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2,6-DIOXASPIRO(3,3)HEPTANE TREATED CELLULOSE FABRIC AND THE PRODUCTION THEREOF

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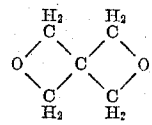
This invention relates to the treatment of cellulosic fabrics, such as those of cotton and regenerated cellulose rayon, for the purpose of imparting to them increased resilience, improved recovery from creasing, wrinkling, and other deformation, and the characteristic of having reduced shrinkage on washing so that partial or complete dimensional stabilization may be effected. The invention also embraces the treated fabrics obtained.

In accordance with the present invention, it has been found that cellulosic fabrics, woven, knitted, or otherwise formed, have reduced shrinkage on washing and acquire resistance to creasing and crushing when they are treated with 2,6-dioxaspiro(3,3)heptane of the formula



For convenience, this compound will be hereinafter referred to by the shorter term dioxaspiroheptane. The extent of modification by means of this compound may be controlled by variation in the proportion of the dioxaspiroheptane and by variation in the amount of catalyst employed during the treatment therewith.

The treatment with dioxaspiroheptane may be effected most advantageously by means of aqueous solutions thereof in which the dioxaspiroheptane is dissolved 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 the like.

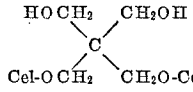
The treatment with dioxaspiroheptane may be carried out in the presence of a catalyst. We have found that the most effective catalysts are metal salts of acids having the composition $H_a(XY_b)$, where H is hydrogen, *a* is an integer which depends on the valence of the complex ion and may have a value 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 I*b*, II, III*b*, 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, oxalic acid, for example, may also be used as catalysts.

Conveniently, the amount of catalyst may vary from about 0.2 to 2% and is preferably in the range of 0.5 to 1% concentration in the aqueous solution of dioxaspiroheptane.

The catalyzed solution of dioxaspiroheptane 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 dioxaspiroheptane to produce changes in the hand or other properties of the fabric.

The aqueous solution containing dioxaspiroheptane 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 fabric 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 machne, or other suitable equipment. After application of the solution, it is desirable to remove the excess solution by squeezing the fabric between rollers, or by shaking or centrifuging it, in order to insure a more even treatment. The fabric treated with solution may 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 250° F. to about 400° 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. 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 dioxaspiroheptane and the hydroxyl groups of the cellulose. Presumably, the hydroxyl group of a cellulose molecule causes an opening of the oxide ring and addition to form some such linkage as may be represented by the following formula:



where Cel represents a cellulose molecule. The two oxide rings in the dioxaspiroheptane may react with hydroxyl groups on the same cellulose molecule, or on different molecules. It is not intended, however, that the present invention be limited to this theory of operation.

The treated fabrics exhibit a high degree of crush resistance and crease recovery with little or no change in the hand or feel of the fabric. The treatment does not discolor the fabric. In addition, the treated fabrics have the important advantage that they do not retain chlorine, so that 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 bleanched are subjected to ironing temperatures. The treated fabrics are also resistant to shrinkage during laundering, and the treatment is very permanent towards laundering, dry-cleaning, and other procedures for cleaning textile fabrics.

The following examples illustrate the present invention, and the parts and percentages therein are by weight unless otherwise noted. The crease recovery values given below were determined by the Shirley Institute procedure (British Standards Handbook No. 11, 1949 ed., page 128).

EXAMPLE 1

A sample of cotton printcloth was saturated with an aqueous solution containing 20% dioxaspiroheptane and 1% zinc perchlorate. It was then put into an oven at 150° C. and baked for 15 minutes. Controls treated with water and 1% zinc perchlorate were similarly prepared.

After being conditioned the samples had the following crease recovery values:

	Degrees
Water control	84
Catalyst control	90
Dioxaspiroheptane	137

The dioxaspiroheptane-treated fabric was insoluble in cuprammonium hydroxide while the controls dissolved readily.

The durability of the treatment was shown by the following tests. Samples of the dioxaspiroheptane-treated fabric were extracted (1) in boiling water for one hour, (2) in 0.1 N HCl at 80° C. for one hour, and (3) in 0.1 NaOH for 24 hours at 20° C. The extracted samples were still insoluble in cuprammonium hydroxide, and had good crease recovery, as shown by the following data:

	Degrees
Water extraction	132
HCl extraction	125
NaOH extraction	123

EXAMPLE 2

(*a*) The procedure of Example 1 is repeated substituting 1% of zinc fluoborate for the zinc perchlorate. Similar crease recovery results were obtained.

(*b*) The procedure of Example 1 is repeated using rayon challis instead of cotton printcloth. The treated fabric was insoluble in cuprammonium hydroxide and had a crease recovery of 120°.

(*c*) A solution containing 10% dioxaspiroheptane and 3% oxalic acid was applied to cotton printcloth and baked for 15 minutes at 150° C. Its crease recovery was improved by this treatment from 83° to 116°.

EXAMPLE 3

Samples of cotton printcloth were saturated with 20% aqueous solutions of dioxaspiroheptane containing various amounts of zinc perchlorate catalyst. They were then cured in an oven at 150° C. for 15 minutes. After being conditioned, the samples were tested for crease recovery. The following results were obtained:

Table A

Concentration of $Zn(ClO_4)_2$ (percent)	Crease recovery (degrees)
0	70
0.50	120
1.00	128

EXAMPLE 4

Samples of cotton printcloth were treated with aqueous solutions of dioxaspiroheptane at various concentrations, each solution containing either 0.5% or 1.0% of zinc perchlorate as catalyst and then baked at 150° C. for 15 minutes. Water and catalyst controls were also prepared. The samples were conditioned and tested for crease recovery with the following results:

Table B

Concentration of dioxaspiroheptane (percent)	Crease recovery (degrees)	
	0.5% catalyst	1.0% catalyst
0 (catalyst control)	76	91
5	106	134
10	112	140
15	109	
20	111	139
Water control	72	82

EXAMPLE 5

Various types of cotton fabrics were treated by saturation in an aqueous solution containing 10% dioxaspiroheptane and 0.75% of zinc perchlorate. After heating in an oven for 15 minutes at 150° C., the results summarized in the following table were obtained:

Table C

Fabric	Count	Crease recovery angles	
		Water	Treated
Printcloth	80 x 80	80	125
Broadcloth	120 x 60	85	123
Muslin	54 x 46	78	99
Lawn	107 x 97	68	128

EXAMPLE 6

A sample of cotton printcloth was impregnated with a solution containing 20% dioxaspiroheptane and 0.75% zinc perchlorate under conditions such that the wet pick-up of the fabric was about 100% of its dry weight. The sample was held on a pin-frame at its orginal dimensions and baked for 15 minutes in an oven at 150° C. A water-treated control was also prepared. The two samples were then washed by the procedure given in Method 5550 of the Federal Specification CCC–T–191*b*. The area shrinkage of the control was 19.7% while that of the treated sample was only 4.6%.

Samples of the treated fabric taken before and after washing were chlorinated in 50 times their weight of a bleach bath containing 0.25% of available chlorine for 15 minutes at room temperature. After being dried, and conditioned, the samples were pressed under an iron at 365° C. for 0.5 minute. Neither sample showed any discoloration or loss of tensile strength after this procedure.

EXAMPLE 7

Samples of cotton printcloth were saturated with aqueous solutions containing 20% dioxaspiroheptane and 1% zinc perchlorate and cured for various lengths of time at 275°, 300°, and 325° F. The crease recovery of the treated fabrics after conditioning is shown in Table D.

Table D

Time of baking (minutes)	Crease recovery (degrees)		
	275° F.	300° F.	325° F.
5	108	126	117
10	115	136	121
15	124	136	137

EXAMPLE 8

A sample of cotton printcloth was treated with a solution containing 10% of dioxaspiroheptane, 1% of zinc perchlorate, and 4% of a partially condensed urea-formaldehyde resin. The treated fabric was cured for 15 minutes at 150° C. After being conditioned, it had a stiffer, firmer, more resilient hand, and a crease recovery of 137°.

EXAMPLE 9

A sample of cotton printcloth was treated with a solution containing a mixture of 5% dioxaspiroheptane and 5% dimethylol-N,N'-ethyleneurea with 1% zinc fluoborate as a catalyst. The application was made on a textile pad and the impregnated fabric was baked for 10 minutes at 150° C. After the fabric was conditioned, its crease recovery angle was 139°.

We claim:

1. The process comprising impregnating a cellulose fabric with an aqueous solution of 2,6-dioxaspiro(3,3)-heptane and a catalyst, and heating the impregnated fabric at a temperature of about 250° to 400° F., until the crease resistance of the fabric is increased.

2. A process as defined in claim 1 in which the fabric is cotton.

3. A process as defined in claim 1 in which the fabric is regenerated cellulose rayon.

4. The process comprising impregnating a cellulose fabric with an aqueous solution containing 1 to 30% by weight of 2,6-dioxaspiro(3,3)heptans and 0.2 to 2% of a catalyst and heating the impregnated fabric at a temperature of about 250° to 400° F. until the crease-resistance of the fabric is increased.

5. A process as defined in claim 4 in which the fabric is cotton.

6. A process as defined in claim 4 in which the fabric is regenerated cellulose rayon.

7. The process comprising impregnating a cellulose fabric with an aqueous solution containing 1 to 30% by weight of 2,6-dioxaspiro(3,3)heptane and, as a catalyst, 0.2 to 2% of a member selected from the group consisting of aluminum and copper sulfates, oxalic acid, and metal salts of an acid of the formula $H_a(XY_b)$, where H is hydrogen, *a* is an integer having a value of 1 to 3, X is a member selected from the group consisting of boron, silicon, sulfur, and chlorine, Y is a member selected from the group consisting of fluorine and oxygen, and *b* is an integer selected from 4 and 6, said metal having an atomic weight of at least 12 and being selected from the group consisting of those in groups I*b*, II, III*b*, IV, and VIII of the periodic table, and heating the impregnated fabric at a temperature of about 250° to 400° F. until the crease-resistance of the fabric is increased.

8. A process according to claim 7 in which the fabric is cotton.

9. A process according to claim 7 in which the fabric is regenerated cellulose rayon.

10. The process comprising impregnating a cellulose fabric with an aqueous solution containing 1 to 30% by weight of 2,6-dioxaspiro(3,3)heptane and 0.2 to 2% of magnesium fluoborate, and heating the impregnated fabric at a temperature of about 250° to 400° F. until the crease-resistance of the fabric is increased.

11. A process as defined in claim 10 in which the fabric is cotton.

12. A process as defined in claim 10 in which the fabric is regenerated cellulose rayon.

13. The process comprising impregnating a cellulose fabric with an aqueous solution containing 1 to 30% by weight of 2,6-dioxaspiro(3,3)heptane and 0.2 to 2% of zinc perchlorate and heating the impregnated fabric at a temperature of about 250° to 400° F. until the crease-resistance of the fabric is increased.

14. A process as defined in claim 13 in which the fabric is cotton.

15. A process as defined in claim 13 in which the fabric is regenerated cellulose rayon.

16. The process comprising impregnating a cellulose fabric with an aqueous solution containing 1 to 30% by weight of 2,6-dioxaspiro(3,3)heptane and 0.2 to 2% of zinc fluoborate and heating the impregnated fabric at a temperature of about 250° to 400° F. until the crease-resistance of the fabric is increased.

17. A process as defined in claim 16 in which the fabric is cotton.

18. A cellulose fabric having improved crease resistance obtained by the process of claim 1.

19. A cotton fabric having improved crease resistance obtained by the process of claim 5.

20. A regenerated cellulose fabric having improved crease resistance obtained by the process of claim 6.

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