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2,826,514

TREATMENT OF TEXTILE MATERIALS AND
COMPOSITION THEREFOR

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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 alkanedial 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 afore-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 a 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 inven-

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tion 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 alkanedial 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 alkanedials, have excellent resistance to creasing and improved resistance to shrinkage. Surprisingly, these properties are obtained by the above-described treatment with little if any loss of other desired properties, such as color and strength, which loss generally occurs with the addition of the above-noted conventional crease-proofing agents and particularly glyoxal, with fabrics such as rayon. The fabrics treated according to the above-described process have a soft feel and good hand and excellent abrasion resistance. It has also been found that the fabrics treated with these alkanedials 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-noted 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 alkanedials containing from 5 to 8 carbon atoms, such as glutaraldehyde, adipaldehyde and suberaldehyde. Glutaraldehyde is by far the more preferred alkanedial to be used in the process.

The alkanedials are applied to the fabric in the form of an aqueous solution. The alkanedials are generally water soluble and the aqueous solutions may be prepared by merely mixing the alkanedials 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, aryl and alkylated aryl 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 alkanedials to be employed in the impregnating solution will vary depending chiefly on the amount of alkanedial to be deposited 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

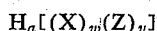
general application, the solution is usually applied but once with pick-ups varying from 55% to 100%.

The curing agent added to the impregnating solution is a metal salt of an inorganic acid such as salts 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, selenious acid, arsenic acid, telluric acid, fluosilicic acid, silicic acid, manganic acid, and the like.

Preferred acids are those of the general formula



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 $(X)_w(Z)_y$, such as sulfuric acid, fluoboric acid, fluosilicic acid, persulfuric acid, phosphoric acid and the like.

Examples of the salts that can be used as curing agents include, among others, zinc fluoborate, magnesium perchlorate, copper fluoborate, zinc fluoborate, cupric chlorate, cupric chromate, cupric fluosilicate, cupric iodate, cupric nitrate, cobaltous nitrate, lead borate, calcium phosphate, magnesium chloroplatinate, cadmium borate, nickel sulfate, stannic fluoborate, zinc chlorate, 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 dialdehydes. Examples of such alcohols, include, among others glycerol, 1,2,6-hexanetriol, 1,4-dihydroxycyclohexane, pentaerythritol, trimethylolpropane, sorbitol, mannitol, 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 alkanetetrols 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 materials 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, diphenylol 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 natural resins and synthetic or semi-synthetic resins, e. g., ester gum, polyhydroxy-polybasic 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 a pH of 2 to 7. The pH may be adjusted to the desired level by adding buffer materials, such as, sodium oxalate, amines, etc.

The application of the aqueous solution containing the alkanedial 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 alkanedial 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 alkanedial 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 alkanedial, such as of the order of 25% to 50% by weight may be deposited.

If the desired amount of the alkanedial 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 alkanedial 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

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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 alkanedial. In most instances, the drying periods of from 1 to 30 minutes should be sufficient.

The dried fabric is then exposed to relatively high temperatures to accelerate the cure of the alkanedial. Temperatures used for this purpose generally range from 100° C. to 200° C., and more preferably from 130° C. to 190° C. At these preferred temperature ranges the cure can generally be accomplished in from 1 to 10 minutes. Exposures of less than 3 minutes, e. g., 1 minute, may probably be used in continuous, commercial processing.

The process of the invention may be applied to the treatment of any textile fabric, colored or white, prepared from fibers having reactive groups, such as OH groups, amine groups, carboxyl groups and the like. Examples of such materials include cotton, wool, regenerated cellulose (rayon), hydroxy-containing cellulose acetate, mixtures thereof and mixtures of these materials without fiber-forming materials, such as ethylene glycol-terephthalate, acid polyesters (Dacron), the acrylic polyvinyls, such as for example the acrylonitrile polymers (Arlon), the polyethylenes, polyurethanes (Perluran), proteins (Caslen), alginic (alginate rayon), non-acrylic polyvinyls, vinyl chloride and vinylidene polymers (Vinyon), mineral fibers (Fiberglas) polyamides, such as the aliphatic dicarboxylic acid-polyamides reaction products (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 improved dimensional stability and may be used for a wide variety of important applications. The woven cotton, rayon and wool fabrics, both colored and white, containing 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 the resin, e. g., 25% to 50% may be used in other applications demanding more crispness and fullness such as the preparation of rugs, carpets, drapes, unholsteries, shoe fabrics, and the like.

To illustrate the manner in which the invention may be carried 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 humidity and 70° F.

Unless otherwise indicated, parts disclosed in the examples are parts by weight.

Example I

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

50 parts of a 30% aqueous solution of glutaraldehyde and 1.12 parts of magnesium perchlorate were added to 50 parts of water. Rayon cloth (filament viscose) was then impregnated with this solution by means of a Butterworth 3-roll laboratory padder (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 0.065% 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 had

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a soft feel, good abrasion resistance, no chlorine retention and good washability. The wrinkle recovery (average warp and fill) was 163 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 122, and a similar sheet of rayon treated with alba-hydroxyadipaldehyde had a wrinkle recovery value of 132.

Similar results are obtained by replacing the magnesium perchlorate with equal amounts of each of the following: zinc fluoborate, cadmium fluoborate and copper 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 discoloration after bleach and scorching. The treated cloth also had soft feel, good abrasion resistance, good washability 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 resistance and good washability. The cloth had a wrinkle recovery of 125 as compared to a value of 111 for alpha-hydroxyadipaldehyde 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 impregnated with this solution by means of a Butterworth 3-roll laboratory padder (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 0.065% 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 had a soft feel, good abrasion resistance, no chlorine retention 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-hydroxyadipaldehyde had a wrinkle recovery value of 143.

Similar results are obtained by replacing the magnesium perchlorate in the above process with equal amounts of each of the following: zinc fluoborate, aluminum sulfate 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-hydroxyadipaldehyde 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 padder (100% pick-up). The impregnated cloth is dried at 60° C. for 5 minutes and cured at 160° C. for 5 minutes. The fin-

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ished product is then washed in a 0.13% solution of Ivory Flakes and 0.065% Na_2CO_3 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 fluoborate in the above process with an equal amount of each of the following: magnesium perchlorate, aluminum sulfate and zinc fluoborate.

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 scorching 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 fluoborate, zinc sulfate and calcium fluoborate.

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 compound 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, sul-

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furic acid, persulfuric acid, phosphoric acid, perchloric acid, chloric acid, chromic acid and nitric acid as curing agent and 20 parts to 40 parts (per 100 parts of glutaraldehyde) of an aliphatic polyhydric alcohol and heating the resulting impregnated fabric to a temperature above 100° C. for a short period.

6. A process as in claim 5 wherein the catalyst is magnesium perchlorate.

7. A process as in claim 5 wherein the catalyst is zinc fluoborate.

8. A process for rendering cellulosic fabrics more crease and shrink proof which comprises impregnating the cellulosic fabric with an aqueous solution containing as the sole polymerizable component glutaraldehyde, 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 a polyhydric alcohol as to deposit from 3 to 20 parts of the glutaraldehyde on the fabric and heating the resulting impregnated fabric to a relatively high temperature for a short period.

9. A process as in claim 8 wherein the polyhydric alcohol is glycerol.

10. A composition for treating textile fabrics to render them more crease resistant comprising an aqueous medium containing as the sole polymerizable component glutaraldehyde, 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.

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