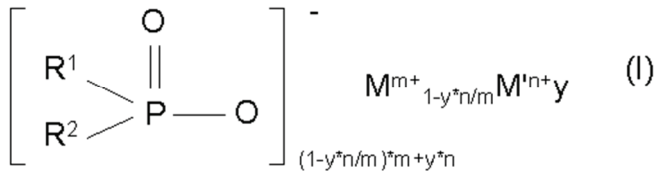
It has been found that, surprisingly, the diorganylphosphinic salts of the invention have a broader processing window in the compounding of flame-retardant polymer molding compounds and in the injection molding of flame-retardant polymer moldings and simultaneously exhibit good flame retardancy.

Summary

In one aspect, there is provided a diorganylphosphinic salt, which conforms to the formula (I)



$$\left[R^1(R^2)P(=O)-O \right]^{-}_{(1-y*n/m)*m+y*n} \; M^{m+}_{1-y*n/m} M'^{n+}_{y} \qquad (I)$$

in which

R^1 and R^2 are the same or different and are C_1-C_{18}-alkyl in linear, branched or cyclic form, C_6-C_{18}-aryl, C_7-C_{18}-arylalkyl and/or C_7-C_{18}-alkylaryl, or together form at least one ring,

y is 0.00001 to 0.091,

m is 1 to 4 and

n is 2 to 3,

M is Mg, Ca, Al, Sb, Sn, Ge, Ti, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na and/or K and

M' is Fe.

In another aspect, there is provided a process for producing diorganylphosphinic salts as described herein, which comprises

a) in a process stage 1 adding 0.9 to 1.1 molecules of olefin per P onto a water-soluble salt of the hypophosphorous acid or the acid itself,

b) in a process stage 2 adding 0.9 to 1.1 additional molecules of olefin per P onto the intermediate from a) to give dialkylphosphinic acid or salt thereof,

c) in a process stage 3 adding one to 9 further olefin molecules onto 0% to 20% of the dialkylphosphinate molecules from process stage 1, so as to form telomers,

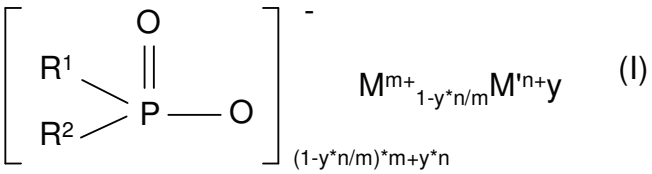
d) in a process stage 4 conducting a crystallization of the intermediate from b) or c) with a metal salt and an iron salt.

In another aspect, there is provided the use of diorganylphosphinic salts as described herein as intermediates for further syntheses, as a binder, as a crosslinker or accelerator in the curing of epoxy resins, polyurethanes and unsaturated polyester resins, as polymer stabilizers, as crop protection compositions, as sequestrants, as a mineral oil additive, as an anticorrosive, in washing and cleaning composition applications, and in electronics applications.

In another aspect, there is provided a flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament and/or fiber comprising 0.5% to 45% by weight of diorganylphosphinic salts as described herein, 0.5% to 95% by weight of thermoplastic or thermoset polymer or mixtures thereof, 0% to 55% by weight of additives and 0% to 55% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.

The invention therefore relates to diorganylphosphinic salts containing 0.0001% to 99.9999% by weight of iron.

The diorganylphosphinic salts preferably conform to the formula (II)



(I)

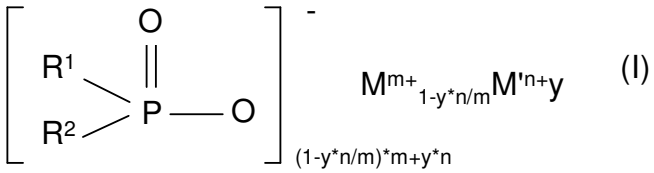
in which

R^1 and R^2	are the same or different and are C_1-C_{18}-alkyl in linear, branched or cyclic form, C_6-C_{18}-aryl, C_7-C_{18}-arylalkyl and/or C_7-C_{18}-alkylaryl, or together form at least one ring,
y	is 0.00001 to 0.091,
m	is 1 to 4 and
n	is 2 to 3,
M	is Mg, Ca, Al, Sb, Sn, Ge, Ti, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na and/or K and
M'	is Fe.

Preferably, R^1, R^2 in formula (I) are the same or different and are independently methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2-methylbutyl, 3-methylbutyl (isopentyl), 3-methylbut-2-yl, 2-methylbut-2-yl, 2,2-dimethylpropyl (neopentyl), hexyl, heptyl, octyl, nonyl, decyl, cyclopentyl, cyclopentylethyl, cyclohexyl, cyclohexylethyl, phenyl, phenylethyl, methylphenyl and/or methylphenylethyl.

Claims

1. A diorganylphosphinic salt, which conforms to the formula (I)



(I)

in which

R^1 and R^2 are the same or different and are C_1-C_{18}-alkyl in linear, branched or cyclic form, C_6-C_{18}-aryl, C_7-C_{18}-arylalkyl and/or C_7-C_{18}-alkylaryl, or together form at least one ring,

y is 0.00001 to 0.091,

m is 1 to 4 and

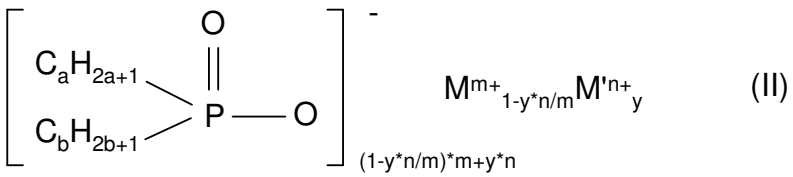
n is 2 to 3,

M is Mg, Ca, Al, Sb, Sn, Ge, Ti, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na and/or K and

M' is Fe.

2. The diorganylphosphinic salt as claimed in claim 1, wherein R^1, R^2 in formula (II) are the same or different and are independently methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2-methylbutyl, 3-methylbutyl (isopentyl), 3-methylbut-2-yl, 2-methylbut-2-yl, 2,2-dimethylpropyl (neopentyl), hexyl, heptyl, octyl, nonyl, decyl, cyclopentyl, cyclopentylethyl, cyclohexyl, cyclohexylethyl, phenyl, phenylethyl, methylphenyl and/or methylphenylethyl.

3. The diorganylphosphinic salt as claimed in claim 1 or 2, which conforms to a formula (II)



(II)

where

a and b are the same or different and are each independently 1 to 9 and the C_aH_{2a+1} and C_bH_{2b+1} groups may be linear or branched and

y is 0.00001 to 0.091,

m is 1 to 4 and

n is 2 to 3,

M is Mg, Ca, Al, Sb, Sn, Ge, Ti, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na and/or K and

M' is Fe.

4. The diorganylphosphinic salt as claimed in one or more of claims 1 to 3, wherein the iron is in the form of iron(II) dialkylphosphinates and/or iron(III) dialkylphosphinates.

5. The diorganylphosphinic salt as claimed in one or more of claims 1 to 3, wherein M and M' are in the form of a homogeneous ionic compound with the (C_aH_{2a+1}) $(C_bH_{2b+1})PO_2$ anions.

6. The diorganylphosphinic salt as claimed in one or more of claims 1 to 5, which further comprises telomer ions, where the telomer ions are those of the empirical formula (VI)

$$H\text{-}(C_wH_{2w})_k\ P(O)(O^{(-)})\ (C_xH_{2x})_l\text{-}H \quad (VI)$$

where, in formula (VI), independently of one another,
k is 1 to 9, l is 1 to 9, w is 2 to 9 and x is 2 to 9.

7. The diorganylphosphinic salt as claimed in claim 6, wherein, in formula (VI), w and x are each 2 to 4 and k and l are each 1 to 4.

8. The diorganylphosphinic salt as claimed in claim 6, wherein, in formula (VI), w and x are each 2 or 3 and k and l are each 1 to 3.

9. The diorganylphosphinic salt as claimed in one or more of claims 6 to 8, which comprises

a) 60 to 99.8999 P% dialkylphosphinic salts of the formula (I) and

b) 0.1 to 40 P% of telomer ions of the formula (VI),

where the sum total of a) and b) is 100 P%, with the proviso that the diorganylphosphinic salts of the formula (I) and the telomer ions of the formula (VI) are each different compounds.

10. The diorganylphosphinic salt as claimed in one or more of claims 1 to 9, wherein the ions M, M‘, $(C_aH_{2a+1})(C_bH_{2b+1})PO_2^-$, $H\text{-}(C_wH_{2w})_kPO_2^-(C_xH_{2x})_l\text{-}H$ and anions of ethylbutylphosphinic acid, dibutylphosphinic acid, ethylhexylphosphinic acid, butylhexylphosphinic acid, ethyloctylphosphinic acid, sec-butylethylphosphinic acid, 1-ethylbutyl(butyl)phosphinic acid, ethyl(1-methylpentyl)phosphinic acid, di-sec-butylphosphinic acid (di(1-methylpropyl)phosphinic acid), propyl(hexyl)phosphinic acid, dihexylphosphinic acid, hexyl(nonyl)phosphinic acid, propyl(nonyl)phosphinic acid, dinonylphosphinic acid, dipropylphosphinic acid, butyl(octyl)phosphinic acid, hexyl(octyl)phosphinic acid, dioctylphosphinic acid, ethyl(cyclopentylethyl)phosphinic acid, butyl(cyclopentylethyl)phosphinic acid, ethyl(cyclohexylethyl)phosphinic acid, butyl(cyclohexylethyl)phosphinic acid, ethyl(phenylethyl)phosphinic acid, butyl(phenylethyl)phosphinic acid, ethyl(4-methylphenylethyl)phosphinic acid, butyl(4-methylphenylethyl)phosphinic acid, butylcyclopentylphosphinic acid, butylcyclohexylethylphosphinic acid, butylphenylphosphinic acid, ethyl(4-methylphenyl)phosphinic acid and/or butyl(4-methylphenyl)phosphinic acid together constitute a homogeneous ionic compound.

11. The diorganylphosphinic salt as claimed in one or more of claims 1 to 10, wherein the telomer ions are in the form of their metal salts, these being metal salts of ethylbutylphosphinic acid, dibutylphosphinic acid, ethylhexylphosphinic acid, butylhexylphosphinic acid, ethyloctylphosphinic acid, sec-butylethylphosphinic acid, 1-ethylbutyl(butyl)phosphinic acid, ethyl(1-methylpentyl)phosphinic acid, di-sec-butylphosphinic acid (di-1-methylpropylphosphinic acid), propyl(hexyl)phosphinic acid, dihexylphosphinic acid, hexyl(nonyl)phosphinic acid, propyl(nonyl)phosphinic acid, dinonylphosphinic acid, dipropylphosphinic acid, butyl(octyl)phosphinic acid,

hexyl(octyl)phosphinic acid, dioctylphosphinic acid, ethyl(cyclopentylethyl)phosphinic acid, butyl(cyclopentylethyl)phosphinic acid, ethyl(cyclohexylethyl)phosphinic acid, butyl(cyclohexylethyl)phosphinic acid, ethyl(phenylethyl)phosphinic acid, butyl(phenylethyl)phosphinic acid, ethyl(4-methylphenylethyl)phosphinic acid, butyl(4-methylphenylethyl)phosphinic acid, butylcyclopentylphosphinic acid, butylcyclohexylethylphosphinic acid, butylphenylphosphinic acid, ethyl(4-methylphenyl)phosphinic acid and/or butyl(4-methylphenyl)phosphinic acid, and the metal of the metal salt comes from the group of Mg, Ca, Al, Sb, Sn, Ge, Ti, Fe, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na and/or K.

12. The diorganylphosphinic salt as claimed in one or more of claims 1 to 11, which has
a particle size of 0.1 to 1000 µm,
a bulk density of 80 to 800 g/L,
a tamped density of 100 g/L to 1100 g/L,
an angle of repose of 5 to 45 degrees,
a BET surface area of 1 to 40 m^2/g,
L color values of 85 to 99.9,
a color values of -4 to +9 and
b color values of -2 to +6.

13. The dialkylphosphinic salt as claimed in one or more of claims 1 to 12, which has
a particle size of 0.5 to 800 µm,
a bulk density of 80 to 600 g/L,
a tamped density of 600 g/L to 800 g/L and
an angle of repose of 10 to 40 degrees.

14. A process for producing diorganylphosphinic salts as claimed in one or more of claims 1 to 13, which comprises
a) in a process stage 1 adding 0.9 to 1.1 molecules of olefin per P onto a water-soluble salt of the hypophosphorous acid or the acid itself,

b) in a process stage 2 adding 0.9 to 1.1 additional molecules of olefin per P onto the intermediate from a) to give dialkylphosphinic acid or salt thereof,

c) in a process stage 3 adding one to 9 further olefin molecules onto 0% to 20% of the dialkylphosphinate molecules from process stage 1, so as to form telomers,

d) in a process stage 4 conducting a crystallization of the intermediate from b) or c) with a metal salt and an iron salt.

15. A process for producing diorganylphosphinic salts as claimed in one or more of claims 1 to 13, which comprises

a) in a process stage 1 adding 0.9 to 1.1 molecules of olefin per P onto a water-soluble salt of the hypophosphorous acid or the acid itself,

b) in a process stage 2 adding 0.9 to 1.1 additional molecules of olefin per P onto the intermediate from a) to give dialkylphosphinic acid or salt thereof,

c) in a process stage 2 adding one to 9 further olefin molecules onto 0% to 20% of the dialkylphosphinate molecules from process stage 1, so as to form telomers,

d) in a process stage 3 conducting a crystallization with a metal salt and/or an iron salt and

e) in a process stage 4 conducting a coprecipitation of the intermediate from d) with a metal salt or an iron salt.

16. A process for producing diorganylphosphinic salts as claimed in one or more of claims 1 to 13, which comprises

a) in a process stage 1 adding 0.9 to 1.1 molecules of olefin per P onto a water-soluble salt of the hypophosphorous acid or the acid itself,

b) in a process stage 2 adding 0.9 to 1.1 additional molecules of olefin per P onto the intermediate from a) to give dialkylphosphinic acid or salt thereof,

c) in a process stage 3 conducting a crystallization with a metal salt and/or an iron salt and

d) then in a process stage 4 physically mixing the telomers.

17. The process as claimed in one or more of claims 14 to 16, wherein the iron salts are fluorides, chlorides, bromides, iodides, iodate, perchlorate, oxides, hydroxides, peroxides, superoxides, sulfates, hydrogensulfates, sulfate hydrates, sulfites, peroxosulfates, nitrides, phosphides, nitrates, nitrate hydrates, nitrites, phosphates, peroxophosphates, phosphites, hypophosphites, pyrophosphates, carbonates, hydrogencarbonates, hydroxide carbonates, carbonate hydrates, silicates, hexafluorosilicates, hexafluorosilicate hydrates, stannates, borates, polyborates, peroxoborates, thiocyanates, cyanates, cyanides, chromates, chromites, molybdates, permanganates, formates, acetates, acetate hydrates, trifluoroacetate hydrates, propionates, butyrates, valerates, caprylates, oleates, stearates, oxalates, tartrates, citrates, basic citrates, citrate hydrates, benzoates, salicylates, lactates, lactate hydrates, acrylates, maleates, salts of succinic acid, salts of glycine, phenoxides, para-phenolsulfonates, para-phenolsulfonate hydrates, acetylacetonate hydrates, tannates, dimethyldithiocarbamates, trifluoromethanesulfonate, alkylsulfonates and/or aralkylsulfonates.

18. The process as claimed in one or more of claims 14 to 17, wherein the metal of the metal salt comes from the group of Al, Fe and/or Zn.

19. The use of diorganylphosphinic salts as claimed in one or more of claims 1 to 13 intermediate for further syntheses, as a binder, as a crosslinker or accelerator in the curing of epoxy resins, polyurethanes and unsaturated polyester resins, as polymer stabilizers, as crop protection compositions, as sequestrants, as a mineral oil additive, as an anticorrosive, in washing and cleaning composition applications, and in electronics applications.

20. The use of diorganylphosphinic salts as claimed in one or more of claims 1 to 13 as a flame retardant, especially as a flame retardant for clearcoats and intumescent coatings, as a flame retardant for wood and other cellulosic products, as a reactive and/or nonreactive flame retardant for polymers, for production of flame-retardant polymer molding compounds, for production of flame-retardant polymer moldings and/or for rendering polyester and pure and blended cellulose fabrics flame-retardant by impregnation.

21. The use as claimed in claim 20, wherein the diorganylphosphinic salts as claimed in one or more of claims 1 to 12 are used together with synergists, where the synergists are melamine phosphate, dimelamine phosphate, pentamelamine triphosphate, trimelamine diphosphate, tetrakismelamine triphosphate, hexakismelamine pentaphosphate, melamine diphosphate, melamine tetraphosphate, melamine pyrophosphate, melamine polyphosphates, melam polyphosphates, melem polyphosphates and/or melon polyphosphates; or melamine condensation products such as melam, melem and/or melon; or oligomeric esters of tris(hydroxyethyl) isocyanurate with aromatic polycarboxylic acids, benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine, melamine cyanurate, urea cyanurate, dicyandiamide and/or guanidine; or nitrogen-containing phosphates of the formula $(NH_4)_yH_{3-y}PO_4$ or $(NH_4PO_3)_z$ with y = 1 to 3 and z = 1 to 10 000; or aluminum phosphites, aluminum pyrophosphites, aluminum phosphonates, aluminum pyrophosphonates; or silicates, zeolites, silicas, ceramic powder, zinc compounds, e.g. zinc borate, zinc carbonate, zinc stannate, zinc hydroxystannate, zinc phosphate, zinc sulfide, zinc oxide, zinc hydroxide, tin oxide hydrate, basic zinc silicate, zinc molybdate, magnesium hydroxide, hydrotalcite, magnesium carbonate, calcium magnesium carbonate; or salts of ethylphosphonic acid, of propylphosphonic acid, of butylphosphonic acid, of n-butylphosphonic acid, of sec-butylphosphonic acid, of hexylphosphonic acid and/or of octylphosphonic acid.

22. The use as claimed in claim 20 or 21, wherein further additives are used, these being antioxidants, UV stabilizers, gamma ray stabilizers, hydrolysis stabilizers, antistats, emulsifiers, nucleating agents, plasticizers, processing auxiliaries, impact modifiers, dyes, pigments and others.

23. The use as claimed in one or more of claims 20 to 22, wherein 0.0001% to 99.7999% by weight of diorganylphosphinic salts as claimed in one or more of claims 1 to 12, 0.1% to 40% by weight of synergists and 0.1% to 40% by weight of additives are used, where the sum of the components is 100% by weight.

24. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament and/or fiber comprising 0.5% to 45% by weight of diorganylphosphinic salts as claimed in one or more of claims 1 to 13, 0.5% to 95% by weight of thermoplastic or thermoset polymer or mixtures thereof, 0% to 55% by weight of additives and 0% to 55% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.

25. The use as claimed in claim 24, wherein the polymer comprises thermoplastic polymers of the HI (high-impact) polystyrene, polyphenylene ether, polyamide, polyester or polycarbonate type, and blends or polymer blends of the ABS (acrylonitrile-butadiene-styrene) or PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene) or PPE/HIPS (polyphenylene ether/HI polystyrene) polymer type, and/or thermoset polymers of the unsaturated polyester or epoxy resin type.