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## CYCLIC PHOSPHONO-CARBOXYLIC AMIDES

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Claims priority, application Great Britain, May 3, 1963, 17,563/63

2 Claims. (Cl. 260—937)

This application is a division of S.N. 362,998, filed Apr. 27, 1964, now abandoned.

This invention relates to substituted phosphono-amides, to processes for their production, the compositions containing such compounds, and to the use of such compositions to impart flame-resistance to cellulose and cellulose-containing materials.

Numerous methods for treating cellulosic materials to impart flame-resistance thereto have been suggested. For example, mixtures of boric acid or ammonium dihydrogen orthophosphate with borax have been used to treat textiles, but the treatment must be repeated after each wash. Methods of preparing wash-proof finishes include precipitation of metal oxides within or on the fibre, e.g. successive precipitation of ferric oxide and a mixture of tungstic acid and stannic oxide or successive precipitation of antimony trioxide and titanium dioxide. These are multi-bath processes involving the use of strongly acidic solutions and are therefore inconvenient. Moreover, because there is a surface deposit on the textile of white metal oxide difficulties are encountered in subsequent dyeing processes.

A known single-bath process involving a metal oxide entails padding a dispersion of a chlorinated hydrocarbon and finely divided antimony oxide onto the fabric and heating to render the finish wash-proof. The active agent in this case is antimony oxychloride which is formed by the interaction of the oxide with the hydrogen chloride liberated from the chlorinated hydrocarbon when flame temperatures are approached. The handle of the finished fabric is deleteriously affected and this is especially so with fine, closely-woven fabrics.

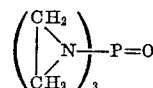
Esterification of cellulosic materials with, for instance, diammonium hydrogen orthophosphate has also been used to impart flame resistance. It has the disadvantage that the treated material is susceptible to ion-exchange in hard water or soap solutions, the inactive calcium or sodium salt being formed. The flame resistance must then be "regenerated" by steeping the material in ammonium chloride solution.

Two more recent wash-fast flame-proofing finishes involve:

(1) Treatment of the cellulosic material with tetrakis(hydroxymethyl)phosphonium chloride in conjunction with an aminoplast. If all the components are used in the same bath the amount of phosphonium salt and aminoplast which has to be absorbed in order to confer adequate flame resistance is undesirably high, causing an increase in weight of the treated fabric of 20–25%. This massive addition can modify the handle of the fabric and, moreover, many fabrics need to be specially pre-treated to render them sufficiently absorbent to take up such a large amount of proofing agent. A means of circumventing this difficulty is disclosed in British specification No. 884,785 and entails the use of a two-stage process in which the fabric is first treated with the aminoplast and then with tetrakis(hydroxymethyl)phosphonium chloride.

(2) Treatment with a mixture of tetrakis(hydroxymethyl)phosphonium chloride and tris(aziridin-1-yl)-phosphine oxide.

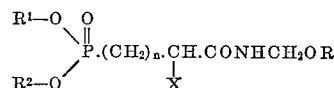
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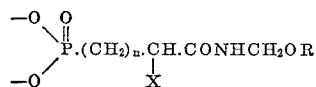
5 The treating bath is prepared immediately before use by mixing aqueous solutions of the two materials. It is unstable and must be kept cool. This process is also two-stage, because the fabric must be softened as an after-treatment. Further, tris(aziridin-1-yl)phosphine oxide is very toxic and excess must be carefully washed from the fibre after the process is completed. Moreover, process workers must be protected.

The present invention provides a new class of substituted phosphono-amides which can be used in conjunction with aminoplasts to confer flame-resistance on cellulosic materials by a process which avoids some or all of the disadvantages of known processes.

The new substituted phosphono-amides are those of the general Formula I:



25 where R represents hydrogen, allyl or alkyl of up to six carbon atoms; n is either 1, when X represents hydrogen, methyl or a —CH<sub>2</sub>CONHCH<sub>2</sub>OR group, or zero, when X represents a —CH<sub>2</sub>CONHCH<sub>2</sub>OR group; and R<sup>1</sup> and R<sup>2</sup> either each represent the same or different alkyl, alkenyl, cycloalkyl, cycloalkenyl, alkoxyalkyl, alkoxy-  
30 alkenyl, aryl, alkoxyaryl, or alkylene residues, which may be substituted by one or more chlorine and/or bromine atoms, the terminal valency of any such alkylene residue being linked to a group of formula II:

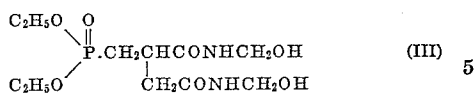


40 the free valency of which, if only one of R<sup>1</sup> and R<sup>2</sup> is alkylene, is linked to a further monovalent R<sup>1</sup> or R<sup>2</sup> residue, or R<sup>1</sup> and R<sup>2</sup> together represent a polymethylene chain containing from two to six carbon atoms which may be linked to a second polymethylene chain containing  
45 two to six carbon atoms, via a spiro carbon, which polymethylene chains may be substituted by one or more chlorine and/or bromine atoms and/or methyl groups, the terminal valencies of the second polymethylene chain, if such be present, being linked to a group of Formula II.

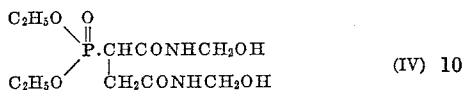
Preferred compounds of Formula I are those wherein R<sup>1</sup> and R<sup>2</sup> either represent identical alkyl groups, particularly those containing up to four carbon atoms, or identical alkenyl or alkylene groups, particularly those  
55 containing from two to four carbon atoms; or together represent a polymethylene group containing from two to six carbon atoms. Also preferred are those compounds wherein R<sup>1</sup> and R<sup>2</sup> together represent a polymethylene chain containing from two to three carbon atoms linked to  
60 a second such polymethylene chain via a spiro-carbon. Further preferred are those compounds of Formula I wherein each of R<sup>1</sup> and R<sup>2</sup> contains up to four chlorine and/or bromine atoms.

Specific examples of preferred compounds are N-hydroxymethyl-3-(diethylphosphono)propionamide, N-hydroxymethyl-3-(diallylphosphono)propionamide, N-methoxymethyl-3-(bis(2,3-dichloropropyl)phosphoro)-  
65 propionamide, N-hydroxymethyl-3-(diethylphosphono)-2-methylpropionamide, N-hydroxymethyl-3-(2,2-dimethyltrimethylenephosphono)propionamide, N-hydroxymethyl-3-(1-methyltrimethylenephosphono)propionamide, N-hydroxymethyl-3-(bis(bromotrichloropropyl)-

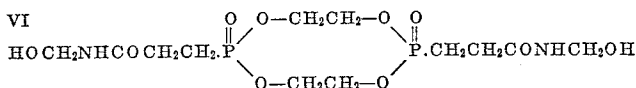
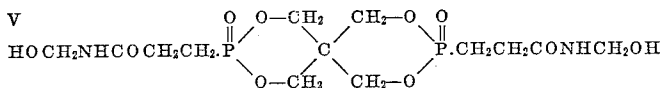
phosphono)propionamide, N-allyloxymethyl-3-(diethylphosphono)propionamide, and those of the formulae:



and

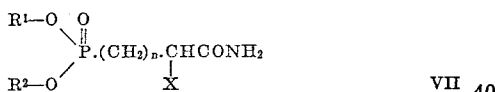


and those of the formulae:

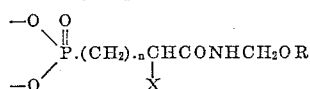


(derived from pentaerythritol diphosphite and from ethylene glycol diphosphite respectively).

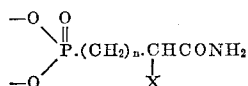
According to a feature of the invention the compounds of the general Formula I wherein R=H are produced by the reaction of compounds of the general Formula VII:



wherein R<sup>1</sup>, R<sup>2</sup>, n and X are as hereinbefore defined except that references to the group



are to be understood as references to the group



in neutral or alkaline solution with formaldehyde or a substance liberating formaldehyde under the reaction conditions.

It is preferred to add the compound of Formula VII to an aqueous solution of formaldehyde, the pH of the reaction mixture being maintained at or above 7.0 by the addition of an alkaline-reacting substance, suitably sodium hydroxide, and to maintain the temperature of the reaction mixture between 40° C. and 60° C. After the reaction is completed, the solution may be cooled and filtered. The product may be incorporated in the flame-proofing compositions hereinafter described as the aqueous solution so obtained.

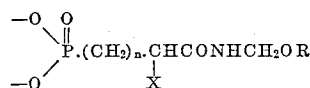
Another preferred method comprises heating a compound of Formula VII with paraformaldehyde in the presence of an alkaline-reacting substance, suitably potassium carbonate or sodium carbonate. Temperatures between about 75° C. and about 150° C. may be employed; if a solvent, such as methanol is added, reaction may be affected at lower temperatures, e.g. about 50° C.

Compounds of the general Formula VII have been described by A. N. Pudovick and D. Kh. Yarmukhametova (Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., 1952, 657-660) and in U.S. patent specifications Nos. 2,754,319 and

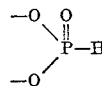
2,754,320. They can be made by reacting a mono- or diphosphite ester of Formula VIII:



wherein R<sup>1</sup> and R<sup>2</sup> are as hereinbefore defined except that reference to the group



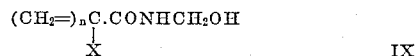
should be understood as references to the group



with acrylamide, methacrylamide, itaconamide, fumaramide or maleamide.

It is usual to conduct the reaction in the presence of a non-acidic condensation catalyst, preferably an alkaline catalyst. The latter may be an alkali metal, an alkaline metal amide, an alkali metal hydride, a secondary or tertiary amine, an alkali metal salt of the phosphite diesters, a quaternary ammonium hydroxide or basic ion-exchange resin and, especially, a solution or slurry of an alkali metal alkoxide in the corresponding alcohol. The reaction, after an induction period, becomes vigorously exothermic and the mixture may be cooled as necessary. A volatile inert solvent, particularly a high-boiling liquid, may be added to moderate the reaction. Addition of a solvent is desirable but not essential, when the unsaturated amide is a solid under the reaction conditions.

According to a further feature of the invention a process for the production of compounds of the general Formula I wherein R=H comprises reacting one to two molar proportions of an N-hydroxymethyl- $\alpha,\beta$ -unsaturated amide of the Formula IX:



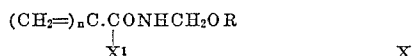
wherein n is either 1, when X<sup>1</sup> represents hydrogen, methyl or a  $\text{---CH}_2\text{CONH}_2\text{OH}$  group, or zero, when X<sup>1</sup> represents a  $\text{=CHCONH}_2\text{OH}$  group, with one molar proportion of a phosphite or diphosphite of Formula VIII.

According to a still further feature of the invention, compounds of the general Formula I wherein R denotes an alkyl group containing from one to six carbon atoms, are produced by reacting a compound of Formula I in which R is hydrogen with an aliphatic monohydric alcohol containing from one to six carbon atoms, in the presence of an acid.

According to another feature of the invention, compounds of the general Formula I wherein R denotes an allyl group are produced by reacting a compound of For-

mula I in which R is hydrogen with allyl alcohol in the presence of an acid.

According to further features of the invention compounds of the general Formula I wherein R denotes an alkyl group containing from one to six carbon atoms or an allyl group are prepared by reacting a compound of Formula VIII with one to two molar proportions of an N-alkoxymethyl- or N-allyloxymethyl- $\alpha,\beta$ -unsaturated amide of the Formula X:



wherein  $n$ ,  $X^1$  and R are as hereinbefore defined.

Compounds of the general Formula IX have been described in British patent specification No. 482,897, and by Kamogawa, Muraas and Sekiya (Textile Res. J., 1960, 30, 774-81). Compounds of the general Formula X have been described by Muller, Dinges and Graulich (Makromol. Chem. 1962, 57, 27).

The invention includes within its scope compositions of utility in imparting flame-resistance to cellulosic materials which contain at least one compound of the general Formula I having one  $-CONHCH_2OR$  group and an aminoplast or at least one compound of the general Formula I having two  $-CONHCH_2OR$  groups and optionally an aminoplast. Preferably such compositions also contain a latent acid catalyst to accelerate curing of the aminoplast and cross-linking of the compound of the general Formula I having to  $CONHCH_2OR$  groups. The latent acid catalysts which may be used are well-known in the process of curing aminoplasts on cellulosic materials and include for example ammonium chloride, ammonium dihydrogen orthophosphate, magnesium chloride, zinc nitrate etc. The aminoplast employed may be a condensation product of formaldehyde with urea or a derivative thereof such as ethyleneurea, or, preferably, with melamine or a derivative, such as an ether, of the said melamine-formaldehyde condensation product. A process for rendering cellulose-containing materials flame-resistant by treatment with such a composition followed by heating the treated material to cure the said aminoplast, and/or to effect cross-linking of the compound of general Formula I containing two  $CONHCH_2OR$  groups is within the scope of the invention.

Compounds of general Formula I containing chlorine and/or bromine atoms may be prepared by using halogen-containing starting materials in the aforesaid processes or by halogenation of the intermediates or final products. Particularly preferred halogen-containing compounds are those obtained by reaction of 3-(diallyl-phosphono)propionamide with a polyhalogenated methane, especially bromotrichloromethane, in the presence of a free-radical catalyst such as benzoyl peroxide, followed by hydroxymethylation.

Compounds of Formula I in which one or more of R,  $R^1$  and  $R^2$  are allyl groups may be polymerised in the presence of a free-radical catalyst to give polymers which may be used for flame-proofing cellulosic materials in the same way as the compounds of Formula I themselves. Such products, compositions thereof with aminoplasts, and the use of such products and compositions as flame-proofing agents, constitute further features of the invention.

The following examples illustrate the invention.

#### Example I.—Preparation of N-hydroxymethyl-3-(diethylphosphono)propionamide

Freshly-prepared ethanolic sodium ethoxide solution (2.90 M, 70 ml.) was added slowly to a solution of acrylamide (568 g., 8 moles) in freshly-distilled diethyl phosphite (2208 g., 16 moles). A vigorous exothermic reaction occurred after about half of the sodium ethoxide solution had been added; the temperature of the reaction mixture was maintained at 80-90° C. by further cautious addition of the catalyst until the exothermic reaction had subsided. The product was isolated by seeding the cooled solution and filtering off the precipitated crystals. These

were washed with benzene and dried. The yield of 3-(diethylphosphono)propionamide was 1277 g. and a further 400 g. was isolated by evaporating the filtrate in vacuo to dryness. The product had a melting-point of 73-74.5° C. Elementary analysis gave the following results: P=15.3%; N=6.7%;  $C_7H_{16}NO_4P$  requires P=14.85%; N=6.7%.

The propionamide (1440 g.) was then added gradually to formalin (36.5%, 564 g.) at 50° C., the pH of the mixture being maintained at 7.5-8.0 by adding approximately 5 ml. of 40% caustic soda solution. After the mixture had been stirred for 2 hours it was allowed to cool to room temperature and filtered. Approximately 2000 g. of an 82.0% solution of N-hydroxymethyl-3-(diethylphosphono)propionamide was obtained.

A sample of the solution was evaporated to dryness in vacuo. Elementary analysis of the residue gave the following results: P=12.3%; N=5.0%;  $C_8H_{18}NO_5P$  requires P=12.95%; N=5.9%.

The infra-red spectrum of the product indicated it to be the required N-hydroxymethyl compound by the presence of the characteristic amide-II band at 1550  $cm^{-1}$  and a broad band at about 3350  $cm^{-1}$  due to the hydroxyl group and NH-stretching of the secondary amide.

#### Example II.—Preparation of N-hydroxymethyl-3-(dimethylphosphono)propionamide

Methanolic sodium methoxide solution (3.04 M, 115 ml.), was added to acrylamide (284 g., 4 moles) in dimethyl phosphite (440 g., 4 moles) and dioxane (400 ml.). A vigorous exothermic reaction ensued when about 90 ml. of the sodium methoxide solution had been added, and the temperature of the reaction mixture was maintained at 80-90° C. by adding further quantities of the catalyst. The mixture was cooled to room temperature and the dioxane distilled in vacuo to leave 3-(dimethylphosphono)propionamide as a white solid; yield, 600 g.

This product (271.3 g., 1.5 moles) was added in portions to 36.5% formalin solution (125 g., 1.5 moles) at 55-60° C. The pH of the mixture was maintained at 8.0 by the addition of 40% caustic soda solution, about 1 ml. being required. The reaction mixture was stirred for 1 hour at 60° C., cooled and filtered to give a solution of the desired product.

#### Example III.—Preparation of N-(hydroxymethyl)-3-(diallylphosphono)propionamide

Proceeding as in Example I, methanolic sodium methoxide solution (4.35 M, 35 ml.) was added to acrylamide (72 g., 1 mole) in diallyl phosphite (162 g., 1 mole) and dioxane (250 ml.), a vigorous exothermic reaction ensuing when 32 ml. of the sodium methoxide solution had been added. The yield of the intermediate was 213.2 g.

The compound (119 g.) was similarly hydroxymethylated with 36.5% formalin solution (41 g.) at 55-60° C. and a solution of the desired product obtained, as described in Example I.

#### Example IV.—Preparation of N-hydroxymethyl-3-(diisopropylphosphono)propionamide

A slurry of sodium isopropoxide in isopropanol (equivalent to 4% W/W of sodium) was added slowly to acrylamide (142 g.) dissolved in di-isopropyl phosphite (332 g., 2 moles) and dioxane (300 ml.). An exothermic reaction set in after some 140 g. of the catalyst had been added, and the total amount of catalyst added before the exothermic reaction had ceased was 160 g. The intermediate was induced to crystallize (in a yield of 456 g.) by adding a small piece of solid carbon dioxide to the cooled solution.

This intermediate (237 g.) was treated with 36.5% formalin solution (82 g.) at 55-60° C., about 0.2 ml. of 40% caustic soda solution being added. The reaction

mixture was stirred for 2 hours at 60° C., cooled and filtered to give a solution of the desired product.

Example V.—Preparation of N-hydroxymethyl-3-(bis(2,3-dichloropropyl)phosphono)propionamide

A 3.6 M methanolic solution of sodium methoxide (8 ml.) was added slowly to acrylamide (7.1 g.) in bis(2,3-dichloropropyl) phosphite (30.4 g.) and dioxane (30 ml.). After evaporation of the solvent in vacuo the residue was added to 36.5% formalin solution (8.2 ml.); the reaction mixture was maintained at pH 8 and 50° C. For ease of stirring the mixture was diluted with water during the reaction. A solution of the desired product was obtained.

Example VI.—Preparation of N-hydroxymethyl-3-(1-methyltrimethylenephosphono)propionamide

A mixture of acrylamide (59.3 g.) and 112 g. of the cyclic phosphite ester of butane-1,3-diol (prepared by transesterifying the diol with diethyl phosphite) in 100 ml. of dioxane was treated with methanolic sodium methoxide solution (5.6 M; 20 ml.), as described in Example I. A vigorous exothermic reaction ensued when about 14 ml. of the catalyst had been added.

The residue obtained by evaporation in vacuo of the solvent was added gradually to 36.5% formalin (67.5 g.). The mixture was maintained at 60° C. and at pH 8 during the addition, then stirred for 2 hours at 50° C., cooled and filtered. A solution of the desired product was obtained.

Example VII.—Preparation of N-hydroxymethyl-3-(dicyclohexylphosphono)propionamide

Phosphorus trichloride (27.5 g., 0.2 mole) in dioxan (40 ml.) was added slowly to cyclohexanol (60 g., 0.5 mole) with vigorous stirring, the hydrogen chloride formed being removed in a stream of nitrogen. The mixture was refluxed for 1½ hours, and then heated at 100° C. under a water pump vacuum and finally at 0.5 mm. pressure. The residue weighed 41.5 g. (84.5% yield).

A mixture of the dicyclohexyl phosphite so obtained (64.5 g., 0.26 mole) and acrylamide (18.6 g., 0.26 mole) was treated until alkaline with a saturated solution in cyclohexanol of sodium cyclohexoxide. A very small quantity of ethanolic sodium ethoxide was then added, further additions being made when the exothermic reaction had subsided. The solution was neutralized with glacial acetic acid, and volatile materials distilled off by heating the mixture at 100° C. under about 12 mm. pressure.

The residue, the infra-red spectrum of which indicated it to be the required 3-(dicyclohexylphosphono)propionamide, was stirred with paraformaldehyde (7.86 g., 0.26 mole) and anhydrous potassium carbonate (0.2 g.) at 120° C. for 2½ hours.

Example VIII.—Preparation of N-hydroxymethyl-1-3-(2,2-dimethyltrimethylenephosphono)propionamide

Neopentyl glycol (312 g., 3 moles), diethyl phosphite (414 g., 3 moles) and 5.5 N-methanolic sodium methoxide solution (6 ml.) were heated together for 6 hours, the ethanol evolved being separated. On fractional distillation of the residue there was obtained 355 g. of the cyclic phosphite of neopentyl glycol, having a B.P. of 132° C. at 2 mm. and an M.P. of about 53° C.

To 15 g. (0.1 mole) of the cyclic phosphite and 7.1 g. (0.1 mole) of acrylamide in 10 ml. of dimethylformamide was added dropwise 5.5-N-methanolic sodium methoxide solution. After the exothermic reaction had subsided, the mixture was cooled and allowed to stand overnight. The desired intermediate separated as a fine white powder, M.P. 190–5° C.

The intermediate (11.05 g., 0.05 mole), paraformaldehyde (1.5 g., 0.05 mole) and methanol (25 ml.) were heated at 50° C. for 1 hour, the mixture being kept at

pH 8.0 by addition of a few drops of concentrated methanolic sodium methoxide solution. The hydroxymethyl derivative remained as a clear, resinous liquid on evaporation of the solvent.

Example IX.—Preparation of the bis(N-hydroxymethylpropionamide) derivative of pentaerythritol diphosphite

(A) Phosphorus trichloride (530 g., 4 moles) was added slowly to pentaerythritol (136 g., 1 mole), and the mixture heated slowly to 63° C. The clear solution so obtained was refluxed for 1½ hours, and unreacted phosphorus trichloride was then distilled off. The residue, which solidified on cooling, was dissolved in chloroform (200 ml.), and a mixture of ethanol (92 g.) in chloroform (100 ml.) was added in portions over about 30 minutes, the rate of addition being adjusted so as to moderate the rate of refluxing. The mixture was filtered and the chloroform distilled off. A pale yellow, clear, resinous liquid remained, the infra-red spectrum of which indicated the presence of P–H bonds.

Acrylamide (108.7 g., 0.75 mole) was added to a solution of this material (172.2 g., 0.75 mole) in dimethylformamide (300 ml.). Concentrated methanolic sodium methoxide solution (30 ml.) was then added dropwise. When the exothermic reaction had subsided, the solvents were distilled off. A glassy solid (280 g.) remained.

This solid was melted and added portionwise to 36.5% formalin (123.5 g.), the mixture being maintained at pH 8.0 by addition of aqueous 40% sodium hydroxide and at 50° C. for 2 hours. The mixture was cooled and filtered, 437.5 g. of a clear resin being obtained.

(B) The desired product was also prepared in the following manner.

Pentaerythritol (68 g., 0.5 mole) was transesterified with diethyl phosphite (276 g., 2 moles) in the presence of concentrated ethanolic sodium ethoxide solution (5 ml.), 90 g. of ethanol being collected over 2½ hours. Unchanged diethyl phosphite was then distilled off. The viscous, colourless residue (105.2 g.) set to a glassy solid on cooling.

The intermediate was reacted with acrylamide (64.5 g.) in dimethyl formamide (200 ml.) as described above, 40 ml. of 4.4 M-methanolic sodium methoxide solution being added. After distilling off the solvents, 185 g. of a resinous material remained. This was then reacted with 36.5% formalin (27.2 g.) as previously described.

Example X.—Preparation of N-hydroxymethyl-3-(n-butyl ethylphosphono)propionamide

A mixture of diethyl phosphite (276 g., 2 moles), n-butanol (148 g., 2 moles) and concentrated ethanolic sodium ethoxide solution (5 ml.) was heated, the ethanol evolved being separated. When ethanol was no longer evolved (i.e., after 3 hours), the residue was fractionated. The fraction boiling at 100–105° C./17 mm. ( $n_D^{25} = 1.4164$ ) was shown by gas liquid chromatography to be n-butyl ethyl phosphite.

A concentrated solution (4 ml.) of sodium ethoxide and sodium n-butoxide (made by dissolving sodium in an equimolar mixture of ethanol and butanol) was added dropwise to n-butyl ethyl phosphite (32.5 g., 0.196 mole) and acrylamide (13.9 g., 0.196 mole). After the vigorous reaction had been completed, volatile materials were distilled off, and the viscous residue induced to crystallize by cooling to 0° C. The crude intermediate melted at about 18° C.

This intermediate (23.9 g., 0.1 mole), paraformaldehyde (3.1 g.) and anhydrous potassium carbonate (0.2 g.) were heated at 120° C. for 2 hours to yield the desired product as a yellow, viscous resin.

Example XI.—Preparation of the bis(N-hydroxymethylpropionamide) derivative of ethylene glycol diphosphite

Diethyl phosphite (82.8 g., 0.6 mole), ethylene glycol (37.2 g., 0.2 mole) and a small piece of sodium were

heated for 5 hours at 135–45° C. and 200 mm. pressure. On fractional distillation of the mixture, 37 g. of a product having B.P. 118° C./0.2 mm. and  $n_D^{25}=1.4750$  were obtained. Petrov et al. (Zhur. Obshchei Khim., 1963, 33, 1485) report a B.P. of 132–6° C./2.5 mm. and  $n_D^{20}=1.4753$ .

This product (37 g., 0.171 mole) was dissolved in tetrahydrofuran (50 ml.), and mixed with acrylamide (24.3 g., 0.342 mole) dissolved in tetrahydrofuran (50 ml.). The mixture was treated with concentrated ethanolic sodium ethoxide solution until an exothermic reaction no longer occurred, and was then neutralised with glacial acetic acid. After removal of volatile materials by heating the mixture at 100° C. at the water pump, the product was hydroxymethylated by being stirred at 120° C. for 2½ hours with paraformaldehyde (10.3 g., 0.342 mole) and anhydrous sodium carbonate (0.3 g.).

**Example XII.—Preparation of N-hydroxymethyl-3-(diethylphosphono)-2-methylpropionamide**

2.6 M-ethanolic sodium ethoxide solution (20 ml.) was added dropwise to methacrylamide (42.5 g., 0.5 mole) dissolved in diethyl phosphite (350 g., 2.53 moles), a vigorous exothermic reaction occurring. Unchanged diethyl phosphite was then distilled off, and the residue allowed to solidify on cooling.

The residue (22.3 g., 0.1 mole), paraformaldehyde (3.0 g.) and anhydrous potassium carbonate (0.1 g.) were stirred together at 120° C. for 2 hours. The product was a yellow viscous liquid.

**Example XIII.—Preparation of N-hydroxymethyl-3-(bis(2-ethoxyethyl)phosphono)propionamide**

Di(2-ethoxyethyl)phosphite was obtained in 198.6 g. yield and having a B.P. of 118–121° C./1.4 mm. by heating 2-ethoxyethanol (180.2 g., 2 moles), diethyl phosphite (138 g., 1 mole) and 2.5 ml. of concentrated ethanolic sodium ethoxide solution for 8 hours, the liberated ethanol being separated.

5.5 m-Methanolic sodium methoxide solution (0.8 ml.) was then added dropwise to di(2-ethoxyethyl) phosphite (22.6 g., 0.1 mole) and acrylamide (7.1 g., 0.1 mole), a vigorous exothermic reaction ensuing. On cooling the mixture it set to a white solid having an M.P. of 41–44° C.

The resultant phosphonopropionamide (14.85 g.) was then added to 36.5% aqueous formaldehyde solution (4.5 g.), the mixture being heated at 50° C. for 1 hour, and maintained at pH 8 by the addition of a few drops of 40% aqueous sodium hydroxide solution.

**Example XIV.—Preparation of N-methoxymethyl-3-(diethylphosphono)propionamide**

3-(diethylphosphono)propionamide (418 g., 2 moles), prepared as described in Example I, paraformaldehyde (60 g., 2 moles) and anhydrous potassium carbonate (2 g.) were stirred together at 120° C. for 2½ hours.

To the cooled reaction product was added methanol (500 ml.), and the pH of the mixture was adjusted to 2.5–3 by adding 5 ml. of methanolic hydrogen chloride solution. The mixture was refluxed for 1½ hours, cooled, neutralised with sodium carbonate, filtered, and excess methanol distilled off. The residue was a light yellow viscous liquid having a nitrogen content of 5.56% (theoretical value, 5.55%).

**Example XV.—Preparation of N,N-bis(hydroxymethyl)-3-(diethylphosphono)methylsuccinamide**

To a mixture of dimethyl itaconate (474 g., 3 moles) and diethyl phosphite (414 g., 3 moles) was added dropwise 5.5 M-methanolic sodium methoxide solution. A vigorous exothermic reaction ensued. The mixture was neutralised with glacial acetic acid, filtered, and the filtrate distilled. The yield of dimethyl 3-(diethylphos-

phono)-methylsuccinate, having B.P. 172–6° C./2 mm. and  $n_D^{25}=1.4448$ , was 713.5 g., i.e., 80%.

Ammonia gas was passed into a mixture of the ester (687.3 g.) and methanol (3 litres) for about six hours, i.e. until the mixture was saturated. The mixture was allowed to stand at room temperature for one week, and was then concentrated. The succinamide crystallized out in a yield of 402.7 g. and was filtered off. The succinamide had an M.P. of 173–8° C. Elementary analysis gave the following results: Found C, 39.80%; H, 7.22%; N, 10.42%; P, 11.68%.  $C_9H_{13}N_2O_5P$  requires C, 40.60%; H, 7.19%; N, 10.52% P, 11.63%.

The succinamide (26.6 g.) was dissolved in methanol (100 ml.), and paraformaldehyde (6.0 g.) was added, followed by a few drops of methanolic sodium methoxide solution to adjust the pH of the mixture to 9.0. The mixture was then stirred to 50° C. for 3 hours.

**Example XVI.—Preparation of N-allyloxymethyl-3-(diethylphosphono)propionamide**

Acrylamide (71 g.), paraformaldehyde (33 g.) and allyl alcohol (68 ml.) were heated at 50° C. for 2 hours, the mixture being maintained at pH 9.0 by addition of a few drops of 40% aqueous sodium hydroxide solution. A further 250 ml. of allyl alcohol, and 1 g. of hydroquinone were added, the solution was acidified with methanolic hydrogen chloride solution to a pH of approximately 2.5, and then heated at 80–90° C. for 6 hours. After neutralization of the mixture with sodium carbonate, followed by filtration, the filtrate was subjected to flash-distillation. N-(Allyloxymethyl)acrylamide was obtained in 80% yield, and having a B.P. of 103–104° C./0.2 mm. and  $n_D^{25}=1.4820$ .

A concentrated ethanolic solution of sodium ethoxide was added dropwise to a mixture of N-(allyloxymethyl)acrylamide (14.1 g.) and diethyl phosphite (138 g.). After the exothermic reaction had ceased, the solution was neutralized with methanolic hydrogen chloride solution, filtered, and unchanged diethyl phosphite distilled off. The residue, (28 g.), was a clear, colorless liquid, shown by infrared spectroscopy to be the addition product of diethyl phosphite and N-(allyloxymethyl)acrylamide.

**Example XVII.—Polymerisation of N-hydroxymethyl-3-(diallylphosphono)propionamide**

To 16.45 g. of N-hydroxymethyl-3-(diallylphosphono)propionamide was added 0.3 g. of ammonium persulphate, and the solution was heated at 70° C. under nitrogen for 4 hours. A clear, viscous, liquid was obtained.

**Example XVIII.—Preparation of N-hydroxymethyl-3-(bis(bromotrichloromethylpropyl)-phosphono)propionamide**

To 3-(diallylphosphono)propionamide, prepared as described in Example III, was added 200 g. of bromotrichloromethane and 2 g. of benzoyl peroxide. The mixture was heated at 65° C. for 3 hours in an atmosphere of nitrogen.

Dioxan and unreacted bromotrichloromethane were then distilled off under reduced pressure, and the residue hydroxymethylated in 100 ml. methanol by reaction with 100 ml. of 36.5% aqueous formaldehyde solution at 70° C. for 2 hours, the mixture being kept at a pH of approximately 8 by addition of 5 ml. of a 50% aqueous solution of sodium hydroxide. On evaporation of volatile materials, the desired product was obtained as a red-brown residue.

**Example XIX.—Preparation of N,N'-bis(hydroxymethyl)-2-(diethylphosphono)succinamide**

Di-n-propyl 2-(diethylphosphono)succinate, having B.P. 134–6° C./0.5 mm. and  $n_D^{25}=1.4398$ , was prepared from di-n-propyl maleate and diethyl phosphite as in Example XV, a concentrated ethanolic solution of sodium ethoxide being used as catalysts.

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The ester was then reacted with methanolic ammonia as in Example XV. The resultant succinamide, which had a B.P. of 187–9° C. was then hydroxymethylated in methanol with paraformaldehyde in the presence of methanolic sodium methoxide solution as described in Example XV.

## Example XX

Mixtures having the following compositions were prepared, the figures representing the weight in grams of the substance added to one litre of water.

|                                                                                     | Mixture No. |     |     |     |     |     |
|-------------------------------------------------------------------------------------|-------------|-----|-----|-----|-----|-----|
|                                                                                     | 1           | 2   | 3   | 4   | 5   | 6   |
| 83% M/V Aqueous solution of N-hydroxy-methyl-3-(diethyl-phosphono)propionamide..... |             | 200 | 200 | 200 | 200 | 200 |
| Product A.....                                                                      |             |     |     | 150 |     |     |
| Product B.....                                                                      | 800         |     |     |     |     |     |
| Product C.....                                                                      | 100         |     | 100 |     |     |     |
| Anhydrous sodium carbonate.....                                                     |             |     |     |     | 20  |     |
| Magnesium chloride hexahydrate.....                                                 |             |     |     |     |     | 20  |

Product A was a commercially-available 75% aqueous solution of an etherified methylolmelamine.

Product B was a conventional flame-proofing agent containing ammonium pyrophosphate.

Product C was a commercially-available water-soluble condensation product of melamine and formaldehyde.

Bleached cotton fabric was padded with each solution to give a weight increase of 80–85%, dried at 80° C., and cured for 4.5 minutes at 155–160° C. The fabric sample from bath No. 1 was also rinsed in cold soft water.

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Product D was a 75% aqueous solution of a highly etherified polymethylolmelamine.

Product E was an aqueous emulsion containing 50% of a copolymer derived from vinylidene chloride and an alkyl acrylate.

Product F was a commercially-available nonionic wetting agent derived from ethylene oxide.

Samples of a bleached cotton fabric and of a bleached spun viscose material with raised woven effects were padded to a weight increase of 80% (cotton) or 100%

(spun viscose), dried at 80° C., cured for 4.5 minutes at 155–160° C., and rinsed for 15 minutes with cold soft water. Samples were also subjected thrice to the washing test C of the Schweizerische Normen-Vereinigung test method (SNV-95821).

## Assessment of samples

|                     | Mixture No. |        |        |        |        |        |
|---------------------|-------------|--------|--------|--------|--------|--------|
|                     | 7           | 8      | 9      | 10     | 11     | 12     |
| Appearance:         |             |        |        |        |        |        |
| Before washing..... | Normal      | Normal | Normal | Normal | Normal | Normal |
| After washing.....  | Normal      | Normal | Normal | Normal | Normal | Normal |
| Handle:             |             |        |        |        |        |        |
| Before washing..... | Soft        | Harsh  | Full   | Full   | Full   | Full   |
| After washing.....  | Soft        | Harsh  | Full   | Full   | Full   | Full   |
| Flammability index: |             |        |        |        |        |        |
| Before washing..... | 2           | 4-5    | 2      | 3      | 1      | 3      |
| After washing.....  | 2           | 3-4    |        | 3      | 1      | 3      |

## Assessment of samples

|                         | Mixture No. |        |        |        |        |        |
|-------------------------|-------------|--------|--------|--------|--------|--------|
|                         | 1           | 2      | 3      | 4      | 5      | 6      |
| Appearance.....         | Normal      | Normal | Normal | Normal | Normal | Normal |
| Handle.....             | Soft        | Soft   | Soft   | Soft   | Soft   | Soft   |
| Flammability index..... | 5           | 3      | 4      | 4      | 2      | 3      |

The flammability index values were assigned according to the arbitrary scale: 5-non-inflammable to 1-easily inflammable.

## Example XXI

Mixtures having the following compositions were prepared, the figures again representing the weight in grams of each material added to one litre of water.

|                                                                                      | Mixture No. |     |     |     |     |     |
|--------------------------------------------------------------------------------------|-------------|-----|-----|-----|-----|-----|
|                                                                                      | 7           | 8   | 9   | 10  | 11  | 12  |
| Aqueous solution (83% W/V) of N-hydroxymethyl-3-(diethylphosphono)-propionamide..... | 400         | 400 | 400 | 400 | 400 | 400 |
| Product A.....                                                                       |             | 150 |     |     |     |     |
| Product C.....                                                                       |             |     | 100 |     |     |     |
| Product D.....                                                                       |             |     |     | 100 |     | 100 |
| Product E.....                                                                       |             |     |     |     | 200 | 200 |
| Product F.....                                                                       |             |     | 5   |     |     |     |
| Ammonium dihydrogen orthophosphate.....                                              | 20          | 20  |     |     |     |     |
| Magnesium chloride hexahydrate.....                                                  |             |     | 20  |     |     |     |
| Ammonium chloride.....                                                               |             |     |     | 2   | 2   | 2   |

## Example XXII

N-(hydroxymethyl) - 3 - (diethylphosphono)-propionamide was incorporated (as an aqueous solution) into decorative paper-melamine formaldehyde laminates. Flame-proofing properties were evaluated by the "Surface Spread of Flame Test" (British standard specification No. 476, Part 1, 1953). The resin employed was used

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as a 50% aqueous solution and prepared by the reaction of melamine (1 part by weight) with formaldehyde (2.45 parts by weight, as an aqueous solution); it was cured at 145° C.

| Method of Impregnation                                                         | Amount of flame-proofing agent added                                           | Result   |
|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|----------|
| Papers pretreated with the solution, dried, treated with the resin, and cured. | 20%, i.e. 2.0% P on weight of paper.                                           | Class 1. |
|                                                                                | 34%, i.e. 5% P on weight of decorative paper layer.                            | Class 2. |
|                                                                                | 38% on weight of decorative paper layer and 53%, i.e. 7% P, on overlay.        | Class 1. |
| Added to solution of resin before using.                                       | 22 g. of solution to 78 g. of resin, i.e. 3% P on resin solids.                | Class 2. |
|                                                                                | Boric acid, 4% on resin solids.                                                | Do.      |
|                                                                                | Boric acid, 5% on resin solids (adjusted to pH 7 by addition of caustic soda). | Do.      |

Both laminates prepared with boric acid had poor surfaces and appeared to have undergone pre-curing.

## EXAMPLE XXIII

A halogenated product, believed to consist essentially of N-hydroxymethyl-3-(bis(bromotrichloromethylpropyl phosphono)propionamide, prepared as described in Example XVIII, was similarly evaluated as a flame-proofing agent. The resin employed was the melamine-formaldehyde resin used in Example XXII and was cured under similar conditions.

| Method of Impregnating                                                                | Amount of flame-proofing agent added | Result   |
|---------------------------------------------------------------------------------------|--------------------------------------|----------|
| Papers pretreated with aqueous solution and dried, then treated with resin and cured. | 18% in decorative paper              | Class 2. |
|                                                                                       | 26% in overlay                       | Do.      |
|                                                                                       | 14% in decorative paper              | Do.      |
| Added to resin solution before curing.                                                | 20% overlay                          | Do.      |
|                                                                                       | 18.8% (1.5% P) on resin              | Class 1. |
|                                                                                       | 37.5% (3% P) on resin                | Class 3. |
|                                                                                       | 62% (5% P) on resin                  | Class 2. |

## EXAMPLE XXIV

Cotton flannelette was padded with an aqueous solution containing, per litre, 300 g. of N-methoxymethyl-3-(diethylphosphono)propionamide, 140 g. of Product D and 5 g. of ammonium chloride. The impregnated fabric was dried and then heated at 150° C. for 5 minutes. The treated fabric met the requirements of British standard specification No. 3119 (1959).

## EXAMPLE XXV

Cotton flannelette was padded with an aqueous solution containing, per litre, 300 g. of N-hydroxymethyl-3-

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(diethylphosphono)propionamide, 140 g. of Product D, 50 g. of a commercially available polyethylene wax emulsion employed as a textile softening agent, and 5 g. of ammonium chloride, to a weight increase of 80%. The treated material was dried at 80° C. and then heated for 5 minutes at 155° C. Part of the material was submitted to the Washing Test of Appendix A of British standard specification No. 3121 (1959). Both washed and unwashed samples, tested in accordance with British standard specification No. 3119 (1959), met the requirements of British standard specification No. 3120 (1959).

## EXAMPLE XXVI

Mixtures having the following compositions were prepared, the figures representing the weight in grams of each material added to one litre of water.

|                                                                | Mixture No. |       |       |       |
|----------------------------------------------------------------|-------------|-------|-------|-------|
|                                                                | 13          | 14    | 15    | 16    |
| N-hydroxymethyl-3-(diethylphosphono)propionamide               | 300         | ----- | ----- | ----- |
| N-hydroxymethyl-3-(dimethylphosphono)propionamide              | -----       | 300   | ----- | ----- |
| N-hydroxymethyl-3-(bis(2-chloroethyl)phosphonopropionamide     | -----       | ----- | 300   | ----- |
| N-hydroxymethyl-3-(1-methyltrimethylenephosphono)-propionamide | -----       | ----- | ----- | 300   |
| Product D                                                      | 135         | 135   | 135   | 135   |
| Ammonium chloride                                              | 5           | 5     | 5     | 5     |

Cotton fabric was padded with each solution to a weight increase of 80%, dried at 80° C. and cured for 4.5 minutes at 160° C. Part of the fabric was washed five times accordingly to test C of SNV-95821. The "flammability indices" of the fabric, determined as in Example XX, were:

| Flammability Index | Mixture No. |     |    |     |
|--------------------|-------------|-----|----|-----|
|                    | 13          | 14  | 15 | 16  |
| Before washing     | 5           | 5   | 5  | 5   |
| After washing      | 4-5         | 4-5 | 4  | 4-5 |

What is claimed is:

1. N - hydroxymethyl - 3 - (2,2-dimethyltrimethylenephosphono)propionamide.
2. N - hydroxymethyl - 3-(1-methyltrimethylenephosphono)propionamide.

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