

PATENT SPECIFICATION

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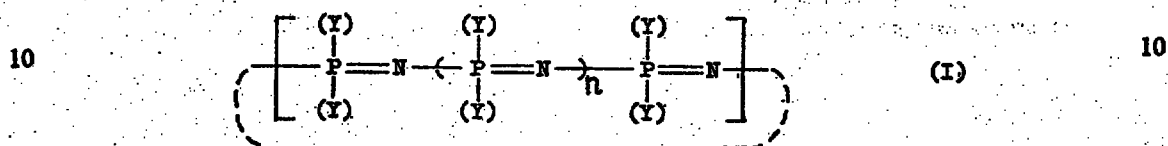
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(54) PHOSPHORNITRILIC ESTERS

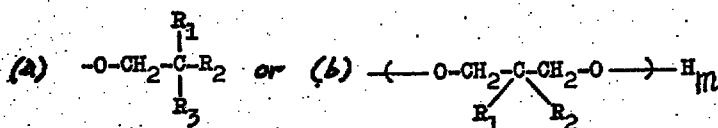
(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phosphornitrilic esters, to a process for the production of these esters and to their use for the flameproof finishing of natural and/or synthetic materials including textiles consisting of natural and/or synthetic fibres.

The present invention provides a phosphornitrilic ester of the formula

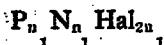


where n represents a whole number from 1 to 10 and each Y represents a chlorine, bromine or fluorine atom or the radical



in which m is zero or 1, the two free valencies (when m is zero) are linked by a single phosphorus atom, thus forming a ring, or each free valency is linked to one of two phosphorus atoms, with the proviso that at least one Y must represent the formula (a) or (b), and each of R₁, R₂ and R₃, independently of each other, represents a halogenated alkyl radical with up to 5 carbon atoms. Each of R₁ and R₂ (optionally also R₃) may suitably be —CH₂Br or —CH₂Cl.

The present invention also provides a process for the production of a phosphornitrilic ester which comprises reacting 1 mole of a phosphornitrilic halide of the formula



(II)

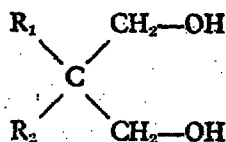
where n₁ represents a whole number from 3 to 12 and

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Price 75p

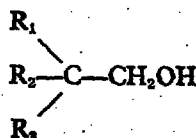


Hal represents a chlorine, bromine or fluorine atom, with at least 1 mole of a propane-1,3 diol of formula



(III)

or of an alcohol of the formula



(IV)

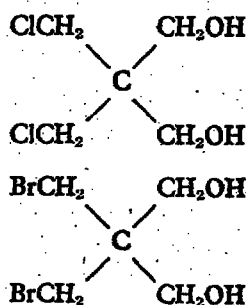
where R_1 , R_2 and R_3 have the above meaning.

The process herein described leads to the formation of a mixture of products having varying degrees of substitution by two different groups derived from the above diol reactant. While some control is possible by suitably arranging the reaction conditions and by employing the appropriate relative amounts of the reactants, nevertheless an absolute control is not possible.

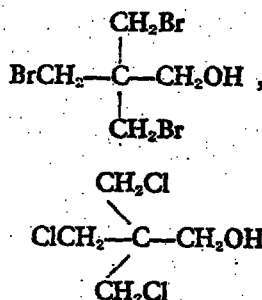
The phosphornitrilic halide may be, for example, the reaction product of an ammonium halide and a phosphorus pentahalide, preferably of NH_4Cl and PCl_5 ; generally, the mixture obtained directly by the reaction can be used, or fractions isolated from the mixture e.g. $P_3N_3Cl_6$, $P_4N_4Cl_8$ or $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12.

An example of a suitable mixture is 60–70% $P_3N_3Cl_6$, 10–15% $P_4N_4Cl_8$ and the remainder $P_xN_xCl_{2x}$ (cf. French Patent 1,281,571). The halogenated radicals R_1 , R_2 and R_3 may be identical or different and may contain 1 to 5 carbon atoms.

Suitable propane-1,3-diols of the formula (III) thus include 2,2-bis-(chloromethyl)-propane-1,3-diol and 2,2-bis-(bromomethyl)-propane-1,3-diol:



Examples of compounds of the formula (IV) are 3-bromo-2,2-bis-(bromomethyl)-1-propanol and 3-chloro-2,2-bis-(chloromethyl)-1-propanol:



One mole of the compound $(PNHal_2)_n$ is reacted with at least 1 mole, prefer-

ably n moles (which leads to a maximum of 50% substitution), of the compound (III) or (IV); an excess of the latter two compounds is not detrimental. It is best to react in an organic solvent which is inert to the phosphornitrilic halide and in the presence of an acid-binding agent which is likewise inert to the compounds in the mixture, in the temperature range of 0°C to 200°C, preferably in the range of 20°C to 100°C, and at excess or reduced pressure as necessary.

Alternatively the reaction can be allowed to proceed at a relatively low temperature and the temperature increased in the final phase to complete the reaction.

The process of the invention may be effected in such a way that

(i) 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 2,2-bis(chloromethyl)-propane-1,3-diol;

(ii) 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 2,2-bis(bromomethyl)-propane-1,3-diol;

(iii) 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 3-bromo-2,2-bis(bromomethyl)-1-propanol;

(iv) 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 3-chloro-2,2-bis(chloromethyl)-1-propanol;

(v) 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_n N_n Cl_{2n}$

consisting of 60—70% $P_3 N_3 Cl_6$, 10—15% $P_4 N_4 Cl_8$ and 30—15% $P_x N_x Cl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 2,2-bis(chloromethyl)-propane-1,3-diol;

(vi) 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_n N_n Cl_{2n}$

consisting of 60—70% $P_3 N_3 Cl_6$, 10—15% $P_4 N_4 Cl_8$ and 30—15% $P_x N_x Cl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 2,2-bis(bromomethyl)-propane-1,3-diol;

(vii) 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_n N_n Cl_{2n}$

consisting of 60—70% $P_3 N_3 Cl_6$, 10—15% $P_4 N_4 Cl_8$ and 30—15% $P_x N_x Cl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 3-bromo-2,2-bis(bromomethyl)-1-propanol; or

(viii) 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_n N_n Cl_{2n}$

consisting of 60—70% $P_3 N_3 Cl_6$, 10—15% $P_4 N_4 Cl_8$ and 30—15% $P_x N_x Cl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 3-chloro-2,2-bis(chloromethyl)-1-propanol.

Examples of suitable organic solvents are ethers, e.g. dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, 1-ethoxy-2-(2'-ethoxy-ethoxy)-ethane or tetrahydrofuran; aromatic hydrocarbons, e.g. benzene, toluene, xylene or mesitylene; halogenated aliphatic or aromatic hydrocarbons, e.g. chloroform, trichloroethylene, chlorobenzene, ortho-dichlorobenzene or bromobenzene; ketones, e.g. propanone-2, butanone-2, 4-methylpentanone-2 or 2,6-dimethyl-heptanone-4; further examples are acetonitrile, dimethyl formamide, dimethyl acetamide, dimethyl sulfoxide, tetramethylene sulphone or phosphoric tris(dimethylamide).

The following are examples of acid-binding agents: hydroxides or carbonates of alkali metals, e.g. potassium, sodium or lithium hydroxide or carbonate, hydroxides or carbonates of alkaline earth metals, e.g. calcium, magnesium or barium hydroxide or carbonate; ammonium hydroxide or carbonate; quaternary ammonium hydroxides, e.g. benzyl trimethyl, tribenzylmethyl or tetra(lower alkyl)-ammonium hydroxide, tri(lower alkyl)-amines, e.g. triethylamine, tributylamine or trimethylamine. Preferred such agents are pyridine, picoline, or quinoline.

When a tertiary amine is used as acid-binding agent it can serve additionally as solvent.

On completion of the reaction the product is precipitated, for example, by dilution with a precipitation agent, preferably water, if necessary with the addition of an acid, or with an alcohol, e.g. methanol, ethanol or iso-propanol, filtered with suction and dried. Alternatively the solvent can be removed by distillation, preferably under reduced pressure, and the residue extracted with an extracting agent, e.g. methylene chloride or chloroform.

The halogenated phosphornitrilic ester obtained by the above procedure is generally a colourless, crystalline solid, which is well soluble in a variety of organic solvents. It may be used as a flameproofing agent for textiles, plastics and synthetic resins, and can be applied to these materials from aqueous suspension, aqueous-organic suspension or solution, or organic solution. Textiles flameproofed with exemplified

products of the invention have been found to be self-extinguishing even after several washes at the boil under the conditions of the German Industrial Standards test 53906.

In the following Examples, which illustrate the invention without thereby limiting its scope, the parts and percentages are by weight and the temperatures in degrees Centigrade.

Example 1

73.5 Parts of 2,2-bis-(chloromethyl)-propane-1,3-diol and 74 parts of pyridine are added consecutively to a solution of 49 parts of $P_3N_3Cl_4$ in 220 parts of tetrahydrofuran at 20°. The reaction mixture is stirred for 22 hours at room temperature and then for 12 hours with reflux, during which time pyridine hydrochloride is formed as a precipitate. The mixture is cooled, and filtered free of salt, after which the filtrate is poured into 1000 parts of water. The product precipitates as a white solid which is isolated and dried.

The dry product has a melting range of 116—120°. It is readily soluble in many organic solvents including aromatic and chlorinated hydrocarbons, acetone, ethyl acetate, tetrahydrofuran, dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide and phosphoric tris-(dimethylamide).

Example 2

150 parts of 2,2-bis-(bromomethyl)-propane-1,3-diol and 110 parts of pyridine are added consecutively to a solution of 66 parts of $P_3N_3Cl_4$ in 300 parts of tetrahydrofuran at 20°. The reaction mixture is stirred for 2 days at room temperature and subsequently for 8 hours at 75°, on which pyridine hydrochloride precipitates. The mixture is cooled and filtered free from salt, then the filtrate is concentrated by evaporation until an oily residue is left. On the addition of 1000 parts of water the reaction product settles out as a yellowish precipitate. The product can be purified and obtained in an almost colourless state by reprecipitation with acetone/water.

Its melting range is about 200° to 220° and it is soluble in the solvents named in Example 1.

Example 3

A solution of 116 parts of a mixture of oligomeric phosphonitrilic chlorides of the approximate composition 60—70% $P_3N_3Cl_3$, 10—15% $P_4N_4Cl_4$ and the remainder $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12, is dissolved at 20° in 600 parts of tetrahydrofuran. To this solution are added consecutively 265 parts of 2,2-bis-(bromomethyl)-propane-1,3-diol and 200 parts of pyridine. The reaction mixture is stirred for 2 days at room temperature and then for 8 hours at 75°; pyridine hydrochloride precipitates during the reaction. Subsequently the mixture is cooled and after being filtered free from salt it is poured into 1000 parts of water causing the reaction product to precipitate as a yellowish product. The product can be purified and obtained almost colourless by reprecipitation from an acetone/water mixture. Its softening range is 80—90° and it is well soluble in many organic solvents such as aromatic and chlorinated hydrocarbons, ethyl acetate, tetrahydrofuran, dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide and phosphoric tris-(dimethylamine).

Example 4

A solution of 34.8 parts of trimeric phosphonitrilic chloride and 195 parts of 3-bromo-2,2-bis-(bromomethyl)-1-propanol in 310 parts of tetrahydrofuran is reacted by adding 52 parts of pyridine and stirring for 20 hours at room temperature and then for 20 hours with reflux. During the reaction pyridine hydrochloride precipitates. The solution is cooled, the pyridine hydrochloride filtered off and the tetrahydrofuran distilled. The oily product remaining is dissolved in acetone, precipitated in ethanol and filtered. From the filtrate one half of the introduced 3-bromo-2,2-bis-(bromomethyl)-1-propanol was regained. The reaction product is a white solid with a softening range between 100—120°, and does not melt up to 200°.

It is soluble in a variety of organic solvents, e.g. acetone, dimethylformamide, dimethylacetamide, dimethylsulfoxide, tetrahydrofuran or dioxane, but is not soluble in water and alcohols, e.g. methanol, ethanol or isopropanol.

Example 5

30 Parts of pyridine are added to a solution of 24.8 parts of trimeric phosphonitrilic chloride and 97.5 parts of 3-bromo-2,2-bis-(bromomethyl)-1-propanol in 265 parts of tetrahydrofuran. The mixture is reacted with stirring for 5 hours at room temperature and then for 38 hours at 75°. During the reaction pyridine hydrochloride precipitates. After cooling, the solution is filtered free of the pyridine hydrochloride

and tetrahydrofuran is distilled off. The oily residue is dissolved in acetone, precipitated in methanol and filtered. No further starting material can be recovered from the filtrate. The reaction product is a white solid which softens at about 150° and has the same solubility properties as the product described in Example 4.

Example 6

116 Parts of a mixture of oligomeric phosphonitrilic chlorides of the approximate composition 60—70% $P_3N_3Cl_6$, 10—15% $P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12 and 325 parts of 3-bromo-2,2-bis-(bromo-methyl)-1-propanol are dissolved in 890 parts of tetrahydrofuran, with the subsequent addition of 100 parts of pyridine. The solution is reacted and the reaction product worked up as specified in Example 5. The product of this reaction softens at 90° and has solubility properties comparable to the products described in Examples 4 and 5.

Example 7

A mixture of 140 parts of the product described in Example 3, 14 parts of sodium dinaphthylmethane disulphonate ("Lyocol O", registered trade mark) and 246 parts of water was ground for 5 hours with ice cooling in a laboratory bead mill in the presence of 400 parts of quartzite beads. The resulting fine dispersion was passed through a glass frit to free it from the quartzite beads, diluted with 220 parts of water and set with 70 parts of a methylol melamine derivative ("Lyofix CH", registered trade mark) and 7 parts of ammonium sulphate. The dispersion was padded on a cotton cretonne fabric (125 g/m²) and on a 50:50 blend fabric of polyester fibre and cotton (220 g/m²) with a pick-up of 75%. The fabrics were dried for 6 minutes at 100° and then treated for a further 5 minutes at 160° for fixation of the finish. Each fabric was washed 10 times for 30 minutes each time with a 5 g/l solution of a domestic detergent ("Dixan", registered trade mark), the cotton fabric at the boil, the blend fabric at 60°. After these repeated washes the finished fabrics were submitted to the flammability test described in German Industrial Standard 53906 and found to be non-flammable. With both fabrics the loss of tensile strength was less than 23—24%.

Example 8

Three different fabrics, and namely cotton fabric, a 50:50 and a 67:33 blend of polyester (polyethylene terephthalate) fibre and cotton were each padded with an aqueous solution of 100 g/l trimethylolmelamine trimethylether and 10 g/l ammonium sulphate and dried for 6 minutes at 100°. The fabrics were then padded with a 200 g/l solution in trichloromethylene of one of the products described in Examples 4, 5 and 6, the liquor pick-up being about 85% of the dry weight, dried for 6 minutes at 100° and treated for 5 minutes at 160° for fixation of the finish.

The finished fabrics were washed 15 times for 30 minutes each time with a 5 g/l solution of a domestic detergent, the cotton fabric at the boil, the blend fabrics at 60°. The finished, washed fabrics are non-flammable in the test referred to in the preceding Example.

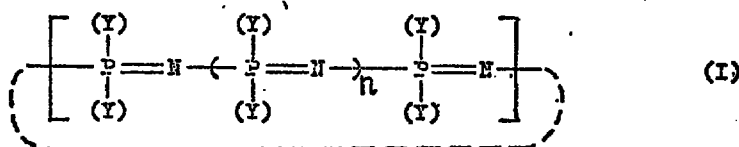
One suitable domestic detergent has the following composition:

- 20% sodium dodecylbenzenesulphonate
- 40% sodium tripolyphosphate
- 8% sodium silicate
- 1% sodium salt of carboxymethyl cellulose
- 21% sodium sulphate
- 10% moisture

The sodium dodecylbenzenesulphonate can be wholly or partly replaced by an alkylsulphate, alkylpolyglycolether sulphate, alkylphenylpolyglycolether sulphate or by a non-ionic detergent.

WHAT WE CLAIM IS:—

1. A phosphonitrilic ester of the formula



and tetrahydrofuran is distilled off. The oily residue is dissolved in acetone, precipitated in methanol and filtered. No further starting material can be recovered from the filtrate. The reaction product is a white solid which softens at about 150° and has the same solubility properties as the product described in Example 4.

Example 6

116 Parts of a mixture of oligomeric phosphonitrilic chlorides of the approximate composition 60—70% $P_3N_3Cl_6$, 10—15% $P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12 and 325 parts of 3-bromo-2,2-bis-(bromomethyl)-1-propanol are dissolved in 890 parts of tetrahydrofuran, with the subsequent addition of 100 parts of pyridine. The solution is reacted and the reaction product worked up as specified in Example 5. The product of this reaction softens at 90° and has solubility properties comparable to the products described in Examples 4 and 5.

Example 7

A mixture of 140 parts of the product described in Example 3, 14 parts of sodium dinaphthylmethane disulphonate ("Lyocol O", registered trade mark) and 246 parts of water was ground for 5 hours with ice cooling in a laboratory bead mill in the presence of 400 parts of quartzite beads. The resulting fine dispersion was passed through a glass frit to free it from the quartzite beads, diluted with 220 parts of water and set with 70 parts of a methylol melamine derivative ("Lyofix CH", registered trade mark) and 7 parts of ammonium sulphate. The dispersion was padded on a cotton cretonne fabric (125 g/m²) and on a 50:50 blend fabric of polyester fibre and cotton (220 g/m²) with a pick-up of 75%. The fabrics were dried for 6 minutes at 100° and then treated for a further 5 minutes at 160° for fixation of the finish. Each fabric was washed 10 times for 30 minutes each time with a 5 g/l solution of a domestic detergent ("Dixan", registered trade mark), the cotton fabric at the boil, the blend fabric at 60°. After these repeated washes the finished fabrics were submitted to the flammability test described in German Industrial Standard 53906 and found to be non-flammable. With both fabrics the loss of tensile strength was less than 23—24%.

Example 8

Three different fabrics, and namely cotton fabric, a 50:50 and a 67:33 blend of polyester (polyethylene terephthalate) fibre and cotton were each padded with an aqueous solution of 100 g/l trimethylolmelamine trimethylether and 10 g/l ammonium sulphate and dried for 6 minutes at 100°. The fabrics were then padded with a 200 g/l solution in trichloromethylene of one of the products described in Examples 4, 5 and 6, the liquor pick-up being about 85% of the dry weight, dried for 6 minutes at 100° and treated for 5 minutes at 160° for fixation of the finish.

The finished fabrics were washed 15 times for 30 minutes each time with a 5 g/l solution of a domestic detergent, the cotton fabric at the boil, the blend fabrics at 60°. The finished, washed fabrics are non-flammable in the test referred to in the preceding Example.

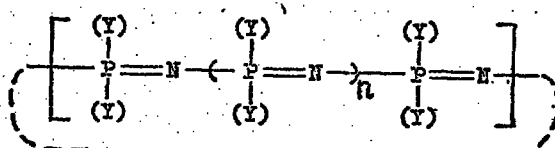
One suitable domestic detergent has the following composition:

- 20% sodium dodecylbenzenesulphonate
- 40% sodium tripolyphosphate
- 8% sodium silicate
- 1% sodium salt of carboxymethyl cellulose
- 21% sodium sulphate
- 10% moisture

The sodium dodecylbenzenesulphonate can be wholly or partly replaced by an alkylsulphate, alkylpolyglycolether sulphate, alkylphenylpolyglycolether sulphate or by a non-ionic detergent.

WHAT WE CLAIM IS:—

1. A phosphonitrilic ester of the formula



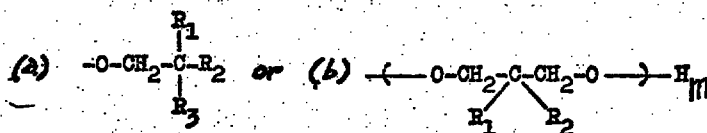


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where n represents a whole number from 1 to 10 and each Y represents a chlorine, bromine or fluorine atom or the radical



in which m is zero or 1, the two free valencies (when m is zero) are linked by a single phosphorus atom, thus forming a ring, or each free valency is linked to one of two phosphorus atoms, with the proviso that at least one Y must represent the formula (a) or (b), and each of R_1 , R_2 and R_3 , independently of each other, represents a halogenated alkyl radical with up to 5 carbon atoms.

2. An ester according to Claim 1, in which each of R_1 and R_2 represents $-CH_2Cl$.

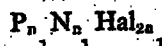
3. An ester according to Claim 1, in which each of R_1 and R_2 represents $-CH_2Br$.

4. An ester according to Claim 1 in which each of R_1 , R_2 and R_3 represents $-CH_2Cl$.

5. An ester according to Claim 1, in which each of R_1 , R_2 and R_3 represents $-CH_2Br$.

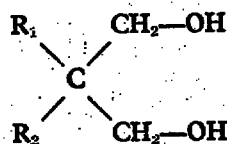
6. A phosphornitrilic ester substantially as herein described with reference to Example 1 or 2.

7. A process for the production of a phosphornitrilic ester, characterized in that 1 mole of a phosphornitrilic halide of the formula



(II)

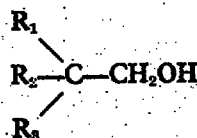
where n_1 represents a whole number from 3 to 12 and Hal represents a chlorine, bromine or fluorine atom, is reacted with at least 1 mole of a diol of the formula



(III)

where R_1 , R_2 and R_3 have the meaning stated in Claim 1.

8. Modification of the process claimed in Claim 7, in which, instead of using a diol (III), there is used an alcohol of the formula



(IV)

where R_1 , R_2 and R_3 have the meaning stated in Claim 1.

9. A process according to Claim 7, in which 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 2,2-bis-(chloromethyl)-propane-1,3-diol.

10. A process according to Claim 7, in which 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 2,2-bis-(bromomethyl)-propane-1,3-diol.

11. A process according to Claim 8, in which 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 3-bromo-2,2-bis-(bromomethyl)-1-propanol.

12. A process according to Claim 8, in which 1 mole of trimeric phosphornitrilic chloride is reacted with 3 moles of 3-chloro-2,2-bis-(chloromethyl)-1-propanol.

13. A process according to Claim 7, in which 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_n N_{n_1} Cl_{2n_1}$ consisting of 60-70% $P_3 N_3 Cl_6$, 10-15%



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$P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 2,2-bis-(chloromethyl)-propane-1,3-diol.

14. A process according to Claim 7, in which 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_nN_nCl_{2n}$ consisting of 60—70% $P_3N_3Cl_6$, 10—15%

5 $P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 2,2-bis-(bromomethyl)-propane-1,3-diol.

15. A process according to Claim 8, in which 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_nN_nCl_{2n}$ consisting of 60—70% $P_3N_3Cl_6$, 10—15%

10 $P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 3-bromo-2,2-bis-(chloromethyl)-1-propanol.

16. A process according to Claim 8, in which 1 mole of a mixture of oligomeric phosphornitrilic chlorides $P_nN_nCl_{2n}$ consisting of 60—70% $P_3N_3Cl_6$, 10—15%

$P_4N_4Cl_8$ and 30—15% $P_xN_xCl_{2x}$, where x is a whole number from 5 to 12, is reacted with 3 moles of 3-chloro-2,2-bis-(chloromethyl)-1-propanol.

17. A process for the production of a phosphornitrilic ester substantially as herein described with reference to Example 1 or 2.

18. A phosphornitrilic ester whenever produced by the process claimed in any one of Claims 7, 9, 10, 13, 14 and 17.

19. A plastics, textile or resin article having incorporated as a flameproofing agent a compound claimed in any one of Claims 1 to 6 and 18.

20. A phosphornitrilic ester substantially as herein described with reference to Example 3.

21. A process for the production of a phosphornitrilic ester substantially as herein described with reference to Example 3.

22. A phosphornitrilic ester whenever produced by the process claimed in Claim 21.

23. A plastics, textile or resin article having incorporated as a flameproofing agent a compound claimed in Claim 20 or 22.

24. A process for the production of a phosphornitrilic ester substantially as herein described with reference to Example 4, 5 or 6.

25. A phosphornitrilic ester whenever produced by the process claimed in any one of Claims 8, 11, 12, 15 and 16.

26. A phosphornitrilic ester substantially as herein described with reference to Example 4, 5 or 6.

27. A plastics, textile or resin article having incorporated as a flameproofing agent a compound claimed in Claim 25 or 26.

28. An article according to Claim 19 substantially as herein described with reference to Example 7.

29. An article according to Claim 19 substantially as herein described with reference to Example 8.

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