curing it at between 130° and 150° C. substantially, for substantially 2 minutes to 6 minutes, the time being inversely related to the temperature.

5. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 a short chain aliphatic organic acid, with an aqueous liquid containing substantially 1.0 to 10.0% glyoxal and a silicofluoride of a member of group IIB of the periodic table (magnesium group) in amount of substantially 0.3-3.0%, each by weight, on the basis of the treating solution and a 100% pick-

up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

6. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 acetate, with an aqueous solution containing substantially 1.0% to 10.0% glyoxal and 0.3% to 3.0% of a silicofluoride of a member of group IIB of the periodic table (magnesium group) each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

7. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 a short chain aliphatic organic acid, with an aqueous solution containing substantially 1.0 to 10.0% glyoxal and a silicofluoride of a member of group VIII of the periodic table (iron group) in amount of substantially 0.3-3.0% each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

8. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile strength and abrasion resistance, 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 acetate, with an aqueous solution containing substantially 1.0 to 10.0% glyoxal and 0.3-3.0% of a silicofluoride of a member of group VIII of the periodic table (iron group) each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° C. and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

9. In the process of stabilizing a textile material against shrinkage upon washing in hot aqueous solutions without significant loss in tensile

strength and abrasion resistance, 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 a short chain aliphatic organic acid, with an aqueous liquid containing substantially 1.0 to 10.0% glyoxal and manganese silicofluoride in amount of substantially 0.3-3.0% each by weight, on the basis of the treating solution and a 100% pick-up based on the dry weight of the goods, mechanically removing surplus impregnating liquid, then drying the textile material after said liquid removal, and curing it at a temperature between 100° and 150° C. substantially, for a period of time inversely related to the temperature until there is a substantial reduction in shrinkage in comparison with the untreated textile material.

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