CROSSLINKING COTTON WITH HALOALKYL PHOSPHINE OXIDES
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Int. Cl. D06m 13/28
26 Claims

ABSTRACT OF THE DISCLOSURE

Improved wet wrinkle recovery is obtained by crosslinking cotton in the presence of a base with certain bis- and tris(haloalkyl)phosphine oxides.

A nonexclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to certain organophosphorus compounds useful as textile finishing agents. Specifically, this invention relates to haloalkyl phosphate oxides. More specifically, this invention relates to a process for crosslinking cellulose fabrics with bis- and tris(haloalkyl) phosphate oxides to impart to the finished products wet wrinkle resistance.

Inventors know of no prior art which would teach the treatment of textiles by any similar process. Details of the work which led to the unexpected discovery of the instant invention have been disclosed by these inventors in their "Crosslinking Cotton with Halomethylphosphine Oxides," which paper appears in the American Dyestuff Reporter 56(17), page 614 (1967).

The principal object of the instant invention is to provide a process for crosslinking fibrous cellulose textiles. A further object of the instant invention is to provide a process for producing fibrous cellulose textiles with an improved wet wrinkle recovery quality.

In the investigative work which led to the instant invention it has been found that phosphate oxides of the graphic formula

$$\text{XCH}_2\text{P}=\text{O}$$

where X is a halogen, will react with cellulose hydroxyl groups to crosslink cellulose. It has also been found that phosphate oxides of the graphic formula

$$\text{XCH}_2\text{P}-\text{CH}_3$$

where X is a halogen, will react with cellulose hydroxyl groups in the presence of alkaline catalysts to crosslink cellulose.

Compounds which are useful reagents in practicing the invention include tris(chloromethyl)phosphine oxide, tris(bromomethyl)phosphine oxide, tris(iodomethyl)phosphine oxide, methyl bis(chloromethyl)phosphine oxide, methyl bis(bromomethyl)phosphine oxide, methyl bis(iodomethyl)phosphine oxide, and the like.

The reaction of the reagents of the invention, above, with cellulose materials takes place between the cellulose hydroxyl groups and the halogen atoms of the phosphate oxides, thereby crosslinking the cellulose through stable ether linkages. Cellulose crosslinking is proven by insolubility of the products of the reaction, which are cellulose derivatives, in a standard 0.5 molar cuprethlenediamine hydroxide aqueous solution—a common cellulose solvent. Cotton fibers, regenerated cellulose, and other natural cellulose fibers can be employed in reducing the invention to practice; nevertheless, the preferred application would be on cotton fabrics.

The tris(chloromethyl)phosphine oxide and methyl bis(chloromethyl)phosphine oxide were unexpectedly found to be soluble in water and in aqueous alkali, and for this reason could be applied to cellulose materials from a single bath. The bromo- and iodo-phosphine oxides are insoluble in water or in aqueous alkali. They can be conveniently applied from miscible organic solvents in which the phosphine oxides are soluble. Dimethylformamide is a particularly suitable solvent for the compounds of this invention. It is preferable that water be present in the solutions of the phosphine oxides so that penetration into cellulose fibers can be achieved. When a combination of water and an organic solvent is used it is necessary to carry out the application to cellulose in two steps. The aqueous alkali may be applied to the cellulose first, followed by the solution of the phosphine oxide, or the phosphine oxide may be applied first followed by the aqueous alkali.

The application of the water soluble phosphine oxides to cotton fabric may be carried out as follows: The cotton fabric is then impregnated with the solution, the fabric dried and cured at temperatures ranging about from 110° to 150° C. for about from 5 to 30 minutes of time.

The application of the water insoluble phosphine oxides to cotton fabric may be carried out as follows: The phosphine oxide is dissolved in a suitable water-miscible organic solvent, and water added in a quantity such that precipitation of the phosphine oxide does not occur. The fabric is then impregnated with the solution, dried, and cured at temperatures about from 110° to 150° C. for about from 5 to 30 minutes of time, the longer times are required for the lower temperatures.

Any alkali hydroxide or alkali carbonate is a suitable catalyst for the reaction of the bis- and tris(haloalkyl)phosphine oxides of the instant invention with cellulose textiles. Sodium carbonate or sodium hydroxide are preferred catalysts. Catalyst concentrations may be varied about from 0.5% to 10%.

The cellulose textile can be impregnated and heated by any apparatus conventionally used for processing such materials.

Repeating the invention, it can be described in general as a process for imparting wet wrinkle resistance to cotton and other cellulose textiles comprising:

(a) impregnating a cotton or other cellulose textile with a solution containing about from 0.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate, and about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(chloromethyl)phosphine oxide, tris(bromomethyl)phosphine oxide, tris(iodomethyl)phosphine oxide, methyl bis(chloromethyl)phosphine oxide, methyl bis(bromomethyl)phosphine oxide, methyl bis(iodomethyl)phosphine oxide, and the like.

(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C., and
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(c) curing the dried impregnated textile for about from 5 to 30 minutes of time at about from 110° to 150° C., using the longer periods of time with the lower temperatures.

The following examples illustrate the methods of carrying out the invention, and are included for purposes of illustration, not as a limitation thereof. Wrinkle recovery tests were carried out by the Monsanto method, ASTM designation D1424–59. All percentages and parts in the examples are by weight.

EXAMPLE 1

Eight solutions were prepared by dissolving tris(chloromethyl)phosphine oxide in aqueous sodium hydroxide of the concentrations indicated in Table I. External cooling was employed when necessary to prevent the solution from heating up spontaneously. Each solution contained 10% of the phosphine oxide. Fabric samples were impregnated with the solutions, dried for 5 minutes at 85° C., and cured in an oven for 5 minutes at 150° C. or 30 minutes at 110° C. The samples were then washed free of alkali, and submitted to wet wrinkle recovery tests, and phosphorus and chlorine analyses. The results obtained are shown in Table I. Highest phosphorus and chlorine content, and wet wrinkle recovery values were obtained at 10% NaOH concentration. Fibers from all of the samples were found insoluble in 0.5 molar cupriethylenediamine hydroxide (“Cuene”).

EXAMPLE 2

Fabric samples were treated in exactly the same way as in Example 1 except that methyl bis(chloromethyl) phosphine oxide was used. Fabric and other data are shown in Table II.

EXAMPLE 3

Tris(bromomethyl)phosphine oxide (5.0 grams) was dissolved in 22.5 grams of dimethyl formamide at 70° C. Water (22.5 grams) was added while holding the temperature at about 70° C. Six samples of cotton printcloth were impregnated with the hot solution and dried for 5 minutes at 85° C. Each sample was then impregnated with a different concentration of aqueous sodium hydroxide, again dried for 5 minutes at 85° C., and cured for 5 minutes at 150° C. Fabric and other data are shown in Table III.

EXAMPLE 4

Methyl bis(iodomethyl)phosphine oxide (5.0 grams) was dissolved in 22.5 grams of dimethyl formamide at 70° C. Water (22.5 grams) was added while holding the temperature at about 70° C. Six samples of cotton printcloth were impregnated with the hot solution and dried for 5 minutes at 85° C. Each sample was then impregnated with a different concentration of aqueous sodium hydroxide, again dried for 5 minutes at 85° C., and cured for 5 minutes at 150° C. Fabric and other data are shown in Table IV.

EXAMPLE 5

A number of samples of cotton printcloth were treated with methyl bis(chloromethyl)phosphine oxide as in Example 2 except that sodium carbonate solutions were used instead of the sodium hydroxide solutions. Crosslinking was observed as present in the treated samples when determined by their insolubility in the “Cuene.”

EXAMPLE 6

A sample of printcloth was treated with tris(bromomethyl)phosphine oxide as in Example 3 except that a 10% sodium carbonate solution was used instead of 10% sodium hydroxide solution. The fibers were insoluble in the “Cuene.” The fabric contained 0.12% phosphorus and 0.23% bromine.

We claim:

1. A process for imparting wet wrinkle resistance to a cellulosic textile comprising

(a) impregnating the cellulosic textile with a solution containing about from 0.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate, and about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(chloromethyl)phosphine oxide, tris(bromomethyl)phosphine oxide, tris(iodomethyl)phosphine oxide, methyl bis(chloromethyl)phosphine oxide, methyl bis(bromomethyl)phosphine oxide, and methyl bis(iodomethyl)phosphine oxide,

(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C., and

(c) curing the dried, impregnated textile for about from 5 to 30 minutes of time at about from 110° to 150° C., using the longer periods of time with the lower temperatures.

2. A process for imparting wet wrinkle resistance to a cellulosic textile comprising

(a) impregnating the cellulosic textile with an aqueous solution containing about from 2.5% to 10% of an alkali catalyst selected from the group consisting of

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### Table I

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<th>NaOH concen., percent</th>
<th>Curing temp., °C</th>
<th>Phosphorus, percent</th>
<th>Chlorine, percent</th>
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### Table III

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</tr>
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</table>
sodium hydroxide and sodium carbonate, and about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(chloromethyl)phosphine oxide, and methyl bis(chloromethyl)phosphine oxide.

(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C., and
curing the dried, impregnated textile for about from 5 to 30 minutes of time at about 110° to 150° C., using the longer periods of time with the lower temperatures.

3. The process of claim 2 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is tris(chloromethyl)phosphine oxide.

4. The process of claim 2 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is tris(chloromethyl)phosphine oxide.

5. The process of claim 2 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is tris(chloromethyl)phosphine oxide.

6. The process of claim 2 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is tris(chloromethyl)phosphine oxide.

7. A process for imparting wet wrinkle resistance to a cellulose textile comprising:

(a) impregnating the cellulose textile with an aqueous solution containing about from 1.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate,
(b) drying the wet, impregnated textile for about 5 to 30 minutes of time at about 85° C., and
c) impregnating the dried textile from step (b) with a 50% aqueous dimethylformamide solution containing about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(bromomethyl)phosphine oxide, and methyl bis(bromomethyl)phosphine oxide;
(d) drying the reimpregnated textile from step (c) for about 5 minutes of time at about 85° C., and
curing the twice-impregnated, twice-dried textile from step (b) with an aqueous solution containing about from 5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate.

8. The process of claim 7 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is tris(bromomethyl)phosphine oxide.

9. The process of claim 7 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is methyl bis(bromomethyl)phosphine oxide.

10. The process of claim 7 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is tris(bromomethyl)phosphine oxide.

11. The process of claim 7 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is methyl bis(bromomethyl)phosphine oxide.

12. A process for imparting wet wrinkle resistance to a cellulose textile comprising:

(a) impregnating the cellulose textile with an aqueous solution containing about from 0.5 to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate,
(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C., and
c) impregnating the dried textile from step (b) with a 50% aqueous dimethylformamide solution at 70° C. containing about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(iodomethyl)phosphine oxide, and methyl bis(iodomethyl)phosphine oxide;
(d) drying the reimpregnated textile from step (c) for about 5 minutes of time at about 85° C., and
curing the twice-impregnated, twice-dried textile from step (b) with an aqueous solution containing about from 0.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate.

13. The process of claim 12 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is tris(iodomethyl)phosphine oxide.

14. The process of claim 12 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is methyl bis(iodomethyl)phosphine oxide.

15. The process of claim 12 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is tris(iodomethyl)phosphine oxide.

16. The process of claim 12 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is methyl bis(iodomethyl)phosphine oxide.

17. A process for imparting wet wrinkle resistance to a cellulose textile comprising:

(a) impregnating the cellulose textile with a 50% aqueous dimethylformamide solution containing about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(bromomethyl)phosphine oxide, and methyl bis(bromomethyl)phosphine oxide,
(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C.,
c) impregnating the dried textile from step (b) with an aqueous solution containing about from 1.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate,
(d) drying the reimpregnated textile from step (c) for about 5 minutes of time at about 85° C., and
curing the twice-impregnated, twice-dried textile from step (b) with an aqueous solution containing about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(iodomethyl)phosphine oxide, and methyl bis(iodomethyl)phosphine oxide.

18. The process of claim 17 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is tris(bromomethyl)phosphine oxide.

19. The process of claim 17 wherein the alkali catalyst is sodium hydroxide and the haloalkylphosphine oxide is methyl bis(bromomethyl)phosphine oxide.

20. The process of claim 17 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is tris(bromomethyl)phosphine oxide.

21. The process of claim 17 wherein the alkali catalyst is sodium carbonate and the haloalkylphosphine oxide is methyl bis(bromomethyl)phosphine oxide.

22. A process for imparting wet wrinkle resistance to a cellulose textile comprising:

(a) impregnating the cellulose textile with a 50% aqueous dimethylformamide solution at 70° C. containing about from 5% to 10% of a haloalkylphosphine oxide selected from the group consisting of tris(iodomethyl)phosphine oxide, and methyl bis(iodomethyl)phosphine oxide,
(b) drying the wet, impregnated textile for about 5 minutes of time at about 85° C.,
(c) impregnating the dried textile from step (b) with an aqueous solution containing about from 0.5% to 10% of an alkali catalyst selected from the group consisting of sodium hydroxide and sodium carbonate.
26. The process of claim 22 wherein the alkali catalyst is sodium carbonate and the halomethylphosphine oxide is methyl bis(iodomethyl)phosphine oxide.

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