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PROCESS FOR CREASE-PROOFING CELLULOSIC FABRICS

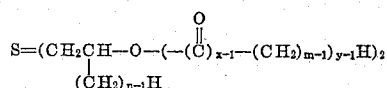
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14 Claims. (Cl. 8-116)

The present invention concerns crease-proofing cellulosic fabrics by the application thereto of compounds of the class of thiodiglycols and esters and ethers thereof.

The compounds with which the cellulosic fabrics are treated in accordance with the present invention are sulfides having the formula



wherein

m is an integer having a value of 1 to 19,

n is an integer having a value of 1 to 2,

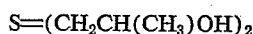
x is an integer having a value of 1 to 2, and

y is an integer having a value of 1 to 2.

Examples of these compounds are thiodiglycol of the formula



bis-(2-hydroxypropyl)sulfide of the formula



the esters of these glycols with organic acids, such as the aliphatic the acids having 1 to 18 carbon atoms, and the ethers of these two glycols with aliphatic alcohols having from 1 to 18 carbon atoms. The diesters formed with formic or acetic acid are especially useful; of the ethers, the dimethyl or diethyl ethers are preferred. The preferred compounds are those of Formula I in which m has a value not over 2.

In the utilization of the compounds of Formula I for the modification of cellulosic fabrics for crease-proofing, crush-proofing, reduction of shrinkage and stabilization against dimensional changes on washing, the following advantages occur. The cellulosic products contain oxygen only in the form of hydroxyl and ether linkages, no ester linkages being present, so that the products are characterized by excellent resistance against alkali. Because of the resistance to alkali, the treated cellulosic fabrics retain their improvement in crease-resistance and shrinkage-reduction even after washing in the usual detergents which are commonly alkaline in character. The treated cellulosic products are also resistant to ordinary acid souring applied in laundries after the washing and rinsing stages. The cellulosic products obtained by treatment with the compounds are not subject to chlorine damage. Since they do not retain chlorine, the use of bleaching agents containing chlorine does not cause deterioration either by way of discoloration or loss in tensile strength even when the treated fabrics which have been bleached are subjected to ironing temperatures. The cellulosic products obtained by treatment with the new compounds are also insoluble because of their cross-linked character so that the improvements in shrinkage and crease-resistance are obtained even after dry-cleaning operations. The treated fabrics also retain excellent hand and feel.

The treatment of the cellulosic fabrics with the sulfides in accordance with the present invention may be effected most advantageously by means of aqueous solutions, dispersions, or emulsions in which the sulfide is dissolved,

2

dispersed or emulsified at a concentration which may vary from 1 to 30% by weight. Preferably, the concentration is from 5 to 15% to obtain the maximum benefits in crease-proofing and shrinkage reduction. The treatment may be carried out in the presence of a catalyst. As a catalyst there may be used metal salts of acids having the composition $H_a(XY_b)$, where H is hydrogen, a is an integer which depends on the valence of the complex ion and may have a value of 1 to 3, X is a non-metal selected from the group consisting of boron, silicon, sulfur, and chlorine, said non-metal being in a state where its valence is from 3 to 7, Y is fluorine or oxygen, and b is an integer having a value of 4 or 6. The metals of these salts are those of groups Ib, II, IIIb, IV, and VIII of the periodic table in T. Moeller, "Inorganic Chemistry," John Wiley & Sons, New York, 1952, which have an atomic weight of at least 12. Salts of perchloric and fluoboric acids are very efficient catalysts, particularly their zinc, lead, copper, and magnesium compounds. Salts of sulfuric acid, such as aluminum and copper sulfate, and of fluosilicic acid, such as magnesium, zinc, and copper fluosilicates, also are active as catalysts. Other acidic compounds, such as phosphoric acid and sodium bisulfate, may also be used as catalysts.

Conveniently, the amount of catalyst may vary from about 0.2% to 5% and is preferably in the range of 0.5% to 1% concentration in the aqueous solution of the sulfide.

The catalyzed solution, dispersion, or emulsion of the sulfide is compatible with solutions or dispersions of most of the common textile finishing agents, such as synthetic polymer latices and aminoplast resins or precondensates, so that they may be applied with the sulfide to produce changes in the hand or other properties of the fabric.

The aqueous solution, dispersion, or emulsion containing the sulfide and catalyst may be applied to the fabric in any suitable manner such as by spraying or impregnation. In general, it is preferable to use some method of impregnation. With piece goods, this is conveniently carried out with the various machines used for treating fabrics in open width, such as pads or jigs. However, it is not required that the impregnation be carried out in open width, and the fabric may be handled in any form. In treating garments or other articles made from cellulosic fabrics, the impregnation may be carried out in a tumble wheel, laundry machine, or other suitable equipment. After application of the solution, dispersion, or emulsion, it is desirable to remove any excess by squeezing the fabric between rollers, or by shaking or centrifuging it, in order to insure a more even treatment. The treated fabric may then be dried, such as by air-drying at normal room temperature or by heating in a drying oven at temperatures of 140° F. and up. The drying and curing operations are preferably done with the fabric open and flat, so that it will have a smooth and even appearance when finished. In a preferred embodiment, the impregnated fabric, immediately after impregnation and without preliminary low-temperature drying is carried in open width by a tenter frame through a curing oven where it is subjected to temperatures of about 212° F. to about 450° F. or higher for a period of time ranging from about one minute to about one-half hour or more, the shorter period being employed at the higher temperature and vice versa. A "flash" cure at 700° to 750° F. for 1 to 20 seconds may be used. Entirely satisfactory results are obtained by heating for ten minutes at about 300° F. This curing operation not only dries the impregnated fabric but apparently causes a reaction between the sulfide and the hydroxyl groups of the cellulose.

The following examples illustrate the present invention, the parts and percentages therein being by weight unless otherwise noted. The crease-recovery values given

below are those determined by the Shirley Institute Procedure (British Standard Notebook No. 11, 1949 edition, page 128) and are the average of warp and filling values

$$\left(\frac{W+F}{2}\right)$$

Example 1

(a) A piece of 80 x 80 cotton printcloth was saturated with an aqueous solution containing 20% of thiodiglycol and 2.0% of zinc perchlorate. It was dried for five minutes at 250° F. and then heated for five minutes at 340° F. to complete the insolubilization and cross-linking of the cellulosic material in the fabric. After conditioning, the sample had a crease-recovery angle of 106°. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

(b) By carrying out the same treatment but with 2% of phosphoric acid as the catalyst, a crease-recovery angle of 111° was reached. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

Example 2

(a) A similar piece of cotton printcloth was saturated with an aqueous solution containing 10% of di-(2-hydroxypropyl) sulfide and 2% of ammonium bisulfate. It was dried for five minutes at 240° F. and then heated for five minutes at 340° F. to complete the insolubilization and cross-linking of the cellulosic material in the fabric. After conditioning, the sample had a crease-recovery angle of 104°. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

(b) By carrying out the same treatment but with 2% of phosphoric acid as the catalyst, a crease-recovery angle of 111° was reached. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

(c) The crease-resistance of rayon was improved in similar fashion when the process of part (a) was repeated replacing the cotton fabric with regenerated cellulose fabrics of spun rayon and filament rayon yarns. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

Example 3

Example 2a was repeated but with the sulfide used at a concentration of 20% and with 2% of zinc perchlorate used as the catalyst. The recovery angle was 120°. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

Example 4

(a) An 80 x 80 cotton printcloth was saturated with an aqueous emulsion containing 15% of the diester of formic acid with thiodiglycol and 2% of zinc perchlorate. After drying, heating, and conditioning as in Example 1, a crease-recovery angle of 115° was obtained. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

(b) Similar results were obtained when the formic acid partial esters and acetic acid esters (mono- and di-) were employed in the same manner.

(c) The process of part (a) was repeated with satisfactory improvement in crease-resistance, substituting the diester of formic acid with di-(2-hydroxypropyl) sulfide.

Example 5

(a) An 80 x 80 cotton printcloth was saturated with an aqueous emulsion containing 15% of the dimethyl ether of thiodiglycol and 2% of zinc perchlorate. After drying, heating, and conditioning as in Example 1, a crease-recovery angle of 101° was obtained. The fabric was resistant to wrinkling and showed no discoloration on washing and ironing.

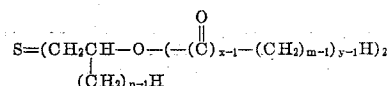
(b) Similar results were obtained when the diethyl,

the monomethyl, and the monoethyl ethers of di-(2-hydroxypropyl) sulfide were used.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

We claim:

1. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of a sulfide of the formula



wherein

m is an integer having a value of 1 to 19,

n is an integer having a value of 1 to 2,

x is an integer having a value of 1 to 2, and

y is an integer having a value of 1 to 2,

20 drying, and heating the impregnated fabric at a temperature of at least about 212° F.

2. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of thiodiglycol, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

3. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of di-(2-hydroxypropyl) sulfide, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

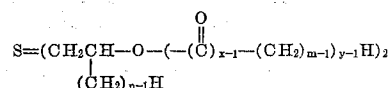
4. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of the dimethyl ether of di-(2-hydroxypropyl) sulfide, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

5. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of a formic acid ester of di-(2-hydroxypropyl) sulfide, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

6. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of a formic acid ester of thiodiglycol, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

7. A process comprising impregnating a cellulose textile with an aqueous medium containing an acid catalyst and 1 to 30% by weight of the dimethyl ether of thiodiglycol, drying, and heating the impregnated fabric at a temperature of at least about 212° F.

8. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with a sulfide of the formula



wherein

m is an integer having a value of 1 to 19,

n is an integer having a value of 1 to 2,

x is an integer having a value 1 to 2, and

y is an integer having a value of 1 to 2.

9. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with thiodiglycol.

10. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with di-(2-hydroxypropyl) sulfide.

11. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with a formic acid ester of di-(2-hydroxypropyl) sulfide.

12. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with a methyl ether of di-(2-hydroxypropyl) sulfide.

13. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with a methyl ether of thiodiglycol.

14. As an article of manufacture, a fabric comprising cellulose fibers modified by reaction with a formic acid ester of thiodiglycol. 5

References Cited in the file of this patent**UNITED STATES PATENTS**

2,785,947	Kress	Mar. 19, 1957
2,785,948	Abrams	Mar. 19, 1957
2,785,949	Kress	Mar. 19, 1957
2,885,443	Kress	May 5, 1959