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AQUEOUS FLAMEPROOFING COMPOSITIONS AND CELLULOSIC MATERIALS TREATED THEREWITH

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The present invention relates to the novel flame-proofing compositions, flammable materials treated therewith and methods of treating such flammable materials to render them flameproof.

It has been proposed in the past to prepare flameproofing compositions utilizing materials such as the adduct of a polyhaloalkane, e. g., bromoform, with an unsaturated phosphate, e. g., triallyl phosphate. Such compositions suffer from the disadvantage that they do not give sufficient permanence to laundering.

It has also been proposed to employ tetrakis-hydroxymethyl phosphonium chloride (THPC) as a flameproofing agent. However, the use of this compound leaves the fabric with relatively poor tear and tensile strength. The combination of THPC with the bromoform adduct previously referred to has the disadvantage of the relatively high cost due to the use of the THPC, the objectionable odor liberated by THPC and the relatively low phosphorus content in the THPC.

It is an object of the present invention to form an improved flameproofing composition.

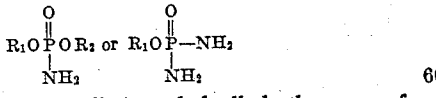
An additional object is to flameproof cellulosic materials in a manner to impart increased permanence to laundering.

A further object is to devise a more economic cellulosic fabric flameproofing composition.

Yet another object is to eliminate the tendering of cellulosic fabrics imparted by the application diethylphosphoramidate (diethyl amido phosphate) and a polymethylol compound thereto.

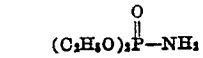
Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by the use of a composition comprising (1) a compound having the formula



where R_1 and R_2 are alkyl or haloalkyl, the sum of the carbon atoms in R_1 and R_2 being less than 8, (2) the adduct of a compound having the formula CX_2YZ, where X is chlorine or bromine, and Y and Z are hydrogen, chlorine or bromine with either a polymerizable neutral unsaturated alcohol ester of phosphoric acid or of an alkene phosphonic acid and (3) a polymethylol amide, azine or azole.

The preferred combination is the use of (1) diethyl phosphoramidate



(2) the 1 to 1 mol ratio bromoform adduct of triallyl phosphate and (3) trimethylolmelamine. It is surprising that the present composition can be successfully applied to cellulosic materials as the combination of diethyl phosphoramidate and trimethylolmelamine alone causes severe tendering of cellulosic fabrics, imparting a stiff board-like quality to the fabric. The novel compositions of the present invention, however, have improved flexibility and superior flameproofing qualities.

The flameproofing compositions of this invention are preferably applied as aqueous dispersions. Preferably the objects to be flameproofed are cellulosic in nature, e. g., cotton textiles, regenerated cellulose fabrics, acetate rayon.

As examples of suitable amidophosphates having less than eight carbon atoms, there can be used diethyl amido phosphate, dipropyl amido phosphate, ethyl propyl amido phosphate, amyl diamido phosphate, di-2-chloroethylamido phosphate, di-2-bromoethylamido phosphate, diisopropyl amido phosphate, ethyl diamido phosphate, propyl diamido phosphate, 2-chloroethyl amido phosphate, etc. These compounds can be prepared in the manner set forth in Kosolapoff, Organophosphorus Compounds (1950), Reaction Method II, pages 279–281, and the articles cited therein. The preferred amidophosphate or phosphonate is diethyl amido phosphate.

As the adduct of the compound having the formula CX_2YZ with the phosphate ester, there can be employed any of the adducts set forth in Frick et al. Patent 2,686,769, e. g., the adducts of CBr_4, CBr_3Cl, CBr_2Cl_2, $CBrCl_3$, CBr_3H, CBr_2H_2, CCl_4, CCl_3H or CCl_2H_2 with neutral unsaturated alcohol esters of phosphoric acid such as trialkenyl phosphates, e. g., triallyl phosphate, trimethyllyl phosphate, triethallyl phosphate, diallyl phosphate, methyl divinyl phosphate, methallyl phosphate, etc. In place of the phosphates in forming the adducts with the CX_2YZ compounds, there can be used polymerizable neutral unsaturated alcohol esters of alkene phosphonic acids, e. g., diallyl propene-2-phosphonate, dimethallyl propene-2-phosphonate, diethallyl propene-2-phosphonate, allyl methallyl propene-2-phosphonate, etc. These phosphonates can be prepared in the manner set forth in Kosolapoff reaction method IA, pages 121–123 and the references cited therein. The preferred adduct is the 1 to 1 mol ratio adduct of bromoform with triallyl phosphate.

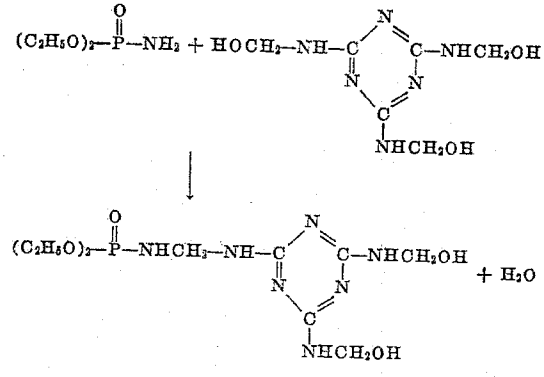
As the polymethylol amide, azine or azole, there can be used the formaldehyde reaction products with amides such as urea, thiourea, guanidine, dicyandiamide, substituted ureas, e. g., methyl urea, ethylene diurea, decamethylene diurea, methylene diurea, oxamide, acetamide, malonic acid amide, phthalamide, succinic acid amide, biuret, sulfamide, toluene sulfonamide. There also can be used any of the amides or substituted ureas disclosed in D'Alelio, United States Patent No. 2,320,816. Likewise, there can be used the reaction products of formaldehyde with aminotriazines such as melamine, ammeline, formoguanamine, acetoguanamine, ammelide, benzoguanamine, sym-triphenyl melamine, sym-triethyl melamine, 2-chloro-4,6-diaminotriazine, diaminotriazine, melam, melon, melem, as well as any of the aldehyde reactable aminotriazines disclosed in D'Alelio, United States Patent No. 2,368,451 and Widmer et al., United States Patent No. 2,197,357. Likewise, there can be used diazines, e. g., 2,4-diamino-1,3-diazine, azoles, e. g., carbamyl guanazole, guanazole, diamino pyrrole, etc. Sufficient formaldehyde is employed to form a polymethylol compound, e. g., sesqui-methylol urea, dimethylol urea, dimethylol melamine, trimethylol melamine, hexamethylol melamine, etc. Generally the amount of formaldehyde need not be more than sufficient to react with all the hydrogen atoms attached to the nitro-

gen atoms. The preferred compound for reaction with formaldehyde is melamine. The preferred reaction product is trimethylol melamine.

The mixture of the diethyl amido phosphate, bromoform adduct of triallyl phosphate and trimethylol melamine is preferably applied to the textile material in the form of an aqueous solution or dispersion. The bromoform-triallyl phosphate adduct is preferably employed as a polymer, e. g. the polymer described in Example I of Frick Patent 2,686,769.

Preferably about 30–50% of the phosphorus deposited upon the cloth, e. g., cotton, should be contributed by the bromoform adduct and the total phosphorus pick-up by the cloth is preferably in the range of about 1–1.5% of the total weight of the cloth. The diethyl phosphoramidate (diethyl amidophosphate) is utilized in an amount of from 1 to 1.5 mols, e. g., 1.25 mols per mol of trimethylol melamine. The bromoform-triallyl phosphate (1 to 1 mol ratio) is preferably used in an amount of 0.25 to 0.5 mol per mol of trimethylol melamine.

It is believed that the trimethylol melamine and diethyl amidophosphate form a thermosetting resin within the textile fiber. The bromoform-triallyl phosphate adduct modifies this composition to give increased flexibility and further gives some additional flame-proofing. The reaction of the amidophosphate with the trimethylol melamine and cellulose is believed to proceed as follows:



The methylol groups are then free to form ethers with cellulose and internal ethers with themselves. Both of the following types of reactions are believed to occur,

$$RNHCH_2OH + HO\text{-cellulose} \rightarrow RNHCH_2—O\ \text{cellulose} + H_2O$$

$$RNHCH_2OH + RNHCH_2OH \rightarrow RNHCH_2—O—CH_2—NHR + H_2O$$

where R is the residue of compound I attached to the methylol grouping CH_2OH, and cellulose stands for the cellulose molecule minus an OH grouping.

In the specification and claims, unless otherwise stated, all percentages and parts are by weight.

Example I

Cotton cloth was dipped in a solution prepared in the following manner:

1 part of diethyl phosphoramidate and 1 part of trimethylol melamine were dissolved in water. To the above solution there was added an equal weight of an emulsion made by mixing 252 parts of triallyl phosphate, 163 parts of bromoform, 12.5 parts of potassium persulfate, 85 parts of polyvinyl alcohol (medium viscosity), 22.5 parts of sodium bicarbonate and 850 parts of water, mechanically stirring the mixture until completely emulsified and then warming the mixture at 85–90° C. for 2.5 hours with continuous stirring. (It should be noted that any of the emulsifying agents and catalysts described in Frick Patent 2,686,769 can be used in place of the polyvinyl alcohol and potassium persulfate of this example.)

The pH of the resulting mixture containing the diethyl phosphoramidate, trimethylolmelamine and polymerized bromoform-triallyl phosphate adduct was adjusted to 5–6 with phosphoric acid.

After the cotton cloth was dipped in the above mixture, the cloth was squeezed through a roll, cured for 3 minutes at 160° C. and dried at 80° C. The dry pick-up of the cloth was about 25%.

In other examples carried out as this one, the dry pick-up of the cotton cloth generally ranged from 20–30%.

In place of phosphoric acid, there can be employed any conventional acidic curing agent for melamine formaldehyde resins, such as those shown in the Widmer patent for example. The curing can be carried out by using temperatures below 160° C. for longer than 3 minutes if desired.

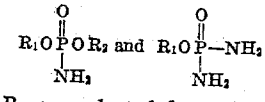
The treated cotton cloth of Example I was flameproof even after 20 launderings.

Example II

Example I was repeated, replacing the cotton cloth with a regenerated cellulose (viscose) fabric. The fabric was also flameproof even after 20 launderings.

I claim:

1. A flameproofing composition comprising a mixture of (*a*) a compound selected from the group consisting of



where R_1 and R_2 are selected from the group consisting of alkyl monochloro alkyl and monobromo alkyl groups, the sum of the carbon atoms in R_1 and R_2 being less than 8, (*b*) the adduct of a compound having the formula CX_2YZ where X is a member of the group consisting of chlorine and bromine and Y and Z are selected from the group consisting of hydrogen, chlorine and bromine, with a compound from the group consisting of polymerizable, neutral, ethylenically unsaturated acyclic alcohol esters of phosphoric acid and polymerizable, neutral, ethylenically unsaturated acyclic alcohol esters of an alkene phosphonic acid and (*c*) a member of the group consisting of polymethylol amides, polymethylol azines and polymethylol azoles dispersed in water, compound (*a*) being used in amount of 1 to 1.5 mols per mol of compound (*c*) and adduct (*b*) being used in an amount of 0.25 to 0.5 mol of compound (*c*).

2. A normally inflammable material that has been flameproofed by impregnating the same with the composition of claim 1.

3. A composition according to claim 1 wherein the polymethylolamide is a polymethylol urea.

4. A composition according to claim 1 wherein the polymethylolamide is a polymethylol melamine.

5. A flameproofing composition comprising a mixture of 1 to 1.5 mols diethyl phosphoramidate, 0.25 to 0.5 mol of the adduct of bromoform with triallyl phosphate and 1 mol of a polymethylolmelamine dispersed in water.

6. A composition according to claim 5 wherein the polymethylolmelamine is trimethylolmelamine.

7. A flameproofed cellulosic material obtained by impregnating the cellulosic material with the composition of claim 5.

8. A flameproofed cellulosic material according to claim 7 wherein the cellulosic material is cotton fabric.

9. A flameproofed cellulosic material according to claim 7 wherein the cellulosic material is regenerated cellulose fabric.

References Cited in the file of this patent

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2,582,961	Burnell et al.	Jan. 22, 1952
2,686,769	Frick et al.	Aug. 17, 1954