

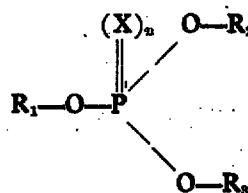
(72) Inventors **WILLIAM ORLANDO DRAKE, HANS-WERNER
FINCK, HORST MAYERHÖFER and WOLFGANG
HEINZ MÜLLER**



(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, 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:—

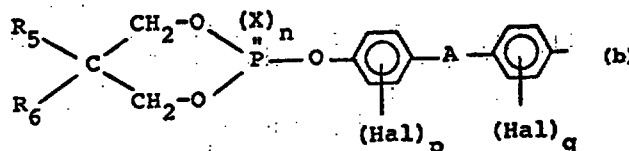
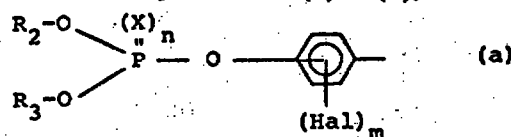
According to the present invention there is provided a flameproofing composition comprising

a) a compound of formula I.



in which

R₁ is (C₁₋₁₈)alkyl; (C₅₋₈)cycloalkyl; phenyl; phenyl-(C₁₋₄)alkyl; phenyl or phenyl-(C₁₋₄)alkyl substituted on the phenyl nucleus with up to 3 halogen atoms, with up to 3 (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms, with up to 3 halogen atoms and an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical, with up to 3 (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms and an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical, or with an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical; or a group of formula (a) or (b).

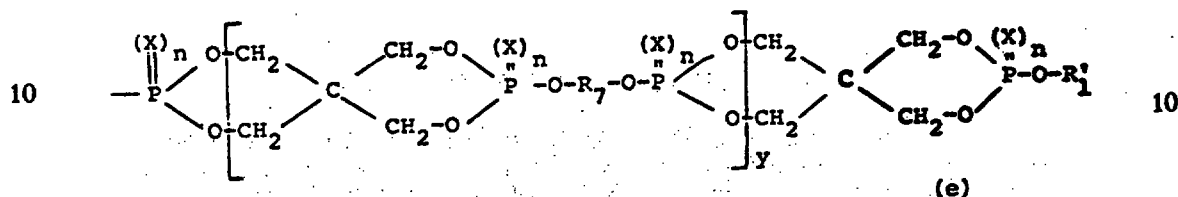
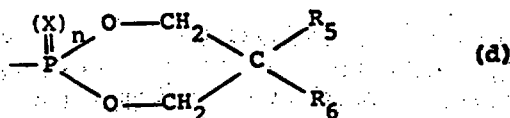
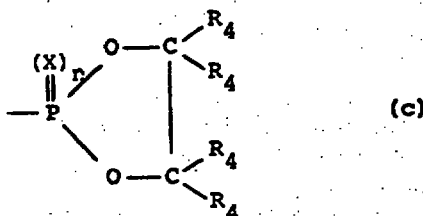


either

R_2 and R_3 each has one of the significances of R_1 , other than a group of formula (a),

or

5 R_2 and R_3 , or both sets of R_2 and R_3 , as appropriate, form together with the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (c), (d), or (e),

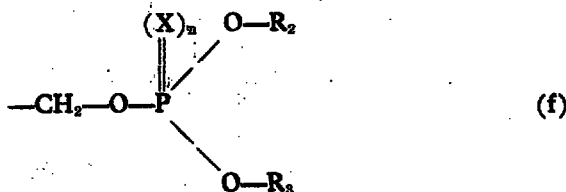


each

R_4 , independently, is hydrogen or (C_{1-4}) alkyl,

R_5 is hydrogen, (C_{1-4}) alkyl, chloromethyl, bromomethyl or phenyl,

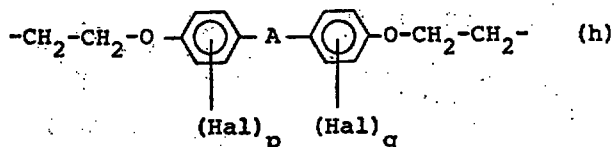
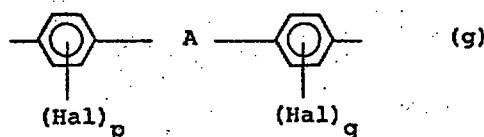
R_6 is hydrogen, (C_{1-4}) alkyl, chloromethyl, bromomethyl or, when R_5 is (C_{1-4}) -alkyl, also a group of formula (f),

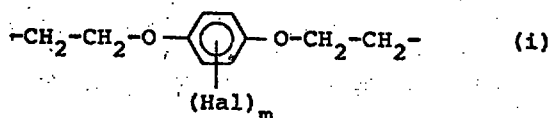


with the proviso that in any radical (d) formed by R_2 and R_3 , the oxygen atoms and the phosphorus atom in the group (f), R_6 is only hydrogen, (C_{1-4}) alkyl, chloromethyl or bromomethyl,

R_1' has one of the significances of R_1 ,

R_7 is straight or branched chain (C_{2-22}) alkylene, cyclohexylene, phenylene, (C_{1-4}) alkylene-1,4-phenylene- (C_{1-4}) alkylene, or a group of formula (g), (h) or (i),





y is zero or an integer 1 to 100,

A is a covalent bond, (C₁₋₄)alkylene, $\text{---CH(C}_6\text{H}_5\text{)---}$, ---O--- , ---S--- or $\text{---SO}_2\text{---}$,

5 each

X, independently, is oxygen or sulphur,

n is zero or 1,

m is zero or an integer 1 to 4

each

10

p and each q, independently, is zero, 1 or 2

and each

Hal, independently, is chlorine or bromine,

with the provisos (i) that only at the most one of the groups (a) and (b) can be linked to any phosphorus atom via an oxygen atom, (ii) that when y in a radical (e) is an integer 1 to 100, each of R₁ and R_{1'}, independently, can also signify a group $\text{---R}_1\text{OH}$, (iii) that when X is oxygen and n=1 in any group (b) or radical (d), then not more than one of R₅ and R₆ in that group (b) or radical (d) may be selected from chloromethyl or bromomethyl, and (iv) that per molecule at the most one radical (e) can be present, and

15

20

b) a haloalkyl aryl ether, of which the aryl radical is unsubstituted or substituted with one or more halogen atoms.

The flameproofing composition of the present invention may optionally additionally comprise other components, e.g.

25

c) a chlorinated aliphatic hydrocarbon containing at least 10 carbon atoms and at least 5 chlorine atoms, and/or d) an organo tin or organo lead compound.

In the compounds of formula I, when R₁, R₂ or R₃ is alkyl, this preferably contains 4 to 18 carbon atoms, and when each of R₁, R₂ and R₃ is alkyl, the sum of the carbon atoms is preferably 24 to 54.

When any of R₁, R₂ and R₃ is cycloalkyl, this is preferably cyclohexyl, of which preferably at the most one is present per molecule.

30

When any of R₁, R₂ and R₃ is substituted phenyl or substituted phenyl-(C₁₋₄)-alkyl, there are preferably one or two substituents, or more preferably there is one substituent, on the phenyl nucleus. Any alkyl substituent preferably contains 1 to 9 carbon atoms or more preferably 1, 4, 5 or 9 carbon atoms. If any R₁, R₂ and R₃ is halo- or alkyl-substituted phenyl further substituted with a (C₁₋₈)alkyl-substituted phenyl radical, each phenyl nucleus preferably bears an alkyl substituent, more preferably butyl. Most preferably the optionally substituted biphenyl radical signified by any of R₁, R₂ or R₃ is unsubstituted. The preferred optionally substituted phenyl or phenyl-(C₁₋₄)alkyl radical is phenyl or benzyl, respectively. Any halogen substituent in R₁, R₂ or R₃ is either chlorine or bromine, of which bromine is preferred.

35

40

Of all the significances, alkyl, optionally substituted phenyl and the groups (a) and (b) are the preferred significances for R₁.

When any R₄ is alkyl, this is preferably methyl. Preferably one R₄ on a carbon atom in the group (c) is hydrogen and the other on the same carbon atom is alkyl.

45

R₅ is preferably alkyl, chloromethyl or bromomethyl more preferably alkyl, the preferred alkyl being methyl.

R₆ is preferably alkyl, chloromethyl, bromomethyl or, when R₅ is alkyl, also a group (f), more preferably alkyl, chloromethyl or bromomethyl, or most preferably, alkyl. The preferred alkyl is methyl.

50

When R₇ is (C₁₋₄)alkylene-1,4-phenylene-(C₁₋₄)alkylene, the (C₁₋₄)alkylene moieties may be straight or branched chain, and, when alkylene, this preferably contains 12 to 18 or most preferably 16 or 18 carbon atoms. When R₇ is cyclohexylene, this is preferably 1,4-cyclohexylene, and when phenylene, preferably 1,2- or 1,4-phenylene, more preferably 1,4-phenylene. Preferably R₇ is alkylene, phenylene or a group (g), (h) or (i), more preferably alkylene, phenylene or a group (g), still more preferably alkylene or phenylene, or most preferably alkylene. In the groups (g) and (h), signified by R₇, and (b), A is preferably a covalent bond, alkylene or ---O--- , more preferably a covalent bond or alkylene. The (C₂₋₄)alkylene radical, signified by A, may be straight or branched chain, and is preferably $\text{---CH}_2\text{---CH}_2\text{---}$ or $\text{---C(CH}_3\text{)}_2\text{---}$, or more preferably the latter radical.

55

60

60

13

4

1,575,356

4

y is preferably zero or 1 to 50, more preferably zero or 1 to 19, still more preferably zero, 1, 2 or 3, and most preferably zero.

The preferences for R_1 , in the group (e), are the same as those given above for R_1 .

n is preferably zero.

All the moieties X in the molecule of formula I preferably have the same meaning, oxygen or sulphur, and any X is preferably oxygen. Most preferably, all the moieties X are oxygen.

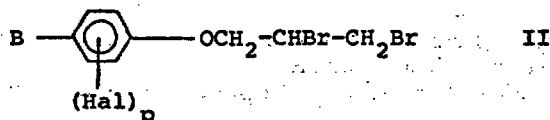
The preferred halogen for any moiety Hal is bromine, and more preferably all the moieties Hal in the molecule of formula I are bromine.

Each of p and q in any group (b), (g) or (h) is preferably 2.

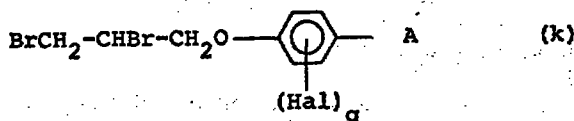
m, in the group (a), is preferably zero, in the group (i) preferably 4.

R_2 and R_3 preferably form together with both the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (d) or (e). Of the compounds containing a radical (d) or (e), those containing two phosphorus atoms per molecule are more preferred, especially those containing two 1,3-dioxaphosphorinane rings or a 3,5,8,10-tetraoxa-4,9-diphosphaspiro-undecane group. Most preferably the compounds of formula I contain a radical (e), in which case R_1 is preferably other than a group (a) or (b).

Preferably the component (b) of the flameproofing composition is selected from compounds of formula II,



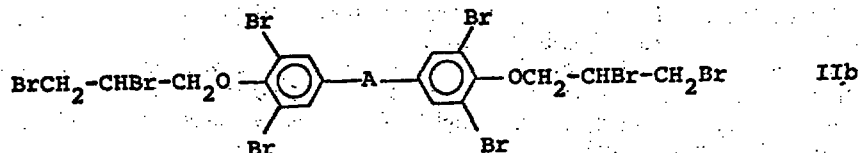
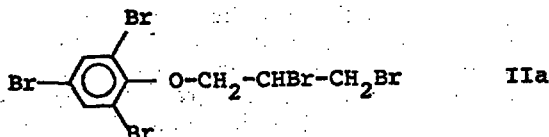
in which B is Hal or a group of formula (k),



and Hal, p, q and A are as defined above.

In the compounds of formula II, Hal, p, q and A have the preferred significances indicated above in relation to these moieties in formula I.

Of the compounds of formula II, those of formulae IIa and IIb are most preferred.



The component c), when present in the flameproofing composition, is selected from chlorinated aliphatic hydrocarbons containing on average at least 10 carbon atoms and at least 5 chlorine atoms. Preferably, it is selected from chloroparaffins with an average chain length of 35-40 carbon atoms, polyvinyl chloride, polyvinylidene chloride and chlorinated polyethylene.

When the component (d) is present in the flameproofing composition, this is preferably selected from di(C_{1-8})alkyl tin carboxylates, di(C_{1-8})alkyl tin mercaptides and lead carboxylates.

Preferred examples of the lead carboxylates are lead stearate and lead phthalate.

Most preferably, the component d) is selected from dibutyl tin maleate, dioctyl tin laurate and dibutyl tin mercaptide.

The compounds of formulae I and II are either known, or can be produced by known methods from available starting materials.

In the preferred flameproofing compositions of the present invention, i.e. those containing one or more compounds of formula I and one or more compounds of formula II, the ratio of compound of formula I: compound of formula II is preferably 1:5 to 3:1, more preferably 1:3 to 2:1 and most preferably 1:3 to 1:1 by weight. When the component c) is also present, the ratio of component c); compound of formula II is preferably 1:5 to 5:1 and more preferably 1:2 to 2:1 by weight. With the component d) present, the ratio of component d): sum of compound of formula I and compound of formula II is preferably 1:30 to 1:3, more preferably 1:20 to 1:4, still more preferably 1:15 to 1:10, and most preferably approximately 1:15 by weight.

The flameproofing compositions of the present invention are useful for the flameproofing of polymeric organic materials and are notable for displaying a greater flameproofing effect than would be expected from the known flameproofing effects of the individual components a) and b).

Accordingly the present invention further provides a method of flameproofing a polymeric organic material comprising treating such material with a flameproofing effective amount of composition of the present invention, as defined above, or sequentially with the individual components of said composition. By the term "treating" is meant either applying on the surface of the substrate to be flameproofed or incorporating, directly or indirectly, into the body thereof in conventional manner.

Also provided by the present invention is a polymeric organic material flameproofed by the method of the present invention, as defined above.

The method of the present invention is particularly suitable for the flameproofing of synthetic polymeric organic materials, more especially polypropylene, polyethylene, polystyrene and acrylonitrile-butadiene-styrene terpolymers, of which polypropylene is preferred. The flameproofed materials may be in the form of moulding or spinning masses as well as in the form of moulded or extruded articles and sheets.

The amount of flameproofing composition used or present in the method or flameproofed polymeric organic material, respectively, is preferably 1 to 9%, and more preferably 2 to 4% by weight of the material to be flameproofed.

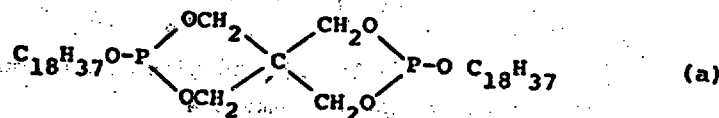
Other agents may be added with the flameproofing composition or individual components thereof besides the components a), b) and optionally c) and/or d) in the method, especially stabilizers against the degradative effects of light.

The present invention further provides a flameproofing master batch composition which comprises the flameproofing composition of the present invention and a part of the substrate to be treated by the method of the present invention. Such a master batch composition is a form of the flameproofing composition conveniently useable in the method, since it avoids the necessity for those engaged in practising the method to initially make up the composition according to recommended ratio specifications before addition to the substrate to be flameproofed, and the master batch composition is readily worked into or applied onto the main body of the substrate by virtue of the presence of the same substrate in the master batch composition. The master batch composition may consist, for example, of a polyolefin which contains 20 to 80, or more preferably 40 to 70% by weight of the flameproofing composition.

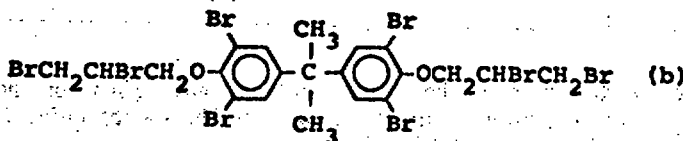
In the following Examples, which illustrate the present invention, the parts and percentages are by weight and the temperatures are expressed in degrees Centigrade.

EXAMPLE 1.

97 Parts of commercial polypropylene (melt flow index 5 at 230° and 2.16 kg/sq cm pressure) are pre-mixed with 1 part of the compound of formula (a),



2 parts of the compound of formula (b),



and 0.2 parts of dibutyl tin maleate in a rolling flask, and then the whole is intimately mixed at 165—175° for 3 minutes in a laboratory rolling mill (Schwabenthau). The resulting sheet of the mixture is cut up into discs of 1 mm thickness in a press (Bucher-

Guyer) at 230° within a period of 3 minutes, and the limiting oxygen index (LOI) determined. This is found to be 23.6, as compared with 17.5 for similar discs of commercial polypropylene not containing the flame-proofing composition.

Another sample of the flameproofed polypropylene is submitted to the vertical test according to DIN 53438; class 1/1 mm, in which the sample self-extinguished within 2 seconds of the removal of the flame.

EXAMPLE 2.

When the dialkyl tin maleate of Example 1 is replaced by a dialkyl tin mercaptide (Irgastab T36, R.T.M.) and the procedure thereof repeated, the sample discs obtained are found to have a LOI of 23.8.

EXAMPLE 3.

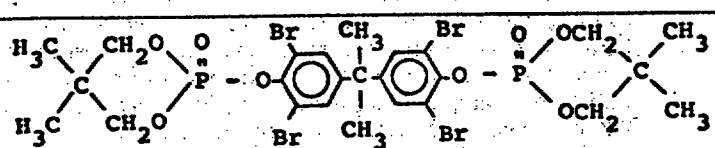
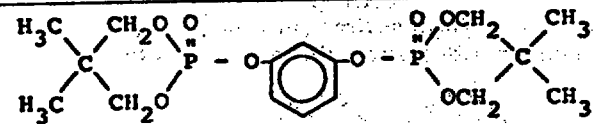
97 parts of commercial polypropylene (melt flow index 5 at 230°, 2.16 kg/sq cm pressure) are mixed with 1.5 parts of the compound of formula (a) and 1.5 parts of the compound of formula (b) as given in Example 1, and the resulting discs tested as described in Example 1. Good results are obtained.

EXAMPLE 4.

97 parts of commercial polypropylene (melt flow index 5 at 230°, 2.16 kg/sq cm pressure), 1.5 parts of the compound of formula (a), 0.5 parts of the compound of formula (b) and 1 part of a waxy chloro paraffin with approximately 40—50 carbon atoms and approximately 20 chlorine atoms, on average, per molecular are mixed and the resulting discs tested as described in Example 1. Good results are obtained.

EXAMPLES 5 to 7.

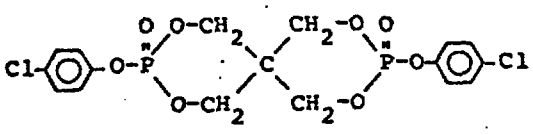
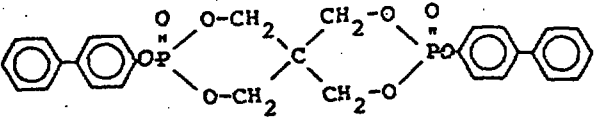
In a similar manner as described in Example 1 the following compositions are produced and tested:

Example No.	Constituents
5	$C_{10}H_{21}O - P(O-C_6H_5)_2$ Compound of formula (b), as given in Example 1 Chloro paraffin as in Example 4
6	 Compound of formula (b), as given in Example 1 Chloro paraffin as in Example 4
7	 Compound of formula (b), as given in Example 1 Chloro paraffin as in Example 4

The weight ratios of the constituents are those given for the constituents in Example 1. Further samples are prepared using the weight ratios as follows: 2:1:0, 1:2:0, 2:1:0.5, 2:0.5:0.5, 1:2:0.5, 1:1:1 and 1:1:2.

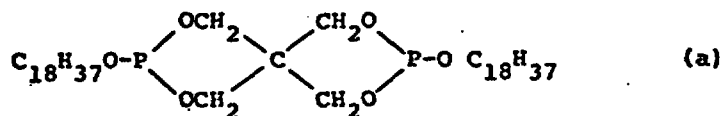
EXAMPLES 8 and 9.

In a similar manner as described in Example 3 the following compositions are produced.

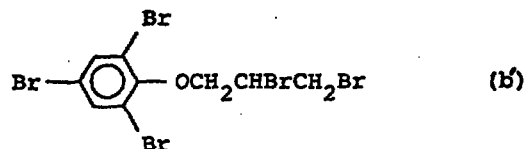
Example No.	Constituents
8	 Compound of formula (b), as given in Example 1
9	 Compound of formula (b), as given in Example 1

EXAMPLE 10.

97 Parts of commercial polypropylene (melt flow index 5 at 230° and 2.16 kg/sq cm pressure) are pre-mixed with 1 part of the compound of formula (a),



2 parts of the compound of formula (b'),

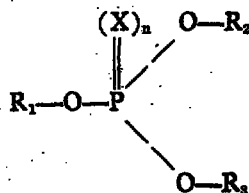


and 0.2 parts of a dialkyl tin mercaptide (Irgastab T 36, R.T.M.) in a rolling flask, and then the whole is intimately mixed at 165—175° for 3 minutes in a laboratory rolling mill (Schwabenthan). The resulting sheet of the mixture is cut up into discs of 1 mm thickness in a press (Bucher-Guyer) at 230° within a period of 3 minutes and the limiting oxygen index (LOI) determined. This is found to be 23.1 as compared with 17.5 for similar discs of commercial polypropylene not containing the flameproofing composition.

Another sample of the flameproofed polypropylene is submitted to the vertical test according to DIN 53438; class 1/1 mm, in which the sample self-extinguished within 1 second of the removal of the flame.

WHAT WE CLAIM IS:—

1. A flameproofing composition comprising a) a compound of formula I,



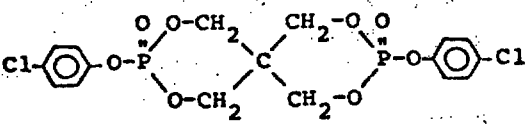
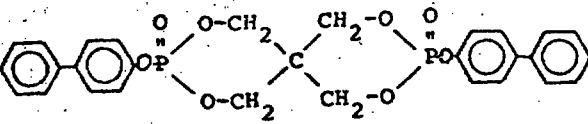


16

1,575,356

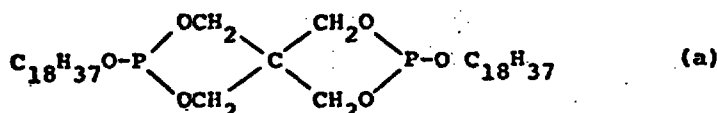
EXAMPLES 8 and 9.

In a similar manner as described in Example 3 the following compositions are produced.

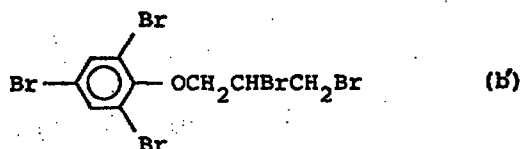
Example No.	Constituents
8	 Compound of formula (b), as given in Example 1
9	 Compound of formula (b), as given in Example 1

EXAMPLE 10.

97 Parts of commercial polypropylene (melt flow index 5 at 230° and 2.16 kg/sq cm pressure) are pre-mixed with 1 part of the compound of formula (a),



2 parts of the compound of formula (b'),

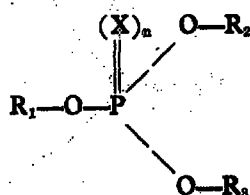


and 0.2 parts of a dialkyl tin mercaptide (Irgastab T 36, R.T.M.) in a rolling flask, and then the whole is intimately mixed at 165—175° for 3 minutes in a laboratory rolling mill (Schwabenthan). The resulting sheet of the mixture is cut up into discs of 1 mm thickness in a press (Bucher-Guyer) at 230° within a period of 3 minutes and the limiting oxygen index (LOI) determined. This is found to be 23.1 as compared with 17.5 for similar discs of commercial polypropylene not containing the flameproofing composition.

Another sample of the flameproofed polypropylene is submitted to the vertical test according to DIN 53438; class 1/1 mm, in which the sample self-extinguished within 1 second of the removal of the flame.

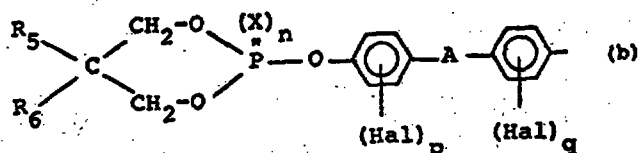
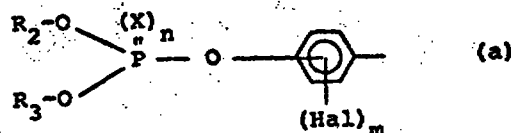
WHAT WE CLAIM IS:—

1. A flameproofing composition comprising a) a compound of formula I,



in which

R₁ is (C₁₋₁₀)alkyl; (C₅₋₉)cycloalkyl; phenyl; phenyl-(C₁₋₄)alkyl; phenyl or phenyl-(C₁₋₄)alkyl substituted on the phenyl nucleus with up to 3 halogen atoms, with up to 3 (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms, with up to 3 halogen atoms and an unsubstituted or (C₁₋₃)-alkyl-substituted phenyl radical, with up to 3 (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms and an unsubstituted or (C₁₋₃)alkyl-substituted phenyl radical, or with an unsubstituted or (C₁₋₃)alkyl-substituted phenyl radical; or a group of formula (a) or (b),

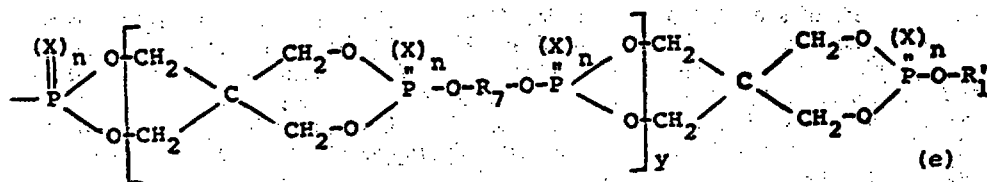
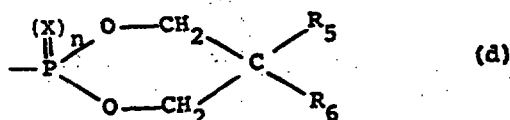
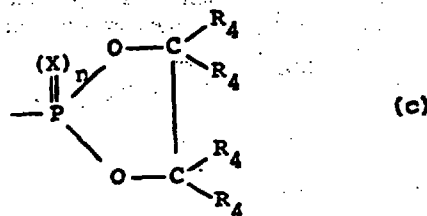


either

R_2 and R_3 each has one of the significances of R_1 , other than a group of formula (a),

or

R₂ and R₃, or both sets of R₂ and R₃, as appropriate, form together with the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (c), (d), or (e).

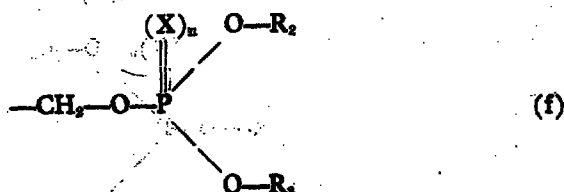


each

R₄, independently, is hydrogen or (C₁₋₄)alkyl,

R₂ is hydrogen, (C₁₋₄)alkyl, chloromethyl, bromomethyl or phenyl,

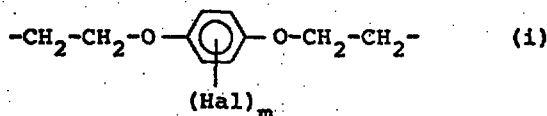
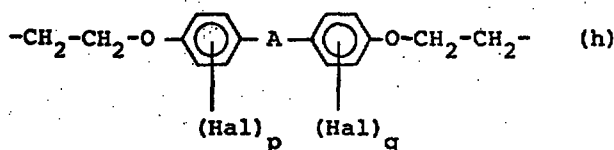
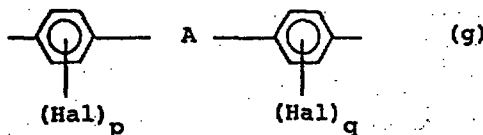
R₆ is hydrogen, (C₁₋₄)alkyl, chloromethyl, bromomethyl or, when R₅ is (C₁₋₄)alkyl, also a group of formula (f),



with the proviso that in any radical (d) formed by R_2 and R_3 , the oxygen atoms and the phosphorus atom in the group (f), R_n is only hydrogen, (C_{1-4}) alkyl, chloromethyl or bromomethyl,

R_1 has one of the significances of R_1 ,

R_1 is straight or branched chain (C_{2-22}) alkylene, cyclohexylene, phenylene, (C_{1-4}) alkylene-1,4-phenylene- (C_{1-4}) alkylene, or a group of formula (g), (h) or (i),



y is zero or an integer 1 to 100,

A is a covalent bond, (C_{1-4}) alkylene, $\text{---CH}(C_6H_5)\text{---}$, ---O--- , ---S--- or $\text{---SO}_2\text{---}$,

each

X, independently, is oxygen or sulphur,

n is zero or 1,

m is zero or an integer 1 to 4,

each

p and each q, independently, is zero, 1 or 2

and each

Hal, independently, is chlorine or bromine,

with the provisos (i) that only at the most one of the groups (a) and (b) can be linked to any phosphorus atom via an oxygen atom, (ii) that when y is a radical (e) is an integer 1 to 100, each of R_1 and R_1' , independently, can also signify a group $\text{---R}_1\text{OH}$, (iii) that when X is oxygen and n=1 in any group (b) or radical (d), then not more than one of R_5 and R_6 in that group (b) or radical (d) may be selected from chloromethyl or bromomethyl, and (iv) that per molecule at the most one radical (e) can be present, and

b) a haloalkyl aryl ether, of which the aryl radical is unsubstituted or substituted with one or more halogen atoms.

2. A flameproofing composition according to Claim 1, additionally comprising c) a chlorinated aliphatic hydrocarbon containing at least 10 carbon atoms and at least 5 chlorine atoms and/or d) an organo tin or organo lead compound.

3. A flameproofing composition according to Claim 2, in which R_1 is (C_{1-18}) alkyl; phenyl; phenyl substituted with up to three halogen atoms, with up to 3 (C_{1-12}) alkyl radicals containing a total of up to 12 carbon atoms, with up to three halogen atoms and an unsubstituted or (C_{1-8}) alkyl-substituted phenyl radical, with up to 3 (C_{1-12}) alkyl radicals containing a total of up to 12 carbon atoms and an unsubstituted or (C_{1-8}) alkyl-substituted phenyl radical, or with an unsubstituted or (C_{1-8}) alkyl-substituted phenyl radical; or a group of formula (a) or (b).

4. A flameproofing composition according to Claim 3, in which R_1 is (C_{4-18}) alkyl; phenyl; mono- or di-substituted phenyl; a group (a) in which R_2 and R_3 form together with both the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (d) or (e), X is oxygen and m is zero; or a group (b) in which R_5 is (C_{1-4}) alkyl, chloromethyl or bromomethyl, R_6 is (C_{1-4}) alkyl, chloromethyl, bromomethyl, or, when R_5 is alkyl, also a group (f), A is a covalent bond, (C_{1-4}) alkylene or ---O--- , X is oxygen, each of p and q is 2, and Hal is bromine.

5. A flameproofing composition according to Claim 4, in which R_1 is (C_{4-18}) alkyl; phenyl; a group (a) in which R_2 and R_3 form together with both the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (d) or (e), X is oxygen and m is zero; or a group (b) in which R_5 is (C_{1-4}) alkyl, R_6 is (C_{1-4}) alkyl, chloromethyl or bromomethyl, A is a covalent bond or



(C₁₋₄)alkylene, and X, p, q and Hal are as defined in Claim 4.

6. A flameproofing composition according to Claim 5, in which R₅ and R₆ are each, independently, (C₁₋₄)alkyl.

7. A flameproofing composition according to any preceding claim, in which R₂ and R₃, or both sets of R₂ and R₃, as appropriate, form together with both the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (d) or (e).

8. A flameproofing composition according to Claim 7, in which in the radical (d) R₅ is (C₁₋₄)alkyl, chloromethyl or bromomethyl, R₆ is (C₁₋₄)alkyl, chloromethyl, bromomethyl, or, when R₅ is alkyl, also a group (f), and in which in the radical (e) R₁' is (C₁₋₁₂)alkyl; phenyl; phenyl substituted with up to three halogen atoms, with up to three (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms, with up to three halogen atoms and an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical, with up to three (C₁₋₁₂)alkyl radicals containing a total of up to 12 carbon atoms and an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical, or with an unsubstituted or (C₁₋₈)alkyl-substituted phenyl radical; or a group (a) or (b), R₇ is straight or branched chain (C₂₋₂₂)alkylene, phenylene, or a group (g), (h) or (i), y is zero or 1 to 50, and X is oxygen.

9. A flameproofing composition according to Claim 8, in which R₅ is (C₁₋₄)alkyl, R₆ is (C₁₋₄)alkyl, chloromethyl or bromomethyl, R₁' is (C₄₋₁₈)alkyl, phenyl, mono- or di-substituted phenyl, or a group (a) or (b), R₇ is straight or branched chain (C₁₂₋₁₈)alkylene, 1,2- or 1,4-phenylene, or a group (g), and y is zero or 1 to 19.

10. A flameproofing composition according to Claim 9, in which R₆ is (C₁₋₄)alkyl, R₁' is (C₄₋₁₈)alkyl, phenyl or a group (a) or (b), R₇ is straight or branched chain (C_{16 or 18})alkylene or 1,4-phenylene, and y is zero, 1, 2 or 3.

11. A flameproofing composition according to Claim 10, in which y is zero.

12. A flameproofing composition according to any of Claims 7 to 11, in which R₅ and R₆ are both methyl.

13. A flameproofing composition according to any preceding claim, in which the compound of formula I contains a radical (e).

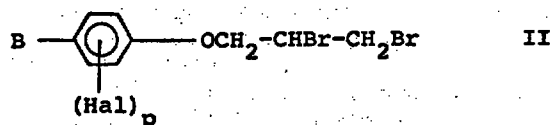
14. A flameproofing composition according to any preceding claim, in which n is zero.

15. A flameproofing composition according to any preceding claim, in which the compound of formula I contains two phosphorus atoms per molecule.

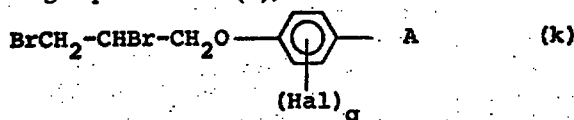
16. A flameproofing composition according to Claim 16, in which the compound of formula I contains two 1,3-dioxaphosphorinane rings or a 3,5,8,10-tetraoxa-4,9-diphosphaspiro-undecane group.

17. A flameproofing composition according to any of Claims 13 to 16, in which the compound of formula I contains a radical (e) and R₁ and R₁' are other than a group (a) or (b).

18. A flameproofing composition according to any preceding claim, in which the component b) is a compound of formula II



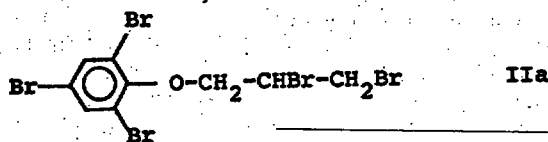
in which B is Hal or a group of formula (k),

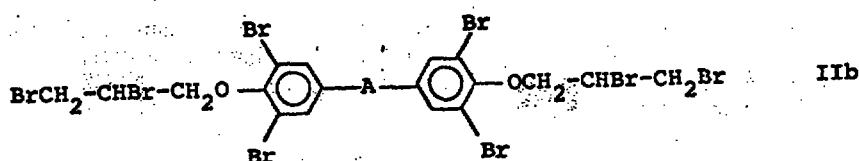


and Hal, p, q and A are as defined in Claim 1.

19. A flameproofing composition according to Claim 18, in which in the compound of formula II, A is a covalent bond, (C₁₋₄)alkylene or —O—, p and q are each 2, and Hal is bromine.

20. A flameproofing composition according to Claim 18 or 19, in which the compound of formula II is one of formula IIa or IIb,





21. A flameproofing composition according to any of Claims 2 to 20, in which the component c) is selected from chloroparaffins with an average chain length of 35 to 40 carbon atoms, polyvinyl chloride, polyvinylidene chloride and chlorinated polyethylene.
22. A flameproofing composition according to any of Claims 2 to 21, in which the component d) is selected from di(C₁₋₈)alkyl tin carboxylates, di(C₁₋₈)alkyl tin mercaptides and lead carboxylates.
23. A flameproofing composition according to Claim 22, in which the lead carboxylates are selected from lead stearate and lead phthalate.
24. A flameproofing composition according to Claim 22 or 23, in which the component d) is selected from dibutyl tin maleate, dioctyl tin laurate and dibutyl tin mercaptide.
25. A flameproofing composition according to Claim 18, in which the ratio of compound(s) of formula I: compound(s) of formula II is 1:5 to 3:1 by weight.
26. A flameproofing composition according to Claim 25, in which the ratio is 1:3 to 2:1 by weight.
27. A flameproofing composition according to Claim 26, in which the ratio is 1:3 to 1:1 by weight.
28. A flameproofing composition according to any of Claims 18 to 27, in which the component c) is present and the ratio of component c); compound of formula II is 1:5 to 5:1 by weight.
29. A flameproofing composition according to Claim 28, in which the ratio is 1:2 to 2:1 by weight.
30. A flameproofing composition according to any of Claims 18 to 29, in which the component d) is present and the ratio of component d): sum of compound of formula I and compound of formula II is 1:30 to 1:3 by weight.
31. A flameproofing composition according to Claim 30, in which the ratio is 1:20 to 1:4 by weight.
32. A flameproofing composition according to Claim 31, in which the ratio is 1:15 to 1:10 by weight.
33. A flameproofing composition according to Claim 32, in which the ratio is approximately 1:15 by weight.
34. A flameproofing composition according to Claim 1, substantially as described herein with reference to any one of Examples 1 to 10.
35. A method of flameproofing a polymeric organic material comprising treating such material with a flameproofing effective amount of a composition according to any preceding claim, or sequentially with the individual components of said composition.
36. A method according to Claim 35, in which the polymeric organic material is a synthetic polymeric organic material.
37. A method according to Claim 36, in which the synthetic polymeric organic material is selected from polypropylene, polyethylene, polystyrene and acrylonitrile-butadiene-styrene terpolymers.
38. A method according to Claim 37, in which the synthetic polymeric organic material is polypropylene.
39. A method according to any one of Claims 35 to 38, in which the amount of flameproofing composition used is 1 to 9% by weight of the material to be flameproofed.
40. A method according to Claim 39, in which the amount is 2 to 4% by weight of the material to be flameproofed.
41. A method according to Claim 35, substantially as described herein with reference to any one of Examples 1 to 10.
42. A polymeric organic material whenever flameproofed by a method according to any one of Claims 35 to 41.
43. A flameproofing master batch composition comprising a flameproofing composition according to any one of Claims 1 to 34 and a part of the substrate to be treated by the method according to any one of Claims 35 to 41.
44. A flameproofing master batch composition according to Claim 43, consisting of a polyolefin which contains 20 to 80% by weight of the flameproofing composition.



46. A flameproofing composition comprising

a) a compound of formula Ia,



R_{1a} is (C₁₋₁₈)alkyl; (C₅₋₈)cycloalkyl; phenyl; phenyl-(C₁₋₄)alkyl; phenyl or phenyl-(C₁₋₄)alkyl substituted on the phenyl nucleus with up to 3 (C₁₋₁₂)-alkyl radicals containing a total of up to 12 carbon atoms, or a group of formula (a') or (b'),



R_{2a} and R_{3a} each has one of the significances of R_{1a} , other than a group of formula (a'),

R_{2a} and R_{3a} , or both sets of R_{2a} and R_{3a} , as appropriate, form together with the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (c), (d') or (e').



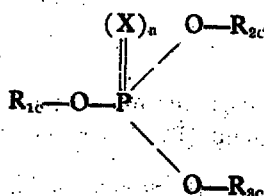
R_4 , independently, is hydrogen or (C_{1-4}) alkyl,
 R_5 is hydrogen, (C_{1-4}) alkyl, chloromethyl, bromomethyl or phenyl,
 R_6 is hydrogen, (C_{1-4}) alkyl, chloromethyl, bromomethyl or, when R_5 is (C_{1-4}) -alkyl, also a group of formula (f')



c) a chlorinated aliphatic hydrocarbon containing at least 10 carbon atoms and at least 5 chlorine atoms.

48. A flameproofing composition comprising

a) a compound of formula Ic,



in which

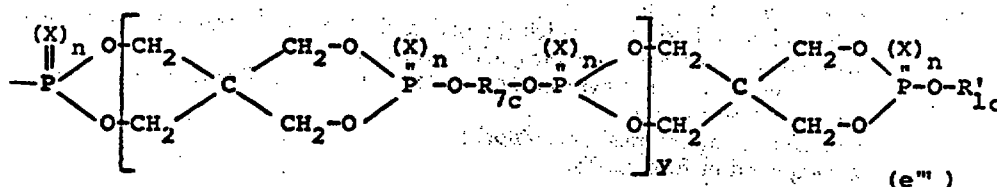
R_{1c} is as defined for R_1 in Claim 1,

either

R_{2c} and R_{3c} each has one of the significances of R_{1c} , other than a group of formula (a),

or

R_{2c} and R_{3c} or both sets of R_2 and R_3 , as appropriate, form together with the oxygen atoms to which they are attached and the common phosphorus atom a radical of formula (c) or (d), as defined in Claim 1, or (e'''),



R_{1c}' has one of the significances of R_{1c} ,

R_{7c} is straight or branched chain (C_{2-22})alkylene, cyclohexylene, phenylene, or a group of formula (g), (h) or (i) as defined in Claim 1,

and

y, X and n are as defined in Claim 1,

with the proviso (i) that at the most one group (a) or one group (b) is present in the molecule, (ii) that when y in any radical (e''') is an integer 1 to 100, each of R_{1c} and R_{1c}' , independently, can also signify a group $-R_{7c}OH$, (iii) that when X is oxygen atom and n=1 in any group (b) or radical (d), then not more than one of R_2 and R_3 in that group (b) or radical (d) may be selected from chloromethyl or bromomethyl, and (iv) that per molecule at the most one radical (e''') can be present,

b) a haloalkyl aryl ether, of which the aryl radical is unsubstituted or substituted with one or more halogen atoms,

c) an organo tin or organo lead compound, and optionally

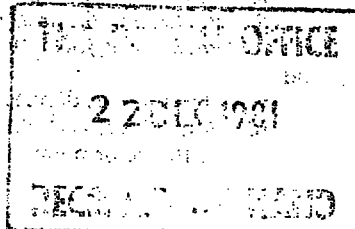
d) a chlorinated aliphatic hydrocarbon containing at least 10 carbon atoms and at least 5 chlorine atoms.

B. A. YORKE & CO.,
Chartered Patent Agents,
98, The Centre,
Feltham,
Middlesex TW13 4EP.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *



ERRATA

SPECIFICATION No. 1,575,356

Page 2, line 13, *for* (C_{1-8}) *read* (C_{1-4})
Page 6, line 20, *for* *moleculer* *read* *molecule*

THE PATENT OFFICE
14th June, 1981

(9)