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Burke

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[54] **HALONEOPENTYL PHOSPHORODIAMIDATE**

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[51] **Int. Cl.** **C07f 9/24**

[58] **Field of Search** 260/950, 953, 959, 963

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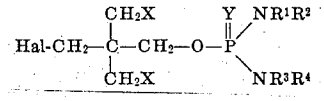
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[57] **ABSTRACT**

Haloneopentylphosphorodiamidate, useful as a flame retardant for cellulosic materials, of the formula



wherein Hal is Cl or Br, X is H, Cl, Br or CH_3, Y is O or S and each of R^1, R^2, R^3 and R^4 independently is H, CH_2OH, CH_2OCH_3 or $CH_2OC_2H_5$.

4 Claims, No Drawings

HALONEOPENTYL PHOSPHORODIAMIDATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to haloneopentylphosphorodiamidates which are useful as flame retardants for cellulosic materials.

2. Description of the Prior Art

Flame retarding chemicals are known to have many applications in carpets and rugs, materials for building construction, electrical and electronic appliances, apparel, paper and wood products, transportation and home furnishings. Apparel, and especially children's apparel, has been the basis of much research directed to making it more flame resistant.

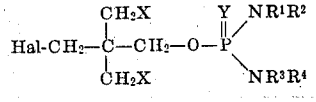
Many flame retardants and processes for their application to textile fabrics are known. In the area of cellulosic fabrics, the most commonly used flame retardants are inorganic compounds, for example, aluminum sulfate, ammonium phosphate, bromide and sulfamate, antimony chloride, antimony oxides, borax, boric acid and zinc borate. Organic compounds which are used as flame retardants for textile fabrics generally are those organic compounds which contain phosphorus, nitrogen and halogen, either singly or in combination. Such compounds include dicyandiamide, thiourea, dibromopropanol, hexabromodiphenyl and tris(2,3-dibromopropyl)phosphate. The above types of flame retardants, although often providing good initial flame retardancy, may not provide durable flame retardancy, the chemical being washed away during laundering; such chemicals need to be applied after each washing. Durable flame retardant finishes for textile fabrics are also known, such as those based on tetrakis(hydroxymethyl)phosphonium chloride or hydroxide and wherein the phosphorus compounds are cured with ammonia on the fabric to form an insoluble fire retardant polymer. Other known durable flame retardant finishes are obtained by coapplying a phosphoric acid derivative with an aminoplast resin which, upon curing, durably fixes the fire retardant chemical on the fabric.

The major problems which often are encountered in the application of flame retardant chemicals to textile materials may include any one or more of the following: (1) unacceptable stiffening of the treated fabric, that is, unsatisfactory fabric aesthetics; (2) weakening of the fiber substrate; (3) unsatisfactory durability to launderings; (4) toxicity, that is, skin sensitization; (5) discoloration of treated fabrics; and (6) high cost.

OBJECTS AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide a compound which is an effective flame retardant for cellulosic materials, especially textile fabrics thereof. It is a further object to provide such a flame retardant which can be applied to fabrics without substantially adversely affecting the fabric aesthetics. Another object is to provide such a flame retardant chemical which is economical to use, durable to laundering and resistant to discoloration.

In summary, the invention herein resides in the discovery and use of a compound of the formula



wherein Hal is Cl or Br, X is H, Cl, Br or CH_3, Y is O or S and each of R^1, R^2, R^3 and R^4 independently is H, CH_2OH, CH_2OCH_3 or $CH_2OC_2H_5$. Preferred compounds herein are of the above formula wherein Hal and X are Br, Y is O and all of the R groups are H or CH_2OH or two are H and two are CH_2OH.

DETAILED DESCRIPTION OF THE INVENTION

The compounds of the above formula wherein all the R groups are H can be prepared by reacting phosphorus oxychloride ($POCl_3$) or thiophosphoryl chloride ($PSCl_3$) with a haloalcohol of the formula $HalCH_2C(CH_2X)_2CH_2OH$, wherein Hal and X are as defined above, to form a phosphorodichloridate, and then with ammonia to form the diamidate. The reactions of $POCl_3$ and $PSCl_3$ with compounds containing reactive hydrogens are well known in the art. The aforesaid haloalcohols are well known; many are commercially available. Although polyhaloalcohols containing both chlorine and bromine atoms are useful, because of their more ready availability polyhaloalcohols containing only one type of halogen are preferred; the preferred halogen is bromine. A convenient preparation of haloalcohols comprises reacting an aldehyde of the formula $A_xCH_{3-x}CHO$ wherein x is 0–2 and A is C_{1-2} alkyl with formaldehyde in an aldol Cannizarro-type condensation under alkaline conditions to produce a polyol which can be halogenated to the desired haloalcohol, for example, by means of HBr, PBr_3, $HCl/ZnCl_2$, PCl_3, PCl_5 or $SOCl_2$.

The aforesaid dichloridate which is an intermediate can be isolated and purified, for example, by distillation, but such isolation is not required for the preparation of the compounds of this invention. The condensation of the dichloridate with ammonia to form the inventive diamidate is preferably carried out at low temperatures, for example, −40°C. to 0°C., to minimize the possible decomposition of the intermediate monoamidate. Moreover, the aforesaid reactions are preferably carried out in the presence of a solvent, such as methylene dichloride, chloroform, carbon tetrachloride, toluene or a xylene, the only requirement for the solvent being that it should be inert to the reactants and the desired product. If desired a catalyst, such as $AlCl_3$ or $AlBr_3$, can be used in the initial phosphorus halide reaction but, generally, a catalyst is not required since the reaction proceeds well at normal temperatures and can be readily carried to substantial completion by increasing the temperature or by increasing the time of reaction or both. The amination reaction proceeds rapidly without a catalyst. In the initial phosphorus halide reaction the evolved hydrogen chloride can be conveniently removed from the reaction system by passing an inert gas, such as nitrogen, through the system. In the amination reaction the hydrogen chloride can be conveniently removed as formed by adding an acid acceptor, such as triethylamine or pyridine, or by the use of an excess of ammonia.

The hydroxymethyl compounds of this invention, that is, compounds of the invention wherein at least one of R^1, R^2, R^3 and R^4 is CH_2OH, can be prepared by reacting the above-described diamidates with formaldehyde. The reaction is preferably carried out in solution under acidic or basic conditions, preferably basic conditions. Since the unsubstituted diamidates, particularly the polyhalo compounds, are not very soluble in

water, these compounds are dissolved in a solvent system comprising water and about 25–75% by weight of an organic solvent which is miscible with water, for example, methanol, ethanol, isopropanol, tetrahydrofuran, ethylene glycol, monomethyl ether of ethylene glycol, monoethyl ether of ethylene glycol, polyethylene glycol, acetone, methyl ethyl ketone, dimethylsulfoxide, dimethylformamide or dimethylacetamide. A convenient form of formaldehyde for use in the methylolation reaction is 37% aqueous formaldehyde. When the reaction is carried out under basic conditions, a convenient pH is 8–12, preferably 9–11. Any soluble alkalizing material can provide the desired basic pH, such as sodium silicate, sodium carbonate, trisodium phosphate, sodium hydroxide or potassium hydroxide; the latter two are preferred. The reaction is carried out at 0–30°C., preferably 10–20°C. Progress of the methylolation reaction can be conveniently followed by periodic broad band proton decoupled P-31 nuclear magnetic resonance (NMR) spectrum analysis of the reaction mixture using 85% phosphoric acid as the external standard. The phosphorodiamidate materials used in the formylation reaction have a characteristic band or multiplet of peaks in the range of −18 to −22 ppm. relative to the standard. As the methylol compound is formed, the peaks in the NMR spectrum shift toward the standard and are centered in the range of −16 to −19 ppm. The number of methylol groups introduced into the phosphorodiamidate molecule will depend upon the molar ratio of formaldehyde to phosphorodiamidate in the reaction mixture; that is, molar ratios of about 1:1, 2:1, 3:1 and 4:1 will provide mono-, di-, tri- and tetramethylol derivatives, respectively.

The methoxymethyl and ethoxymethyl compounds of the invention can be made by reaction of the appropriate non-methylolated phosphorodiamidate with chloromethyl methyl ether or chloromethyl ethyl ether, respectively, in an alkaline medium, for example, at a pH of 8–12, preferably 9–11, or by etherification of the above-described hydroxymethyl compounds with methanol or ethanol, respectively, in an acidic alcoholic medium, for example, at a pH of 1–5, preferably 2–3.

Typical compounds of the present invention include those shown in Table I as well as their thiono analogs. The preferred compounds are 2,2-bis(bromomethyl)-3-bromopropylphosphorodiamidate and its methylol derivatives, particularly the bis methylol derivative.

TABLE I

2,2-dimethyl-3-chloropropylphosphorodiamidate
2-methyl-2-chloromethyl-3-chloropropylphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropylphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropyl-N-methylolphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropyl-N,N-dimethylolphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropyl-N,N′-dimethylolphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropyl-N,N,N′,N′-tetramethylolphosphorodiamidate
2,2-bis(chloromethyl)-3-chloropropyl-N-methoxymethylphosphorodiamidate
2,2-bis(chloromethyl)--chloropropyl-N,N′-di(methyoxymethyl)-phosphorodiamidate
2,2-dimethyl-3-bromopropylphosphorodiamidate
2-methyl-2-bromomethyl-3-bromopropylphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropylphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N-methylolphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N,N-dimethylolphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N,N′-dimethylolphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N,N,N′,N′-tetramethylolphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N,N′-dimethoxymethylphosphorodiamidate
2,2-bis(bromomethyl)-3-bromopropyl-N,N,N′,N′-tetramethoxymethylphosphorodiamidate

Any suitable method can be used to incorporate a compound of the invention into the cellulosic material being treated. A convenient method is to apply the compound in solution, thus ensuring good penetration into the cellulosic substrate. Since the compounds of the invention, particularly the polyhalogenated compounds, have low solubilities in water, a solvent comprising water and about 25–75% by weight of a water miscible organic solvent, such as methanol, ethanol, isopropanol, ethylene glycol, monomethyl ether of ethylene glycol, monoethyl ether of ethylene glycol, polyethylene glycol, tetrahydrofuran, acetone, methyl ethyl ketone, dimethylsulfoxide, dimethylformamide or dimethylacetamide, is conveniently used. The preferred water miscible solvents are isopropanol and dimethylformamide. A sufficient amount of the composition should be applied to the cellulosic material to provide the desired amount of flame resistance. The amount of the compound of the invention applied should be 3.5–10% by weight, based on the weight of fabric, preferably 5–9%. The solution of the compound can be applied by spraying or dipping but the preferred method is by a conventional padbath technique. Wet pick-up of solution is usually 60–200% by weight, based on the weight of fabric, preferably 80–120%.

The flame resistance imparted to a combustible cellulosic material by a compound of this invention, particularly a methylol or alkoxymethyl derivative, is made durable to laundering by fixing or curing the compound after it has been applied to the substrate. Curing is carried out for a sufficient time and at such a temperature that the compound is insolubilized on the substrate. Representative of such an operation, the substrate which is impregnated with a solution of a compound of the invention is dried at 20°–115°C. Curing is effected at 150°–190°C., preferably 160°–190°C., in the presence of an acidic curing catalyst for 2–10 minutes, preferably 2–4 minutes. The catalyst is usually dissolved in the solution of phosphorodiamidate before the solution is applied to the material being treated. The amount of catalyst used is 0.5–5 weight %, preferably 1–2.5%, based on the weight of the solution. Suitable catalysts are protonic and Lewis acids and include organic acids, such as oxalic, tartaric, glycolic, lactic, succinic, citric and malic acids and their ammonium salts; salts of inorganic acids, such as the ammonium salts of hydrochloric, phosphoric and sulfuric acids, zinc fluoroborate, zinc chloride, zinc nitrate, magnesium chloride and

magnesium nitrate; and the hydrochlorides of 2-amino-2-methyl-1-propanol and tris(2-hydroxyethyl-)amine. The preferred catalysts include ammonium chloride and 2-amino-2-methyl-1-propanol hydrochloride.

When the compounds of this invention are used to impart a significant degree of flame resistance to combustible cellulosic materials, they usually are applied as a liquid composition in combination with other agents conventional in the art for enhancing flame resistance and for improving the durability of the effect. The liquid composition generally comprises the phosphorodiamidate, a curing catalyst, a conventional aminoplast resin precursor, described below, and a volatile carrier solvent which can wet, penetrate and swell the cellulose and which is readily removable by volatilization at fixation temperatures. Other adjuvants, such as nonionic wetting agents, may also be advantageously incorporated into the treating solution. The liquid composition generally contains 1.5–20% by weight, preferably 3–15%, of the phosphorodiamidate of the invention in combination with an aminoplast resin precursor, the weight of the aminoplast resin precursor being 50–150% of the weight of the phosphorodiamidate, preferably 75–140%.

Aminoplast resin precursors (that is, resin intermediates) useful herein are water soluble polymethylol compounds containing at least 2 moles of condensed formaldehyde, for example, as N-hydroxymethyl groups of C_{1-4} alkyl ethers thereof. Typical of these aminoplast resin intermediates are the partial or complete ethers of polymethylol derivatives of amides, such as urea, thiourea, guanidine and dicyandiamide. Particular examples of such precursors include dimethylolurea, tetramethylolurea, di(methoxymethyl)-urea, dimethylol guanidine, trimethylol guanidine and dimethyloldicyandiamide. Derivatives of substituted ureas can also be used, such as formaldehyde condensates, and their ethers, of ethyleneurea, methyleneurea, acetylenediurea, diurea, oxydimethyleneurea (uron) and iminodimethyleneurea (triazone). Particular examples of such condensates include dimethylolethyleneurea, dimethylolmethyleneurea, tetramethylolacetylenediurea, trimethyloldiurea, di(methoxymethyl)uron and di(methoxymethyl)triazone. Derivatives of triazines, such as derivatives of melamine, diaminotriazine, formoguanamine and 2-chloro-4,6-diaminotriazine, can also be used. These represent a preferred class of aminoplast resin intermediates or precursors. Specific examples include formaldehyde adducts such as di- and trimethylolmelamine, optionally partially methylated, hexamethoxymelamine, tetramethyloldiaminotriazine and tetramethylol-2-chloro-4,6-diaminotriazine.

If desired the methylol compounds of the invention can be prepared in situ for application to cellulosic substrates. For example, a solution of an invention compound of the above formula wherein all the R groups are H can be mixed in isopropanol with the requisite amount of formaldehyde (as a 37% aqueous solution), the pH of the mixture being adjusted to 10–11 using aqueous sodium hydroxide. The amount of formaldehyde used will depend upon whether the mono-, di-, tri or tetramethylol compound is desired. The above mixture is then stirred at room temperature for 1–2 hours, readjusting the pH to 10–11 if necessary. Resin precursor is then added, if desired, the concentration of the compound is adjusted to the desired level and the pH is adjusted to 7–8. Finally, the acid catalyst is added and the resulting solution is used as a padding bath to treat the cellulosic material which is to be made flame resistant.

Cellulosic fabrics which are treated with a compound of this invention have fabric characteristics, for example, hand, softness and drape, substantially indistinguishable from the untreated fabrics and the imparted flame resistance is durable to laundering. Moreover, since in the compounds of the invention the halogen atom (or atoms) is attached to a carbon atom which is adjacent to a carbon atom which does not contain any hydrogen atom, that is, each carbon atom containing a halogen atom is α to a fully substituted carbon atom, the compounds of the invention exhibit good thermal and photolytic stability because there can be no α,β-elimination of hydrogen halide. Elimination of hydrogen halide may lead to discoloration of the fabric and formation of a corrosive atmosphere. The unusual and unexpected effectiveness of the compounds of the invention as durable flame retardants for cellulosic materials appears to relate to the presence of both halogen and phosphorodiamidate moieties in the compounds.

The compounds of this invention are particularly effective on all forms of cellulose which swell and become flexible upon exposure to the carrier solvent (water or an organic solvent as described above) used to prepare the solution or liquid composition. When complete penetration of the cellulosic material is achieved, the flame resistance is imparted throughout the material. Suitable cellulosic materials include natural fibers, purified wood pulp and rayon. In the textile field, natural fibers include the preferred fiber cotton, linen, viscose rayon, cuprammonium rayon, jute, hemp and ramie. Such materials can be treated in the form of raw fiber, carded stock, rovings, thread, yarn and felts as well as in the form of knitted and woven fabrics. Cellulosic materials which have been treated with the compounds of this invention are especially useful for tents, stage scenery, upholstery fabrics, slipcovers, draperies, wearing apparel for personnel in close relation to fire or heat, bedding, nightclothes, tarpaulins, insulation, padding, rope, string and twine.

The following experiments demonstrate the utility of the compounds of this invention in combination with trimethylolmelamine as flame retardants for cellulosic materials. The experiments included use of the Vertical Flame Test and determination of Limiting Oxygen Index.

Limiting Oxygen Index (LOI) is determined with a 5 × 2 inch piece of fabric spread lengthwise in a vertical plane and supported along its vertical edges. The spread fabric is positioned inside a transparent cylindrical column open only at the top. The top of the column is 1 or more inches above the spread fabric. The interior of the column is provided with an upward flow, from its base, of a gaseous mixture of pure oxygen and pure nitrogen. The volume flow rate of each gas making up the mixture is intrumented and manually adjustable. To test fabric in this apparatus, the spread fabric is ignited from the top while gas mixture flows up the column. The flow rates of the nitrogen and oxygen are adjusted until the flame on the ignited fabric just goes out. The ratio of the volume flow of oxygen to the sum of the volume flows of oxygen and nitrogen is then calculated. This value, called the Limiting Oxygen Index,

is the average of two determinations. As a standard of reference, untreated 8 oz. cotton twill which was used in these experiments to test the effectiveness of the compounds of this invention has an LOI value of 0.180 ± 0.002 and is completely burned up in the vertical flame test. Any treated cotton having an LOI value of greater than 0.180 is considered to exhibit some flame resistance. Air contains about 21 mole % of oxygen; therefore, fabrics with LOI values below about 0.210 can be expected to burn freely in a candle-like manner (from the top to the bottom) in air.

The Vertical Flame Test and char length determination are carried out in a 12 × 12 inch cabinet which is 30 inches high (30.5 cm. × 30.5 cm. × 76.2 cm.) and has a glass front. Gas circulation is provided by a 4 inch (10.2 cm.) high opening beneath the glass front and a 6 inch (15.2 cm.) diameter baffled hole at the top of the cabinet. It is provided with holder brackets on which a specimen holder is hung. The specimen holder provides a 2 inch (5.1 cm.) wide by 14 inch (35.6 cm.) high vertical open space and vertical side clips to hold edges of fabric which span this open space. Samples are ignited by a 6 inch (15.2 cm.) high Bunsen burner having a 0.375 inch (0.95 cm.) inside diameter tube and a luminous flame 1.5 inches (3.8 cm.) long. To conduct the test, a 2.75 inch × 10 inch (7.0 × 25.4 cm.) fabric sample is held in the specimen holder by its vertical edges and the specimen holder is hung centrally by the holder brackets. The igniting flame is applied so that 0.75 inch (1.9 cm.) of the lower end of the fabric is in the flame. This exposure is continued for 3.0 seconds and the flame is removed. After the flame has extinguished itself, the sample is removed from the holder. A hook with an attached weight is inserted into the sample on one side of the charred area 0.25 inch (0.6 cm.) from the outside edge and 0.25 inch (0.6 cm.) from the lower edge. For 2.0 to 6.0 oz. per square yard (74–222 g./m.²) fabric a 0.50 pound (0.227 kg.) weight is used. The corner of the cloth at the opposite edge of the char from the load is gently raised until the sample and weight are clear of supporting surface. The length of the tear which occurs is measured (in inches) and reported as char length. The char lengths reported below are the averages of 2 or 4 determinations with no sample burning the entire length. If any one sample burns the entire length (BEL), all samples are so rated.

In the following experiments parts shown are by weight unless otherwise indicated. Laundering, also expressed as home washing (HW), was carried out by exposing the fabric to a standard laundering cycle employing a washing solution of 100 g. of a commercial detergent ("Tide") per 15 gallons of water and tumble drying the washed fabric.

EXPERIMENT 1

Six padbaths were prepared of the following compositions, the catalyst being 2-amino-2-methyl-1-propanol hydrochloride:

	1	2	3	4	5	6
Compound of Example 1	4	6	8	8	10	10
dimethylformamide	42	42	42	42	40	44
trimethylolmelamine	8	8	8	4	8	0
catalyst	2	2	2	2	2	2
water	44	42	40	44	40	44

Cotton twill strips 5 inches × 10 inches (12.7 cm. × 25.4 cm.) were padded in each of the above solutions to a wet pick-up of about 87%, based on the weight of fabric. The fabrics were dried at 100°C. for 10 minutes and cured at 165°C. for 4 minutes. The treated fabric hand was about the same as that of the untreated fabric. LOI determinations, Vertical Flame Tests and elemental analyses were carried out initially, after one home wash and after 20 home washings. The results are summarized in Table II.

TABLE II

	Pad Bath No. 1	2	3	4	5	6
Initial Add-On						
Compound of Ex. 1	3.9	5.2	7.5	7.3	9.2	8.9
Trimethylolmelamine	7.0	7.0	7.0	3.5	7.0	0
% Bromine						
Initial	2.12	3.05	3.92	4.13	4.68	4.87
After 1 HW	—	—	—	—	—	0.98
After 20 HW	1.89	2.71	3.40	2.53	3.84	0.78
% Retained after 20 HW	89	89	87	61	82	16
LOI						
Initial	0.219	0.242	0.254	0.238	0.261	0.237
After 1 HW	0.224	0.243	0.262	0.221	0.270	0.173
After 20 HW	0.223	0.241	0.256	0.216	0.286	0.174
Char Length (inches)						
Initial	7.5	2.5	1.2	3.9	1.4	3.3
After 1 HW	8.3	2.8	1.6	7.4	0.8	BEL
After 20 HW	9.1	2.9	1.5	9.0	0.5	BEL

The control sample of fabric burned the entire length. The use of Pad Bath No. 1 containing a compound of this invention provided a significant improvement (before washing) over the control. The use of a compound of this invention without trimethylolmelamine (Pad Bath No. 6) provided a marked improvement (before washing) over the control; however, the treated fabric lacked durability, that is, the flame resistant characteristic was not permanent. In addition to char length, the

bromine content after washing also provides an indication of the durability of treatment.

EXPERIMENT 2

A padbath solution was prepared so as to contain the compound of Example 2 (11.6 g.), dimethylformamide (18.9 g.), trimethylolmelamine (8 g.), 2-amino-2-methyl-1-propanol hydrochloride (2 g.) and water (59.5 g.). Three strips of 5 inch × 10 inch (12.7 cm. × 25.4 cm.) 8 oz. cotton twill fabric were padded to a wet pick-up of 87%, based on weight of fabric. The fabrics were dried at 100°C. for 10 minutes and cured at 165°C. for 4 minutes. The treated fabric hand was about the same as that of the untreated fabric. LOI determinations, Vertical Flame Tests and elemental analyses for phosphorus, bromine and nitrogen were carried out initially, after 1 home wash and after 20 home washes. The results are summarized in Table III.

TABLE III

Initial Add-on	
Compound of Example 2	9.0
Trimethylolmelamine	7.0
% Bromine	
Initial	3.94
After 1 HW	3.34
After 20 HW	3.36
% Phosphorus	
Initial	0.44
After 1 HW	0.50
After 20 HW	0.40
% Nitrogen	
Initial	3.18
After 1 HW	3.11
After 20 HW	3.06
LOI	
Initial	0.242
After 1 HW	0.253
After 20 HW	0.253
Char Length (inches)	
Initial	1.7
After 1 HW	0.7
After 20 HW	3.1

As shown by the above, the compound of Example 2 in combination with trimethylolmelamine provides both effective and durable flame retardancy on cotton twill.

In the following examples, parts are parts by weight except where otherwise stated. Broad band proton decoupled P-31 NMR spectra are reported in ppm. relative to 85% phosphoric acid in the manner previously described.

EXAMPLE 1

A mixture of tribromoneopentyl alcohol (162.5 g.; 0.5 mole), phosphorus oxychloride (335 g.; 2.18 moles) and potassium chloride (2.5 g.) was heated to reflux (110°C.) for 2.5 hours. The excess $POCl_3$ was removed by vacuum stripping, initially at 110°C. and 60 mm. pressure and then at 103°C. and 0.9 mm. pressure. The product, a viscous yellow liquid (217 g.), was confirmed to be 2,2-bis(bromomethyl)-3-bromopropyl-phosphorodichloridate on the basis of its P-31 NMR spectrum which showed as its major peak a triplet ($J = 6H_z$) at −6.1 ppm. relative to phosphoric acid, collapsing to a singlet on proton decoupling. The structure was further confirmed by the proton NMR spectrum which showed a doublet ($J = 6H_z$) at 4.4 δ and a singlet at 3.6 δ with area ratios 2.03:6.0.

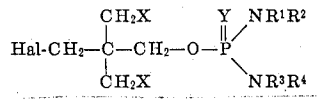
Ammonia (35 g.; 2.06 moles) was added slowly at −10°C. to −15°C. to a solution of 2,2-bis(bromomethyl)-3-bromopropylphosphorodichloridate (221 g.; 0.5 mole), prepared as described above, in 1,000 ml. of carbon tetrachloride. The ammonia addition was continued until the mixture was strongly alkaline, about 4 hours. The solids were isolated by filtration; the ammonium chloride was removed by slurrying the solids with water until the filtrate was free of chloride ion. The recovered product 2,2-bis(bromomethyl)-3-bromopropylphosphorodiamidate (96.5 g.) exhibited a m.p. of 138°–146°C. (144°–148°C. after recrystallization from isopropanol). Calc'd. for $C_5H_{12}O_2N_2PBr_3$: C, 14.9; H, 2.9; N, 6.95; P, 7.6; Br, 59.6%. Found: C, 15.8; H, 3.8; N, 7.3; P, 7.8; Br, 61.3%. The P-31 (singlet at −17.6 ppm.) and the proton NMR spectra exhibited by the product were consistent with the expected structure.

EXAMPLE 2

2,2-Bis(bromomethyl)-3-bromopropylphosphorodiamidate (10.1 g.; 0.025 mole), prepared as in Example 1, was dissolved in a mixture of dimethylformamide (20 ml.) and water (20 ml.). To the solution at room temperature were added 4.2 g. (0.05 mole) of formaldehyde (37% aqueous solution) and the pH was adjusted to 10.0 with 20% aqueous sodium hydroxide. After standing for 1 hour the pH was adjusted to 6.5 with 10% aqueous hydrochloric acid. The desired product 2,2-bis(bromomethyl)-3-bromopropyl-bis-(hydroxymethyl)phosphorodiamidate was obtained by removing the solvent at 50°–65°C. at 10–20 mm. pressure. The structure was confirmed by P-31 and proton NMR spectra. In using the compound of this example, if desired, it can be applied to the cellulosic material being treated without isolating it from the solvent in which it is prepared.

I claim:

1. Compound of the formula



wherein Hal is Cl or Br, X is H, Cl, Br or CH_3, Y is O or S and each of R^1, R^2, R^3 and R^4 independently is H, CH_2OH, CH_2OCH_3 or $CH_2OC_2H_5$.

2. The compound of claim **1** wherein Hal and X are Br, Y is O and all of the R groups are H.

3. The compound of claim **1** wherein Hal and X are Br, Y is O, R^1 and R^2 are H and R^3 and R^4 are CH_2OH.

4. The compound of claim **1** wherein Hal and X are Br, Y is O and all of the R groups are CH_2OH.

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