TREATMENT OF TEXTILE MATERIALS AND COMPOSITION THEREFOR

Carl W. Schroeder, Oakland, Calif., assignor to Shell Development Company, New York, N. Y., a corporation of Delaware

No Drawing. Application November 17, 1955 Serial No. 547,551

10 Claims. (Cl. 117—103)

This invention relates to the treatment of textile materials. More particularly, the invention relates to a method for treating textile materials to render them crease and shrink resistant.

Specifically, the invention provides a new and highly efficient method for treating textile materials to render them crease and shrink resistant which comprises impregnating the textile fabric with an aqueous solution containing an alkanal containing from 5 to 8 carbon atoms, and preferably glutaraldehyde, and a metal salt of an inorganic acid, as curing agent, and preferably a polyhydric alcohol, and then heating the impregnated fabric for a short period. The invention further provides improved textile fabrics prepared by the above-described process.

Many textile fabrics, such as those prepared from cotton and rayon, have rather poor resilience, i.e., they are easily creased or wrinkled when crushed or otherwise subjected to localized physical force. In addition, many of the fabrics have poor dimensional stability as exemplified by poor resistance to shrinkage. In order to overcome these shortcomings it has been common practice to treat the fabric with materials, such as urea- or melamine-formaldehyde resin and glyoxal that could be subsequently insolubilized within the fabric fibers. These materials, however, have certain disadvantages which have placed a considerable limitation on their utilization in this field. Some of these materials, for example, fail to give the high degree of crease and shrink resistance necessary for many applications. Others cause a permanent discoloration of the treated fabrics. Still others do not affect the color of the fabric initially but after the fabric has been bleached and ironed or hot-air dried, the fabric becomes charred or discolored. Still others give erratic results and are not reproducible. Still others weaken the fabrics, such as rayon, so that they have low tensile strength. In addition, many of the fabrics treated with these materials have a harsh feel and poor abrasion resistance. Many of the fabrics treated with the material also have poor washability, i.e., the material is easily lost from the fabric after a few washings with soap and water.

It is an object of the invention, therefore, to provide a new method for treating textile materials. It is a further object to provide a process for imparting unexpectedly high crease resistance to textiles such as rayon and cotton. It is a further object to provide a method for preparing crease resistant fabrics without causing discoloration of the fabric. It is a further object to provide a method for rendering textile materials crease resistant without having any deleterious effect on tensile strength. It is a further object to provide a method for rendering textile fabrics crease resistant which is reproducible, i.e., gives the same type of crease resistance on repeated operations. It is a further object to provide a method for rendering fabrics crease resistant without a harsh feel. Other objects and advantages of the invention will be apparent from the following detailed description thereof.

It has now been discovered that these and other objects may be accomplished by the novel process of the invention which comprises impregnating the textile fabric with an aqueous solution containing an alkanal containing from 5 to 8 carbon atoms and a metal salt of an inorganic acid as curing agent, and preferably a polyhydric alcohol, and then heating the impregnated fabric to a relatively high temperature for a short period.

Fabrics treated in this manner, even with relatively small quantities of the alkanaldehydes, have excellent resistance to creasing and improved resistance to shrinkage. Surprisingly, these properties are obtained by the above-described treatment with little or no loss of other desired properties, such as color and strength, which loss generally occurs with the addition of the above-mentioned conventional crease-proofing agents and particularly glyoxal, with fabrics such as rayon. The fabrics treated according to the above method are soft and have a good hand and excellent abrasion resistance. It has also been found that the fabrics treated with these alkanaldehydes have no ability to retain chlorine and the treated fabrics may be bleached or otherwise exposed to chlorine without danger of being discolored, charred or weakened during subsequent heat treatments. Finally, the above-described process is reproducible and gives some superior results after every operation.

The crease and shrink proofing agents employed according to the process of the invention comprise the alkanaldehydes containing from 5 to 8 carbon atoms, such as glutaraldehyde, adipaldehyde and suberinaldehyde. Glutaraldehyde is by far the more preferred alkanaldehyde to be used in the process.

The alkanaldehydes are applied to the fabric in the form of an aqueous solution. The alkanaldehydes are generally water soluble and the aqueous solutions may be prepared by merely mixing the alkanaldehydes with water. In other cases, it may be helpful to add solvents, such as acetone, ethyl alcohol and dioxane to the water, or to employ emulsifying agents to assist in the formation of the water solution. If emulsifying agents are employed, they are preferably those that are free of nitrogen and strong acidic groups, such as the monooleate of sorbitan polyoxyethylene, the trioleate of sorbitan polyoxyethylene, sorbitan tristearate, sorbitan monolaurate, polyoxyethylene esters of alkylphenols, carboxymethylcellulose, starch, gum arabic, polyvinyl alcohol, acryl and alkylated acryl sulfonates, such as cetyl sulfonate, oleyl sulfonate, sulfonated mineral oils, copolymers of vinyl methyl ether, maleic anhydride and the like, and mixture thereof. The emulsifying agents are generally employed in amounts varying from 0.1% to 10% by weight and more preferably from 1% to 5% by weight.

The amount of the alkanaldehydes to be employed in the impregnating solution will vary depending chiefly on the amount of alkanaldehyde to be impregnated on the fabric and this in turn will depend upon the number of applications and the pick-up allowed per application. As indicated hereinafter, the amount of material to be applied to the fabric will generally vary from about 3% to about 20% for soft goods. If a 100% pick-up is allowed and the solution is applied but once, the impregnating solution should contain the material in amounts varying from 3% to 20% in order to apply these same percentages to the cloth. On the other hand, if say only a 50% pick-up is allowed and the solution applied but once, the impregnating solution should contain the material in amounts varying from 6% to 40% in order to apply the material in the preferred amounts of 3% and 20%. In
general application, the solution is usually applied but once with pick-ups varying from 55% to 100%.

The impregnating solution is a metal salt of an inorganic acid such as sulfates of metals having an atomic weight between 24 and 210 and inorganic acids the anion portion of which contains at least two dissimilar elements having an atomic weight above 2. The metals used in preparing such salts include, among others, magnesium, potassium, copper, zinc, aluminum, nickel, cadmium, strontium, vanadium, barium, calcium, iron, cobalt, chromium and the like. The particularly preferred metals are those of groups I to IV and VIII of the periodic table of elements, such as aluminum, zinc, magnesium, mercury, tin, calcium, copper, potassium, iron, nickel, lead and cobalt. Particularly preferred are the non-alkali metals having an atomic weight between 24 and 207.

The acid portion of the above-described salts may be any monobasic or polybasic inorganic acid the anion portion of which contains at least two dissimilar elements having an atomic weight above 2. One of the dissimilar elements in the anion radical is preferably a non-metal (e.g., as described in chapter VI of Ephraim "Inorganic Chemistry," 1939 edition), such as boron, silicon, sulfur, nitrogen, selenium, tellurium and phosphorus. One of the other dissimilar elements is preferably an element which tends to gain electrons in its outer orbit and thereby assume a negative charge, such as oxygen, fluorine and chlorine. Oxygen, for example, has only 6 electrons in the L level and tends to gain two electrons to complete the level. Fluorine has 7 electrons in the L level and tends to gain one electron to complete that level.

Examples of the above-described acids include among others, fluoboric acid, persulfuric acid, sulfuric acid, fluoberyllic acid, boric acid, hydrochlorous acid, iodic acid, periodic acid, phosphoric acid, phosphorous acid, selenic acid, arsenic acid, telluric acid, fluosilicic acid, silicic acid, magnesium and the like.

Preferred acids are those of the general formula

$$H_2(\text{X})\text{a}(\text{Z})_b$$

wherein X is a non-metal having an atomic weight above 2, Z is an element which tends to gain from 1 to 2 electrons in its outer orbit, w is an integer, y is an integer greater than 1, and a equals the valency of the radical (X)a(Z)b, such as sulfuric acid, fluoroboric acid, fluorosilicic acid, persulfuric acid, phosphoric acid and the like.

Examples of the salts that may be used as curing agents include, among others, zinc fluoroborate, magnesium perchlorate, copper fluoroborate, zinc fluoroborate, cupric chloride, cupric chromate, cupric fluorosilicate, cupric iodate, cupric nitrate, cobaltous nitrate, lead borate, calcium phosphate, magnesium chloroplatinate, cadmium borate, nickel sulfate, stannic fluoroborate, zinc carbonate, aluminum sulfate, ferric phosphate, ferrous sulfite, mercuric sulfate and the like and mixtures thereof.

The amount of the curing agent employed will vary depending upon the type of agent selected. In general, the amount of the curing agent will vary from about 0.5% to 30% by weight of the polyaldehyde. Preferably the curing agent is used in amounts varying from 1% to 15%.

Unexpected resistance to discoloration of the cloth is also obtained by adding polyhydric alcohols to the aqueous medium containing the di-aldehydes. Examples of such alcohols, include, among others, glycerol, 1,2,6-hexanetriol, 1,4-dihydroxycesolohexane, pentaerythritol, trimethylolpropane, sorbitol, mannotol, trimethylene glycol, hexylene glycol, inositol, ethylene glycol, and the like. Particularly preferred additives of this type are the aliphatic and cycloaliphatic polyhydric alcohols containing from 2 to 6 hydroxyl groups, and no more than 12 carbon atoms. Especially preferred are the alkanediols, alkanetriols and alkane tetrols containing up to 8 carbon atoms. The alcohols are preferably added to the aqueous medium in amounts varying from 20 to 40 parts per hundred parts of dialdehyde, and more preferably in amounts varying from 20 to 30 parts per hundred parts of dialdehyde.

The solution employed in the treatment of the textile fabrics according to the process of the invention may also contain plasticizers to improve the flexibility of the fabrics, although these should not be present in such proportions as to render the finished fabrics soft or sticky at temperatures and humidities to which they may be exposed. It is found, however, that the substances employed in the present invention yield products which are sufficiently flexible for most purposes without the use of plasticizers. Among plasticizers that may be used according to the present invention may be mentioned organic and inorganic derivatives of phenols, for example, diphenyl propane and triphenyl and tricresyl phosphates, alkyl phthalates, derivatives of polyhydric alcohols, such as mono-, di- and tri-acetin. The compositions may also contain natural resins, and other nitrocelluloses and synthetic or semi-synthetic resins, e.g., ester gum, polyhydroxy-polysylic acid resins, phenol aldehyde and urea-aldehyde resins.

Textile softening agents may also be added in varying amounts to improve the feel of the treated fabrics. Examples of these agents include, among others, pentadecyl phenol, octadecyl succinic acid, octadecenyl succinic acid, sulfonated waxes and sulfonated alcohols, dimerized long-chain unsaturated acids, non-ionic fatty acid esters of higher polyglycerols.

Other crease-proofing agents or resins utilized for treating fabrics, such as for example urea-aldehyde, melamine-aldehyde, ketone-aldehyde and phenol-aldehyde resins, glyoxal and the like, may also be employed in combination with the polyaldehydes in the padding solution.

The process gives highest results when padding solution is acidic between pH 2 and 7. The pH may be adjusted to the desired level by adding buffering materials, such as sodium oxalate, amines, etc.

The application of the aqueous solution containing the alkanaldehyde and curing agent to the textile fabric may be effected in any suitable manner, the method selected depending upon the results desired. If it is desired to apply the solution only to one surface of the material, as, for example, when it is desired to treat the back only of a fabric having a face of artificial or natural silk and a cotton back, the application may be effected by spraying or by means of rollers, or the composition may be spread upon the surface by means of a doctor blade. When, however, it is desired to coat both surfaces of the material, or if the material is to be thoroughly impregnated with it, the fabric may be simply dipped in the solution or run through conventional-type padding rollers. The solutions may also be applied locally to the material, for example, by means of printing rollers or by stencilling.

The amount of the alkanaldehyde to be deposited on the fabric will vary over a wide range depending upon the degree of wrinkle resistance and shrink resistance desired in the finished material. If the fabric is to have a soft feel, such as that intended for use for dresses, shirts, etc., the amount of alkanaldehyde deposited will generally vary from 3% to 20% by weight of the fabric. If stiffer materials are required such as for the shoe fabrics, draperies, and the like, still higher amounts of the alkanaldehyde, such as of the order of 25% to 50% by weight may be deposited.

If the desired amount of the alkanaldehyde deposited in the fabric is not obtained in one application, the solution can be applied again or as many times as desired in order to bring the amount of the alkanaldehyde up to the desired level.

After the desired amount of solution has been applied to the fabric, the treated fabric is preferably dried for a short period to remove some or all of the dispersing liquid, such as water, and the like. This is generally accomplished by exposing the wet sheets to hot gas either
slack or framed to dimension at temperatures ranging up to 120° C. The period of drying will depend largely on the amount of pick-up permitted during the application of the solution, and the concentration of the alkali-
dial. In most instances, the drying periods of from 1 to 30 minutes should be sufficient.

The dried fabric is then exposed to relatively high tem-
peratures to accelerate the cure of the alkali-dial. Tem-
peratures used for this purpose generally range from
100° C. to 200° C., and preferably from 130° C. to
190° C. At these preferred temperature ranges the cure
may generally be accomplished in from 1 to 10 min-
utes. Exposures of less than 3 minutes, e. g., 1 minute, may probably be used in continuous, commercial proc-
cessing.

The process of the invention may be applied to the treatment of any textile fabric, colored or white, pre-
pared from fibers having reactive groups, such as OH
groups, amine groups, carboxyl groups and the like. Ex-
amples of such materials include cotton, wool, regen-
erated cellulose (rayon), hydroxy-containing cellulose
acetate, mixtures thereof and mixtures of these materials
without fiber-forming materials, such as ethylene glycol-
terephthalate, acid polysters (Dacron), the acrylic poly-
vinyls, such as for example the acrylonitrile polymers
(Arkon), the polyethylenes, polyurethanes (Perluran),
polymers (Cotwood), however, non-acrylic poly-
vinyls, vinyl chloride and vinylidene polymers (Vin-
yon), mineral fibers (Fiberglas) polyamides, such as the
aliphatic dicarboxylic acid-polyamides reaction prod-
ucts (nylon). While the invention has been particularly
described with relation to the treatment of woven fabrics,
it may also be applied to other materials, for example,
knitted or netted fabrics.

The materials treated according to the process of the
invention will have excellent crease resistance and im-
proved dimensional stability and may be used for a wide
variety of important applications. The woven cotton,
rayon and wool fabrics, both colored and white, con-
taining conventional amounts of resin, e. g., from 3% to 25%
by weight, may be used, for example, in the preparation of
soft goods, such as dresses, shirts, coats, sheets, and
the like, while the fabrics containing much larger amounts
of resin, e. g., 25% to 50% may be used in other ap-
plications demanding more crispness and fullness such as
the preparation of rugs, carpets, drapes, upholstery,
shoe fabrics, and the like.

To illustrate the manner in which the invention may be
handled out, the following examples are given. It is to
be understood, however, that the examples are for the
purpose of illustration and the invention is not to be
regarded as limited to any of the specific materials or
conditions recited therein.

The wrinkle recovery values reported in some of the
examples were determined by the Monsanto recovery
method. The tests were carried out at 65° relative hu-
midity and 70° F. Unless otherwise indicated, parts disclosed in the ex-
amples are parts by weight.

**Example I**

This example demonstrates the superiority of glutar-
aldehyde as a crease-proofing agent for rayon.

50 parts of a 30% aqueous solution of glutar-
aldehyde and 1.12 parts of magnesium perchlorate were added to 50 parts of water. Rayon cloth (filament vis-
 Wo) was then immersed in this solution, and impregnated with this solution by means of a Butterworth 3-roll laboratory paddler (100% pick-
up). The impregnated cloth was dried at 60° C. for 5

minutes and cured at 160° C. for 5 minutes. The treated cloth was then washed in a 0.31% solution of Ivory

Flakes and 0.0635% Na₂CO₃ solution at 70° C. for 12

minutes and then rinsed three times in warm water to
remove any soluble material.

The cloth treated in the above-described manner had

a soft feel, good abrasion resistance, no chlorine reten-
tion and good washability. The wrinkle recovery (av-

gerage warp and fill) was 165 compared to a value of

100 for the control. A similar sheet of rayon treated

with glyoxal according to the above procedure had a

wrinkle recovery value of 122, and a similar sheet of

rayon treated with ala-hydroxydipaldehyde had a wrinkle

recovery value of 132.

Similar results are obtained by replacing the magne-
sium perchlorate with equal amounts of the follow-
ing: zinc fluoborate, cadmium fluoborate and cop-
per fluoborate.

**Example II**

Example I was repeated with the exception that the

aqueous medium contained 20 parts of glycerol per 100

parts of glutaraldehyde. In this case, the treated cloth

had a much whiter color and better resistance to discol-

oration after bleach and scouring. The treated cloth also

had soft feel, good abrasion resistance, good wash-

ability and excellent wrinkle and shrink resistance.

**Example III**

16 parts of a 30% aqueous solution of glutaraldehyde

and 0.5 part of magnesium perchlorate were added to

84 parts of water and this mixture applied to filament

viscose rayon as in Example I. In this case, the rayon

treated with the glutaraldehyde also had the same color

as before the treatment, a soft feel, good abrasion resis-
tance and good washability. The cloth had a wrinkle

recovery of 125 as compared to a value of 111 for alpha-

hydroxydipaldehyde treated rayon.

**Example IV**

50 parts of a 30% aqueous solution of glutaraldehyde

and 1.12 parts of magnesium perchlorate were added to

50 parts of water. Spun viscose rayon was then im-

pregnated with this solution by means of a Butterworth

3-roll laboratory paddler (100% pick-up). The impreg-

nated cloth was dried at 60° C. for 5 minutes and cured

at 160° C. for 5 minutes. The treated cloth was then

washed in a 0.31% solution of Ivory Flakes and 0.0635%

Na₂CO₃ solution at 70° C. for 12 minutes and then

rinsed three times in warm water to remove any soluble

material.

The cloth treated in the above-described manner had

a soft feel, good abrasion resistance, no chlorine reten-
tion and good washability. The wrinkle recovery was 152

compared to a value of 100 for the control. A similar

sheet of rayon treated with glyoxal according to the

above process had a wrinkle recovery value of 137, and

a similar sheet of rayon treated with alpha-hydroxy-
dipaldehyde had a wrinkle recovery value of 143.

Similar results are obtained by replacing the magne-
sium perchlorate in the above process with equal amounts

of each of the following: zinc fluoborate, aluminum sul-
fate and copper fluoborate.

**Example V**

33 parts of a 30% aqueous solution of glutaraldehyde

and 1.12 parts of magnesium perchlorate were added to

67 parts of water and this mixture applied to the spun

viscose rayon cloth as in Example III. In this case, the
treated cloth had good color, a soft feel, good abrasion

resistance and good washability. The cloth had a wrinkle

recovery value of 148 as compared to 137 for cloth

treated with alpha-hydroxydipaldehyde and 127 for cloth

treated with glyoxal.

**Example VI**

33 parts of a 30% aqueous solution of glutaraldehyde

and 1.12 parts of zinc fluoborate are added to 67 parts of

water. 5.6 yd./lb. white cotton gingham (80 x 80

count) cloth is then impregnated with this solution by

means of a Butterworth 3-roll laboratory paddler (100%

pick-up). The impregnated cloth is dried at 60° C. for 5

minutes and cured at 160° C. for 5 minutes. The fin-

ished cloth proved to have excellent wrinkle and

shrink resistance.
ished product is then washed in a 0.13% solution of Ivory Flakes and 0.065% Na₂CO₃ solution at 70° C. for 12 minutes and then rinsed three times in warm water to remove any soluble material.

The cloth treated in the above-described manner has good color and a soft feel, excellent crease resistance, good washability and no chlorine retention.

Similar results are obtained by replacing the zinc fluoroborate in the above process with an equal amount of each of the following: magnesium perchlorate, aluminum sulfate and zinc fluoroborate.

Example VII

50 parts of a 30% solution of glutaraldehyde, 1.12 parts of magnesium perchlorate, and 15 parts of glycerine are added to 50 parts of water and this solution applied to cotton cloth as in Example III. In this case the treated cloth had much whiter color and better resistance to discoloration after bleach and scouring and had a soft feel, excellent crease resistance, good washability and no chlorine retention.

Similar results are obtained by replacing the magnesium perchlorate with each of the following catalysts: cadmium fluoroborate, zinc sulfate and calcium fluoroborate.

I claim as my invention:

1. A process for rendering textile fabrics more crease and shrink proof which comprises impregnating the fabric with an aqueous solution containing as the sole polymerizable component glutaraldehyde and a salt of a non-alkali metal having an atomic weight between 24 and 207 and an acid of the group consisting of fluoboric acid, boric acid, fluosilicic acid, sulfuric acid, persulfuric acid, phosphoric acid, perchloric acid, chloric acid, chromic acid and nitric acid as curing agent and heating the resulting impregnated fabric to a relatively high temperature for a short period.

2. A process as in claim 1 wherein the aqueous solution also contains a polyhydric alcohol.

3. A process as in claim 1 wherein the fabric is cotton.

4. A process as in claim 1 wherein the fabric is rayon.

5. A process for rendering textile fabrics more crease and shrink proof which comprises impregnating the fabric with an aqueous solution containing as the sole polymerizable component glutaraldehyde, from 1% to 20% by weight of a salt of a non-alkali metal having an atomic weight between 24 and 207 and an acid of the group consisting of fluoboric acid, boric acid, fluosilicic acid, sulfuric acid, persulfuric acid, phosphoric acid, perchloric acid, chloric acid, chromic acid and nitric acid as curing agent and heating the resulting impregnated fabric to a relatively high temperature for a short period.

References Cited in the file of this patent

UNITED STATES PATENTS

1,219,451 Gardos Mar. 20, 1917
2,350,350 Gresham June 6, 1944
2,411,818 Weiss Nov. 26, 1946
2,436,076 Pfeffer Feb. 17, 1948
2,541,457 Beer Feb. 13, 1951
2,548,455 Walker Apr. 10, 1951
2,752,259 Condo et al. June 26, 1956
2,774,691 Schroeder et al. Dec. 18, 1956

FOREIGN PATENTS

1,058,002 France Nov. 4, 1953