United States Patent

Weyker et al.

[15] **3,650,819**

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[54] DURABLE FIRE-RETARDANT FINISH FOR CELLULOSIC TEXTILE MATERIALS

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[22] Filed: **Oct. 8, 1968**

[21] Appl. No.: **765,961**

[52] **U.S. Cl.**.....**117/136**, 117/137, 117/139.4, 117/143 R

[51] **Int. Cl.**.....**C09k 3/28**, D06m 13/26

[58] **Field of Search**.....117/136, 139.4, 143 R, 76 T, 117/62, 63

[56] **References Cited**

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2,530,261	11/1950	Morton et al.	117/137 X
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Drake et al., " Imparting Crease Resistance," Textile Research Journal, Vol. 29, No. 2, pps. 155- 164, Feb., 1959.

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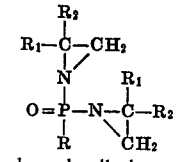
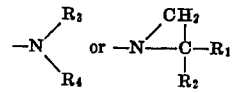
[57] **ABSTRACT**

A method for providing a hard water wash durable cyanamide-phosphoric acid, flame-retardant finish for cellulosic textile materials which comprises aftertreating the textile material bearing the cyanamide-phosphoric acid finish with an aziridinyl phosphine oxide of the formula:



wherein R is alkyl, aryl, cyclo alkyl,



R_1 and R_2 are hydrogen or lower alkyl; and R_3 and R_4 are alkyl, or, taken together with the nitrogen, represent a heterocyclic ring, followed by a curing step.

6 Claims, No Drawings

DURABLE FIRE-RETARDANT FINISH FOR CELLULOSIC TEXTILE MATERIALS

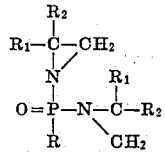
This invention relates to fire-retardant finishes for textile materials. More particularly, it relates to a method for improving the wash fastness for a cyanamide-phosphoric acid fire-retardant finish for cellulosic textile materials.

The cyanamide-phosphoric acid finish ("Pyroset CP," of American Cyanamid Co.) of U.S. Pat. 2,530,261 imparts very good fire-retardant properties to cellulosic textile materials. The finish, however, suffers from poor durability to laundering when hard water is used. The wash fastness with soft water is good.

There is moderate improvement in durability of the finish to washing in hard water when sodium hexametaphosphate ("Calgon," of Hagan Chemicals & Controls, Inc.) is used in the hard wash water. A slight improvement is found when a sequestering agent, such as the sodium salt of ethylenediamine-tetracetic acid, is used in the hard water.

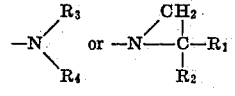
The loss in fire retardancy due to laundering in hard water is believed to be due to an ion exchange, i.e., base exchange, with ammonium ion replaced by calcium. Analysis shows a decrease in nitrogen content and an increase in calcium content of the fabric as the washings in hard water are repeated. Also, the rate of loss of fire retardancy increases as the hardness of the wash water increases. Ion exchange with sodium ions is much slower than with calcium ions. This explains why the fire retardancy is more durable to washing with soft water, or with hard water plus "Calgon" or a sequestering agent. Other metal ions are also harmful, zinc ions having been shown to be more harmful than calcium ions.

It has now been discovered that the wash durability in hard water of the cyanamide-phosphoric acid textile finish can be greatly improved by aftertreating the textile material bearing the cyanamide-phosphoric acid finish with an aziridinyl phosphine oxide of Formula I:



Formula I

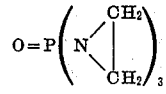
wherein R is alkyl, aryl, cyclo alkyl,



;

R_1 and R_2 are hydrogen or lower alkyl; and R_3 and R_4 are alkyl, or, taken together with the nitrogen, represent a heterocyclic ring, followed by a curing step.

Compounds of Formula I include bis(1-aziridinyl)alkylphosphine oxides, such as bis(1-aziridinyl)ethylphosphine oxide, bis(1-aziridinyl)butylphosphine oxide, etc.; bis(1-aziridinyl)-arylphosphine oxides, such as bis(1-aziridinyl)phenylphosphine oxide, bis(1-aziridinyl)-p-tolyphosphine oxide, bis(1-aziridinyl)-p-chlorophenylphosphine oxide, bis(1-aziridinyl)-2-naphthylphosphine oxide, etc.; bis(1-aziridinyl)cycloalkylphosphine oxides, such as bis(1-aziridinyl)cyclohexylphosphine oxide, etc.; bis(1-aziridinyl)disubstituted-aminophosphine oxides, such as bis(1-aziridinyl)(dibutylamino)phosphine oxide, bis(1-aziridinyl)(dioctylamino)phosphine oxide, bis(1-aziridinyl)piperidinophosphine oxide, bis(1-aziridinyl)morpholinophosphine oxide, bis(2methyl-1-aziridinyl)piperidinophosphine oxide, bis(2,2-dimethyl-1-aziridinyl)piperidinophosphine oxide, etc.; and tris-(1-aziridinyl)phosphine oxides, such as tris(1-aziridinyl)phosphine oxide itself, tris(2-methyl-1-aziridinyl)phosphine oxide, tris(2,2-dimethyl-1-aziridinyl)phosphine oxide, etc. The preferred polyaziridinyl phosphine oxide is tris(1-aziridinyl)phosphine oxide of Formula II:



Formula II

The aziridinyl phosphine oxides of Formula I can be prepared by the procedures described in U.S. Pat. Nos. 2,606,900; 2,606,902; 2,654,738 and 2,663,705.

The procedure for applying the cyanamide-phosphoric acid is described in U.S. Pat. No. 2,530,261. Our results indicate that at least 10 percent to 30 percent, preferably at least 20 percent, of cyanamide, and at least 5 percent to 25 percent, preferably at least 15 percent, of phosphoric acid (H_3PO_4) should be applied to the textile material. The percentages are based on the weight of the material. It is advantageous to apply the two agents simultaneously from aqueous solution by any of the procedures conventionally used to apply aqueous textile finishes, such as by padding, dipping, spraying, etc.

The temperature of the aqueous solution of cyanamide and phosphoric acid is preferably at about 10°–20° C. or below, and not over 30° C.

After the fabric has been treated with the aqueous solution of cyanamide and phosphoric acid, it is dried by any convenient method, as in an oven at 90°–105° C., and is then heated at an elevated temperature to effect a cure of the finish on the textile material. A temperature between 105° C. and 200° C., preferably between 125° C. and 175° C., is employed for the curing operation depending on fabric weight. The time required is between about 1 and 20 minutes, depending on the temperature used and fabric weight. Alternatively, the drying step can be omitted and cure times extended slightly to accomplish drying and curing in one operation.

The textile material should contain at least 50 percent cellulosic fibers. It can be in the form of a woven or knitted fabric, nonwoven fabric, yarns, etc.

The aziridinyl phosphine oxide is applied to the textile material bearing the cured cyanamide-phosphoric acid from a suitable solvent medium using any conventional procedure such as by padding, dipping, spraying, etc. Where the aziridinyl compound is sufficiently soluble in water, it is advantageous to use an aqueous solution of the compound. This particularly applies to the preferred compound, tris(1-aziridinyl)phosphine oxide of Formula II. When the compound is not sufficiently soluble in water, an inert solvent such as chlorinated hydrocarbons and glycol ethers can be used.

The amount of aziridinyl phosphine oxide used should be between 1 percent and 25 percent, preferably between 5 percent and 20 percent, based on the weight of the textile material.

The temperature of the solution of aziridinyl compound is preferably at about room temperature, but it can be higher or lower within practical limits.

The treated textile material is dried by any convenient method, as in an oven at 105° C., and is then heated at an elevated temperature to effect a "cure" of the aziridinyl phosphine oxide finish on the textile material. A temperature between 105° C. and 200° C., preferably between 125° C. and 150° C., is recommended for the curing operation. The time required is between about 1 and 5 minutes, depending on the temperature used and weight of the fabric. If desired, the drying and curing operation can be done in one operation.

Before applying the aziridinyl phosphine oxide it is desirable to rinse the cyanamide-phosphoric acid treated textile material in water. This procedure removes phosphoric acid and increases the effectiveness of the aziridinyl compound.

The aziridinyl phosphine oxide treatment not only improves the durability of the cyanamide-phosphoric acid fire-retardant finish, but it also increases the wrinkle recovery properties of the fabric, thus providing the fabric with durable wash and wear properties.

The following specific examples are given to illustrate the invention and are not intended to be limitative.

EXAMPLE I

A. Treatment of Fabric with Cyanamide and Phosphoric Acid

A pad bath was prepared by mixing 1,200 g. of 50 percent aqueous cyanamide solution, 328 g. of ice and 472 g. of 85 percent phosphoric acid. The bath was padded onto 80 × 80 cotton percale obtaining an 80 percent wet pickup. The treated fabric was dried, and the finish was cured by heating the fabric at 150° C. for 3 minutes.

B. Treatment of Fabric with Tris(1-aziridinyl)phosphine Oxide

A 10 percent aqueous solution of tris(1-aziridinyl)phosphine oxide was padded onto the fabric from Treatment A obtaining an 80 percent wet pickup. The treated fabric was dried and the finish was cured by heating the fabric at 125°C. for 3 minutes.

The durability of the fire-retardant finish to laundering was determined by repeatedly washing the fabric in an automatic washing machine using hard water, the water having a calcium ion content of about 70 p.p.m. After each washing operation, the fire resistance of the fabric was determined by a vertical flame test according to Standard Test Method AATCC 34–1966. The washings and flame testing were continued as long as the char length of the burned fabric was less than 6 inches. The limit of wash durability was reached when the char length was 6 inches.

The fire resistance of the fabric obtained by Treatment A plus B was durable for about 40 launderings in hard water. For comparison, the fire resistance of the fabric from Treatment A alone was durable for about five launderings in hard water.

EXAMPLE II

A series of aqueous solutions containing 2.5 percent, 5 percent, 7.5 percent, 10 percent, 15 percent and 20 percent of tris(1-aziridinyl)phosphine oxide (APO) were padded onto 80 × 80 cotton percale which had been treated with cyanamide and phosphoric acid according to the procedure of Example I. A wet pickup of about 80 percent was obtained. The treated fabrics were dried and cured at 125° C. for 3 minutes.

The durability of the fire-retardant finishes to laundering in hard water was determined by the procedure of Example I.

The wrinkle recovery of the treated fabrics was measured by Tentative Test Method AATCC 66–1959T after 30 washes.

The results are shown in Table I.

TABLE I

APO in Bath	Durability of Fire Resistance	Wrinkle Recovery Degrees, W&F
2.5%	15 washes	—
5.0%	35 washes	264
7.5%	40 washes	269
10.0%	40 washes	269
15.0%	40 washes	275
20.0%	40 washes	264

The fabric treated only with cyanamide and phosphoric acid had a wrinkle recovery of about 230° C.

EXAMPLE III

A. Treatment of Fabric with Cyanamide and Phosphoric Acid

The procedure of Part A of Example I was followed with the exception that the finish was cured by heating the fabric at 150° C. for 5 minutes and the fabric was not rinsed in water after the curing step.

B. Treatment of Fabric with Tris(1-aziridinyl)phosphine Oxide

The procedure of Part B of Example I was followed with the exception that the finish was cured by heating the fabric at 150° C. for 5 minutes.

The durability of the fire-resistant finishes of Treatment A and A + B were determined by the procedure of Example I. The results are shown in Table II.

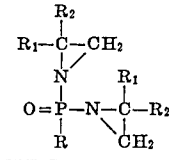
TABLE II

Treatment	Durability of Finish
A	2 washes
A + B	9–12 washes

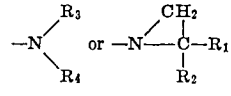
While certain specific embodiments and preferred modes of practice of the invention have been set forth, it will be understood that this is solely for purposes of illustrating the invention, and that various changes and modifications may be made without departing from the spirit of the disclosure or the scope of the appended claims.

We claim:

1. A method for improving the durability of a cyanamide-phosphoric acid fire-retardant textile finish on a cellulosic textile material comprising impregnating the textile material containing the cyanamide phosphoric acid finish with an aziridinyl phosphine oxide of the formula:



where R is alkyl, aryl, cycloalkyl,



R_1 and R_2 are hydrogen or lower alkyl; and R_3 and R_4 are alkyl or, taken together with the nitrogen, represent a heterocyclic ring, and heating the textile finish at a temperature between 105° C. and 200° C.

2. The method of claim 1 where the aziridinyl phosphine oxide is tris(1-aziridinyl)phosphine oxide.

3. The method of claim 1 wherein said aziridinyl phosphine oxide is employed as an aqueous solution.

4. The method of claim 1 wherein said aziridinyl phosphine oxide is employed in an inert organic solvent.

5. The method of claim 1, including a water rinse prior to said impregnation with said aziridinyl phosphine oxide.

6. Cellulosic textile materials treated by the method of claim 1.

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