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Stockel et al.

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[54] **DURABLE FLAME RETARDANT FINISH
FOR CELLULOSIC TEXTILE
MATERIALS**

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[56]

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2,809,941	10/1957	Reeves et al.	117/136 X
3,236,676	2/1966	Coates et al.	117/137 X
2,892,803	1/1959	Reeves et al.	117/136 X
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[57]

ABSTRACT

Flame retardant finishes for cellulosic textile materials containing tetrakis(hydroxymethyl)phosphonium phosphate, tris(hydroxymethyl)phosphine, and at least one organic nitrogenous compound.

7 Claims, No Drawings

DURABLE FLAME RETARDANT FINISH FOR CELLULOSIC TEXTILE MATERIALS

This invention relates to flame retardant finishes for cellulosic textile materials. More particularly, it relates to aqueous flame retardant finishes containing tetrakis (hydroxymethyl)phosphonium phosphate, tris(hydroxymethyl)phosphine, and at least one organic nitrogenous compound. It further relates to aqueous solutions containing tetrakis(hydroxymethyl)phosphonium phosphate and tris(hydroxymethyl)phosphine, and to the process for making these solutions.

Tetrakis(hydroxymethyl)phosphonium chloride, abbreviated THPC and obtained by reacting 1 mole of tris(hydroxymethyl)phosphine, abbreviated THP, 1 mole of formaldehyde and 1 mole of hydrochloric acid, is a component of certain flame retardant finishes for textile materials. When applied with organic nitrogenous compounds which contain trivalent nitrogen atoms bearing at least two members of the group consisting of hydrogen atoms and methylol groups, the treated textile materials have flame retardant properties which are durable to repeated launderings. The preferred nitrogenous compounds are melamine, urea and water-soluble methylol melamines and methylol ureas. (U.S. Pat. No. 2,809,941 is a basic reference). These finishes provide good flame retardancy which is durable to laundering, but the finishes impart a stiff and "boardy" hand and cause an objectionable, and sometimes severe, strength loss of the treated fabrics. Textile strength, tear strength and abrasion resistance are reduced.

In U.S. Pat. Nos. 2,892,803 and 3,236,676, it was suggested that tetrakis(hydroxymethyl)phosphonium phosphate of the formula $(\text{HOCH}_2)_3\text{PCH}_2\text{OH}\cdot\text{H}_2\text{PO}_4$ (abbreviated THPP) is the equivalent of THPC in flame retardant finishes containing nitrogenous compounds. Finishes containing THPP impart good flame retardancy which is durable to laundering, but again the treated fabrics are stiff and "boardy" and suffer from undesirable strength losses.

In copending, commonly assigned application, Ser. No. 861,481, filed Sept. 26, 1969, a flame retardant finish for textile materials is disclosed comprising an aqueous solution of THP, a methylolated nitrogenous compound and, optionally, urea. Methylolated nitrogenous compounds include methylolated melamines and methylolated ureas. The finish provides flame retardancy only when about three times the usual amount of methylolated nitrogenous compound is used. A very stiff hand is obtained.

It is, therefore, an object of this invention to provide a flame retardant finish for cellulosic textile materials which is durable to laundering.

A further object is to obtain such a finish which imparts a good "hand" to the textile material, i.e., it does not make the textile stiff.

Another object is to provide such a finish which is not injurious to the durability of the fabric to wear.

These and other objects of the invention will become apparent as the description thereof proceeds.

It has now been discovered that when an aqueous solution containing tetrakis(hydroxymethyl)phosphonium phosphate, tris(hydroxymethyl)phosphine and at least one organic nitrogenous compound having trivalent nitrogen bearing at least two members of the group consisting of hydrogen atoms and methylol groups, is applied to cellulosic textile materials, the materials become flame retardant without appreciable change in the hand or severe strength loss and the flame retardancy is durable to repeated launderings. This is a particularly surprising discovery in view of the comments above about each phosphorus compound when employed separately. Optionally, and often preferably, the flame retardant finish of this invention contains free formaldehyde.

Aqueous solutions of tetrakis(hydroxymethyl)phosphonium phosphate (THPP), tris(hydroxymethyl)phosphine (THP) and, optionally, formaldehyde can be prepared by reacting THP with formaldehyde and orthophosphoric acid (H_3PO_4) in

aqueous medium. Sufficient phosphoric acid is used to provide between 0.15 and 0.60 mole, preferably between 0.25 and 0.4 mole, of real orthophosphoric acid per mole of THP. The formaldehyde should be used in an amount sufficient to provide at least as many moles of formaldehyde as moles of orthophosphoric acid. Preferably at least twice as many moles of formaldehyde as orthophosphoric acid should be employed, i.e., between 0.5 and 1.25 mole of formaldehyde per mole of THP. The formaldehyde can be in the form of an aqueous solution or as paraformaldehyde. Sufficient water is present to provide a product solution with the desired concentration of solids, up to a maximum of about 78 percent. When the exothermic reaction subsides, the temperature of the mixture is held at about 50° C. for about 1 hour.

The product is an aqueous solution which can be used in preparing the flame retardant finishes. The amount of THPP present in the product depends on the amount of orthophosphoric acid used. Each mole of THPP requires by theory 1 mole of phosphoric acid and 1 mole of formaldehyde. For each mole of THPP formed, the amount of THP in the product is reduced by 1 mole. In actual practice, a little more than 1 mole of THP per mole of phosphoric acid is converted to tetrakis(hydroxymethyl)phosphonium compound.

The nitrogenous compounds of use in this invention include the organic amido compounds which are conventionally employed in the form of their methylol derivatives as thermosetting aminoplast textile finishes. They include the melamines, ureas, cyclic ureas, carbamates, triazinones, etc., and their methylol and alkylated methylol derivatives. The preferred nitrogenous compounds are urea, melamine, and water-soluble methylol melamines and methylol ureas. Representative methylol compounds include monomethylol urea, dimethylol urea, tetramethylol urea, dimethylol melamine, partially methylated trimethylol melamine, and the like. Combinations of two or more nitrogenous compounds may be employed.

The preferred aqueous flame retardant finishes of this invention contain urea and methylolated melamine. In preferred embodiments of this invention, the aqueous reaction product of 1.0 mole of THP, 0.3 mole of orthophosphoric acid and 1.0 mole of formaldehyde is combined with urea and a methylolated melamine such as dimethylol melamine or a partially methylated trimethylol melamine.

Sufficient flame retardant finish should be applied to the cellulosic textile material to provide between about 1 and 10 percent, preferably between about 2 and 4 percent, of phosphine-derived phosphorus based on the weight of the textile material. The phosphorus from phosphoric acid is disregarded. Sufficient nitrogenous compound is used to provide between about 3 and 15 percent, preferably between about 5 and 10 percent, of nitrogen based on the weight of the textile material. In the case of the preferred flame retardant finishes, at least 1 percent of nitrogen is provided by the urea and the methylolated melamine provided between about 1 and 10 percent, preferably between about 2.5 and 6 percent, of nitrogen, both based on the weight of the textile material.

From these percentages it is a simple matter to calculate the amounts of phosphorus-containing compounds and nitrogenous compounds to be used in preparing the flame retardant finishes. Of the total phosphorus-containing compounds (i.e., THP plus THPP) between about 0.15 and 0.60 mole percent, preferably between 0.25 and 0.40 mole percent, is THPP, and between about 0.85 and 0.40 mole percent, preferably between about 0.75 and 0.60 mole percent, is THP. The ratio of nitrogen of the nitrogenous compounds to phosphine-derived phosphorus on a parts by weight basis is between 15/1 and 3/10, preferably between 5/1 and 5/4.

The cellulosic textile materials should contain at least 20 percent 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 flame retardant finish can be applied to the textile material from the same bath or from separate baths by padding, dipping, spraying, etc. The fabric can be dried at a temperature between about 75° and 210° C. or higher. The drying time can range from several minutes at the lower temperatures to as low as 15 seconds at the highest temperature. The determining factor for time is the reduction of the moisture content to some finite level, e.g., 5–10 percent. Overdrying is not desirable. The finish is cured at a temperature between about 125° and 200° C., preferably between about 150° and 175° C. The time required for curing the finish is between 5 and 1 minutes, depending on the temperature and the weight of the textile material.

EXAMPLE 1

Paraformaldehyde (91 percent real formaldehyde) (133 g.) was slowly added to a mixture of 133 g. of 93 percent tris(hydroxymethyl)phosphine, 38 g. of 85 percent of orthophosphoric acid and 50 g. of water while maintaining a temperature of 50° C. When all of the paraformaldehyde was added, the temperature was maintained for about 1 hour. The molar ratio of tris(hydroxymethyl)phosphine/formaldehyde/phosphoric acid was 1/1/0.33. The product was an aqueous solution containing 73 percent solids.

EXAMPLE 2

Three preparations A, B and C were made by reacting together the amounts of tris(hydroxymethyl)phosphine (THP), orthophosphoric acid (H_3PO_4), aqueous formaldehyde (CH_2O) and water shown in Table I. The moles of real reactants are also shown.

TABLE I

	A		B		C	
	g.	moles	g.	moles	g.	moles
THP (89%)	150	1.075	150	1.075	150	1.075
H_3PO_4 (85%)	41.3	0.358	62.2	0.538	124.4	1.075
CH_2O (44%)	78.5	1.15	78.5	1.15	78.5	1.15
Water	20.3	—	25.3	—	38	—
Molar ratio*	1/1/0.33		1/1/0.5		1/1/1	

*Molar ratio of THP/ CH_2O / H_3PO_4 .

A mixture of phosphoric acid and formaldehyde was added in each preparation to a mixture of THP and water while keeping the temperature below about 42° C. by external cooling. The mixture was then allowed to slowly cool to about 25° C. The product solutions contained 70 percent solids.

EXAMPLE 3

Three preparations A, B and C were made by reacting together the amounts of tris(hydroxymethyl)phosphine (THP), aqueous formaldehyde (CH_2O), orthophosphoric acid (H_3PO_4) and water shown in Table II. The moles of real reactants are also shown.

TABLE II

	A		B		C	
	G.	Moles	G.	Moles	G.	Moles
THP (89%)	90	0.645	90	0.645	90	0.645
CH_2O (44%)	43.8	0.645	29.2	0.430	21.9	0.323
H_3PO_4 (85%)	24.8	0.215	24.8	0.215	18.6	0.161
Water	13.4	—	17.0	—	20.5	—
Molar ratio*	1/1/0.33		1/0.67/0.33		1/0.5/0.25	

*Molar ratio of THP/ CH_2O / H_3PO_4 .

The procedure of Example 2 was followed. The product solutions contained 70 percent solids.

EXAMPLE 4

An aqueous pad bath was prepared containing 18.1 percent solids of the product of Example 1, 8.7 percent of urea and 9.3 percent of dimethylol melamine. The pad bath was applied to 80×80 cm. cotton percale by a standard padding procedure

obtained an 80 percent wet pickup. The treated fabric, containing 14.5 percent solids of the product of Example 1 (2.0 percent phosphine-derived phosphorus), 7.4 percent of dimethylol melamine (3.75 percent melamine-derived nitrogen) and 4.8 percent of urea (2.24 percent urea-derived nitrogen), was dried at 107° C. and then heated for 1.5 minutes at 175° C.

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 drier. After each 10th 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 inches.

The flame retardancy of the treated fabric was durable for more than 90 washes. The textile strength of the fabric (W+F) was 82 pounds, the warp tear strength was 345 g., the fill tear strength was 160 g., the abrasion resistance of the warp plus fill was 56 percent of that of the untreated fabric, and the hand was relatively soft.

The same fabric treated with a similar finish containing tetrakis(hydroxymethyl)phosphonium chloride instead of the product of Example 1 had a flame retardancy also durable for more than 90 washes. However, the tensile strength of the fabric (W+F) was 67 pounds, the warp tear strength was 180 g., the fill tear strength was 100 g., the abrasion resistance of warp plus fill was 35 percent of that of the untreated fabric, and the hand was stiffer than that of the above treated fabric.

EXAMPLE 5

The pad bath of Example 4 was applied to 35/65 Dacron/cotton fabric by the procedure of Example 4.

The flame retardant finish was durable for more than 90 washes. A similar finish containing tetrakis(hydroxymethyl)phosphonium chloride instead of the product of Example 1 was durable for less than 60 washes.

EXAMPLE 6

Three pad baths were prepared containing the percentage amounts of the product of Example 1 (Prod. Ex. 1), a partially methylated trimethylolmelamine (TMM) and urea shown in Table III.

TABLE III

	A	B	C
Prod. Ex. 1 (solids)	15.1%	15.1%	15.1%
TMM	7.8%	7.8%	7.8%
Urea	3.0%	6.0%	9.0%

The pad baths were applied to cotton sheeting obtaining a 94 percent wet pickup. The treated fabrics A, B and C, containing 14.2 percent solids of the product of Example 1, 7.3 percent of partially methylated trimethylol melamine, and 2.8, 5.6 and 8.4 percent, respectively, of urea, were dried for 4 minutes at 107° C. and then heated at 165° C. for 4 minutes.

The fabrics contained 2.25 percent of phosphine-derived phosphorus, 2.35 percent of melamine-derived nitrogen and 3.65, 4.95 and 6.25 percent, respectively, of total nitrogen.

The flame retardancy of Fabric A was durable for less than 10 washes, of Fabric B and C for at least 90 washes. The treated fabrics had relatively soft hands.

A similar finish containing tris(hydroxymethyl)phosphine (THP) instead of the product of Example 1 provided a flame

retardancy durable for less than 10 washes. When the amount of methylolated melamine was tripled, the flame retardancy was greatly improved, but the hand of the fabric was stiff.

EXAMPLE 7

A pad bath was prepared containing 21.0 percent solids of the product of Example 1, 10.9 percent of partially methylated trimethylolmelamine and 8.35 percent of urea. The pad bath was applied to cotton twill obtaining a 67 percent wet pickup. The treated fabric, containing 14.2 percent solids of the product of Example 1, 7.3 percent of partially methylated trimethylolmelamine and 5.6 percent of urea, was dried at 107° C. for 4 minutes and then heated at 165° C. for 4 minutes.

The flame retardancy of the treated fabric was durable for more than 90 washes. The hand of the fabric was relatively soft.

EXAMPLE 8

Two pad baths A and B were prepared containing 15.0 percent and 18.0 percent solids, respectively, of the product of Example 1, 9.3 percent of dimethylolmelamine and 8.7 percent of urea. Pad bath A containing 2.50 percent of phosphine-derived phosphorus was applied to cotton broadcloth (Fabric U), cotton flannel (Fabric V), and 80×80 cotton percale (Fabric X-A) obtaining wet pickups of 96, 101 and 90 percent, respectively. Pad bath B containing 3.0 percent of phosphine-derived phosphorus was applied to 50/50 polyester/cotton fabric (Fabric Y), 35/65 polyester/cotton flannel (Fabric Z) and 80×80 cotton percale (Fabric X-B) obtaining wet pickups of 103, 106 and 95 percent, respectively. The treated fabrics were dried at 107° C. for 4 minutes and then heated at 165° C. for 4 minutes.

The durability to washing of the flame retardancy of the treated fabrics is shown in Table IV.

TABLE IV

Fabric	% phosphine-derived Phosphorus on the fabric	Durability No. of washes
U	2.40	25-40
V	2.52	70-80
X-A	2.25	50-70
X-B	2.85	<100
Y	3.09	80-100
Z	3.18	<100

The example demonstrates that the wash durability of the flame retardant finishes of this invention depend not only on the amount of phosphine-derived phosphorus applied to the fabric but also on the fiber composition and the construction of the fabric.

EXAMPLE 9

Twelve pad baths were prepared containing sufficient amounts of the products of Examples 2 and 3 to provide 2.5 percent of phosphine-derived phosphorus in the baths. The baths also contained dimethylolmelamine (DMM) and urea or a partially methylated trimethylolmelamine (TMM) and urea. The details are shown in Table V.

TABLE V

Pad Bath	Prod. of Example	Percent based on weight of pad bath		Urea
		DMM	TMM	
A	2-A	9.3%	—	8.7%
B	2-A	—	9.3%	8.7%
C	2-B	9.3%	—	8.7%
D	2-B	—	9.3%	8.7%
E	2-C	9.3%	—	8.7%

F	2-C	—	9.3%	8.7%
G	3-A	9.3%	—	8.7%
H	3-A	—	9.3%	8.7%
I	3-B	9.3%	—	8.7%
J	3-B	—	9.3%	8.7%
K	3-C	9.3%	—	8.7%
L	3-C	—	9.3%	8.7%

The pad baths were applied to 2.85 ounces mercerized cotton sheeting obtaining a 95 percent wet pickup. The treated fabrics were dried at 107° C. for 4 minutes and then heated at 165° C. for 4 minutes. The fabrics contained about 2.3 percent phosphine-derived phosphorus.

All of the fabrics possessed an acceptable flame retardancy durable for at least 100 washings.

The hands of the fabrics were examined and the results are shown in Table VI.

TABLE VI

Fabric	Hand	Molar Ratio*
A	slightly firm	1/1/0.33
B	slightly/moderately firm	1/1/0.33
C	firm	1/1/0.5
D	firm	1/1/0.5
E	extra firm	1/1/1
F	extra firm	1/1/1
G	slightly firm	1/1/0.33
H	slightly/moderately firm	1/1/0.33
I	slightly firm	1/0.66/0.33
J	slightly/moderately firm	1/0.66/0.33
K	very slightly firm	1/0.5/0.25
L	slightly/moderately firm	1/0.5/0.25

* Molar ratio THP/Formaldehyde/Phosphoric Acid

This example demonstrates the advantages of the finishes of this invention, which contain both THPP and THP, over finishes containing only THPP (Fabrics E and F). The example also demonstrates by Fabrics C and D, that the preferred usage of phosphoric acid is less than 0.5 mole per mole of THP.

When the above procedure was followed using sufficient tetrakis(hydroxymethyl)phosphonium chloride to provide 2.5 percent of phosphine-derived phosphorus in the pad bath and TMM, the treated fabric disintegrated after 40 washings.

When the above procedure was followed using sufficient tris(hydroxymethyl)phosphine to provide 2.5 percent of phosphorus in the baths, there was no flame retardancy when DMM was used, and the flame retardancy was not durable for 10 washes when TMM was used.

We claim:

1. An aqueous flame retardant finish for cellulosic textile materials comprising tris(hydroxymethyl)phosphine, tetrakis(hydroxymethyl)phosphonium phosphate and at least one organic nitrogenous compound having trivalent nitrogen bearing at least two members selected from the group consisting of hydrogen atoms and methylol groups.

2. The finish of claim 1 wherein the nitrogenous compound is selected from the group consisting of urea, melamine, a water-soluble methylol urea or a water-soluble methylol melamine.

3. The finish of claim 1 wherein the nitrogenous compound is a mixture of urea and methylolated melamine.

4. The finish of claim 1 where of the total phosphorus-containing compounds between about 0.15 and 0.60 mole percent is tetrakis(hydroxymethyl)phosphonium phosphate and between about 0.85 and 0.40 mole percent is tris(hydroxymethyl)phosphine.

5. The finish of claim 1 where the ratio of nitrogen in the nitrogenous compound to the phosphine-derived phosphorus is between about 15/1 and 3/10 on a parts by weight basis.

6. A process of treating cellulosic textile materials to render them flame retardant which comprises applying to said textile the flame retardant finish of claim 1.

7. A textile material obtained by the process of claim 6.

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