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3,737,284

TRIS(HYDROXYMETHYL)PHOSPHINE PHOSPHATES AS FLAME RETARDANTS FOR TEXTILE MATERIALS

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4 Claims

ABSTRACT OF THE DISCLOSURE

Durable flame retardant finishes for textiles comprising aqueous solutions of tris(hydroxymethyl)phosphine, phosphoric acid and a methylolated nitrogenous cellulose reactant.

This application is a continuation-in-part of application Ser. No. 50,360, filed June 26, 1970 and now abandoned.

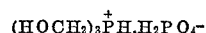
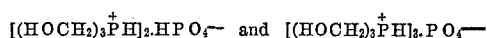
Copending, commonly assigned application Ser. No. 861,481, filed Sept. 26, 1969, now U.S. Pat. 3,619,113 (1971), relates to flame retardant finishes for cellulosic textile materials comprising aqueous solutions of tris(hydroxymethyl)phosphine and methylolated nitrogenous cellulose reactants. The finishes of the copending application Ser. No. 861,481, provide flame retardants durable for a maximum of about 50 launderings, but normally of the order of 15–20 launderings.

This invention relates to durable flame retardant finishes for cellulosic textile materials, to the method of applying the finishes and to the textile material treated with the finishes. More particularly, the flame retardant finishes of this invention are aqueous solutions of tris(hydroxymethyl)phosphine (THP), phosphoric acid and a methylolated nitrogenous cellulose reactant.

The object of the present invention is to provide tris(hydroxymethyl)phosphine-based flame retardant finishes that are more durable to laundering than the finishes of the copending application Ser. No. 861,481.

It has been discovered that textile finishes containing tris(hydroxymethyl)phosphine, orthophosphoric acid and a methylolated nitrogenous cellulose reactant impart excellent flame retardant properties to cellulosic textile materials which are more durable to laundering than the textile finishes containing only tris(hydroxymethyl)phosphine and a methylolated nitrogenous cellulose reactant.

The finishes of this invention are aqueous solutions of tris(hydroxymethyl)phosphine, orthophosphoric acid and methylolated nitrogenous cellulose reactants. The relatively dilute application solutions can be prepared by dissolving the individual components, which are normally concentrated aqueous solutions in water. Solutions of tris(hydroxymethyl)phosphine and orthophosphoric acid form salts or complexes when they are combined in aqueous solution. Three types of salts or complexes are theoretically possible and presumably can be formed depending on the molar ratio of tris(hydroxymethyl)phosphine and orthophosphoric acid employed. The three complexes or salts have the following compositions:



The above complexes contain 1, 2 or 3 moles of tris(hydroxymethyl)phosphine per mole of orthophosphoric acid.

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Mixtures of the complexes can be used. The preferred ratio is two moles of tris(hydroxymethyl)phosphine per mole of phosphoric acid because of efficiency in imparting flame resistance to textiles and the relative economics of the complexes.

Tris(hydroxymethyl)phosphine is a known compound, its preparation having been disclosed as early as 1960 (U.S.S.R. Pat. 138,617). Its preparation by reaction of phosphine with formaldehyde is described in German Pat. 1,035,135.

The amount of tris(hydroxymethyl)phosphine applied to the cellulosic textile material should be between 5% and 35%, preferably between 10% and 15%, based on the weight of the textile material.

The amount of phosphoric acid applied to the cellulosic material should be between 5% and 20%, preferably between 10% and 12%, based on the weight of the textile material.

The total phosphorus applied should be between 2% and 5%, preferably between 2.5% and 4%, based on the weight of the textile material.

The methylolated nitrogenous cellulose reactant is a thermosetting aminoplast resin precursor including melamine-formaldehyde condensates, urea-formaldehyde condensates, alkyl carbamate-formaldehyde condensates, etc. The preferred nitrogenous reactants are melamine-formaldehyde condensates such as dimethylolmelamine, dimethylated trimethylolmelamine, tetrakis(methoxymethyl)melamine, partially methylated pentamethylolmelamine, etc.

The amount of methylolated nitrogenous cellulose reactant applied to the cellulosic textile material will depend on the nitrogen content of the reactant. Sufficient reactant should be applied to provide on a weight basis between 50% and 300% of nitrogen, preferably between 100% and 200%, based on the phosphorus applied to the textile material.

The addition of urea to the application bath improves the stability of the bath. It also improves the durability of the flame retardancy and reduces strength losses of the treated fabric. The amount of urea added to the bath should be at least 3%, preferably between 3% and 10%, based on the weight of the textile material.

The application solutions should contain, per 100 grams of solution, between 0.05 and 0.15 gram-mole, preferably between 0.08 and 0.12 gram-mole, of tris(hydroxymethyl)phosphine; between 0.033 and 0.15 gram-mole, preferably between 0.09 and 0.1 gram-mole, of phosphoric acid; between 0.025 and 0.15 gram-mole, preferably between 0.04 and 0.075 gram-mole, of methylolated melamine, and, if used, between 0.13 and 0.25 gram-mole, preferably between 0.15 and 0.18 gram-mole of urea. These values are based on the assumption that the wet pickup by the cellulosic textile material to which they are applied is 100% based on the weight of the textile material.

The cellulosic textile material should contain at least 50% cellulosic fibers. By cellulosic fibers is meant such fibers as cotton, regenerated cellulose (rayon), linen, jute, etc. Blends of cellulosic fibers or blends of cellulosic fibers with noncellulosic fibers, both natural and synthetic, such as silk, wool, nylon, polyester, acrylic, etc., may be used.

The components of the fire retardant finish can be applied to the textile material from the same bath or from separate baths by padding, dipping, spraying, etc. For maximum durability, it is advantageous to dry the textile at a temperature of about 75° to 115° C., preferably at 100° to 110° C., for a time of from about 2 to 10 minutes depending on the construction of the fabric, before the finish is cured at a temperature from about 125° to 175°

C., preferably at 140° to 160°. The time required for curing is between 1 and 5 minutes, depending on the temperature used and the weight of the fabric.

EXAMPLE 1

(A) An aqueous solution was prepared by mixing 133 g. of 93% tris(hydroxymethyl)phosphine, 57 g. of 85% orthophosphoric acid and 50 g. of water. The molar ratio of tris(hydroxymethyl)phosphine to phosphoric acid was 2/1. The product contained 72% "solids."

(B) An aqueous solution was prepared by mixing 133 g. of 93% tris(hydroxymethyl)phosphine, 38 g. of 85% orthophosphoric acid and 50 g. of water. The molar ratio of tris(hydroxymethyl)phosphine to phosphoric acid was 3/1. The product contained 70% "solids."

EXAMPLE 2

An aqueous pad bath was prepared containing 12.4% of tris(hydroxymethyl)phosphine (THP), 5.8% of 85% orthophosphoric acid ($\text{THP}/\text{H}_3\text{PO}_4=2/1$), 8.9% of dimethylolmelamine and 8.5% of urea. The pad bath was applied to 80 x 80 cotton percale obtaining a wet pickup of about 80%. The padded fabric, containing about 10.0% of THP, 4.6% of phosphoric acid, 7.1% of dimethylolmelamine and 6.8% of urea, was dried at 107° C. for 4 minutes and then heated at 150° C. for four minutes.

The durability of the flame retardant finish to laundering was determined by repeatedly washing the fabric in an automatic washing machine, using water at 140° F. and a commercial detergent, and drying in a tumble dryer. After each fifth washing and drying operation, the flame resistance of the fabric was determined by a vertical flame test according to Standard Test Method AATCC 34-1966. The limit of wash durability is reached when the char length is over 6". After 100 washings, the char length was 3.1".

The hand of the fabric was only very slightly altered by the treatment.

EXAMPLE 3

An aqueous pad bath was prepared containing 13.0% of tris(hydroxymethyl)phosphine, 9.3% of 85% orthophosphoric acid ($\text{THP}/\text{H}_3\text{PO}_4=1.25/1$), 9.3% of dimethylolmelamine and 8.7% of urea. The pad bath was applied to 80 x 80 cotton percale obtaining a wet pickup of about 80%. The padded fabric contained about 10.4% of THP, 7.4% of phosphoric acid, 7.4% of dimethylolmelamine and 7.0% of urea. The fabric was dried at 107° C. for 4 minutes and then heated at 150° C. for 4 minutes.

The durability of the flame retardant finish to laundering was determined by the procedure of Example 2. After 60 washings, the char length was 5.7".

EXAMPLE 4

Two aqueous pad baths were prepared containing the percentage amounts of the reactants shown in Table I.

TABLE I

Pad bath.....	A	B
THP-H ₃ PO ₄ :		
Product of Example 1A, solids.....	15.6	16.4
Product of Example 1B, solids.....		9.3
Dimethylolmelamine.....	9.3	6.0
Urea.....	6.0	3/1
THP/H ₃ PO ₄	2/1	

The pad baths were applied to 80 x 80 cotton percale obtaining wet pickups of about 80%. The padded fabrics A and B, containing 12.5% and 13.1% of THP-H₃PO₄, 7.4% and 7.4% of dimethylolmelamine, and 4.8% and 4.8% of urea, respectively, were dried at 107° C. for 4 minutes and then heated at 150° C. for 4 minutes. After 100 washings by the procedure of Example 1, the char lengths were 5.1" and 5.0", respectively.

We claim:

1. A flame retardant finish for cellulosic textile materials comprising an aqueous solution of tris(hydroxymethyl)phosphine, orthophosphoric acid, and a methylolated nitrogenous cellulose reactant, 1 to 3 moles of said tris(hydroxymethyl)phosphine per mole of said phosphoric acid.

2. A process for imparting flame retardant properties to cellulosic textile materials comprising applying a finish containing tris(hydroxymethyl)phosphine, orthophosphoric acid, and a methylolated nitrogenous cellulose reactant and heating the treated textile material at an elevated temperature, 1 to 3 moles of said tris(hydroxymethyl)phosphine per mole of said phosphoric acid.

3. A flame retardant as in claim 1 where the methylolated nitrogenous cellulose reactant is a methylolated melamine.

4. A cellulosic textile material treated by the process of claim 2.

References Cited

UNITED STATES PATENTS

3,619,113	9/1971	Stockel et al.	117-136 X
2,582,961	1/1952	Burnell et al.	117-136
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