Claims

1. A flame retardant mixture comprising

a) 0.0001% to 74.8% by weight of component A),

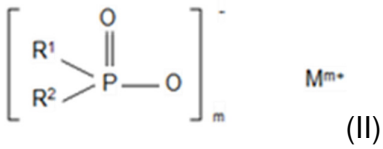
b) 0.0001% to 25% by weight of component B1),

c) 0.1% to 40% by weight of component C) and

d) 0.1% to 40% by weight of component D),

where the sum total of A), B1), C) and D) is 100% by weight, with the proviso that A), B1) and C) are different compounds;

wherein component A) are dialkylphosphinic acid salts conform to the formula (II)



(II)

where

R^1 and R^2 are the same or different and are C_1-C_{18}-alkyl in linear, branched or cyclic form,

m is 1 to 4 and

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

wherein component B1) is selected from the group consisting of: iron(II) dialkylphosphinates, iron(III) dialkylphosphinates, iron(II) monoalkylphosphinates, iron(III) monoalkylphosphinates, iron(II) alkylphosphonates, iron(III) alkylphosphonates, iron(II) phosphite, iron(III) phosphite, iron(II) phosphate and iron(III) phosphate;

wherein component C) is selected from the group consisting of telomers of the formula (III)

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

where in formula (III), independently of one another,

k is 1 to 9, l is 1 to 9,

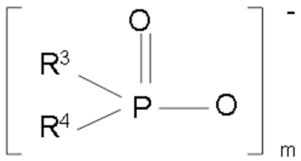
w is 2 to 9, x is 2 to 9,

and

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

and the $(C_wH_{2w})_k$, $(C_xH_{2x})_l$ groups may be linear or branched;

and the telomers are those of the formula (I)



M^{m+} (I)

where

R^3, R^4 are the same or different and are C_6-C_{10}-arylene, C_7-C_{20}-alkylarylene, C_7-C_{20}-arylalkylene and/or C_3-C_{16}-cycloalkyl or -bicycloalkyl,

M is Mg, Ca, Al, Sb, Sn, Ge, Ti, Fe, Zr, Zn, Ce, Bi, Sr, Mn, Li, Na, K and/or a protonated nitrogen base; and

wherein component D) consists of synergists.

2. The flame retardant mixture 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, butyl, 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, and / or cyclohexylethyl.

3. The flame retardant mixture as claimed in claim 1 or 2, wherein component B1) is present in the form of iron(II) bis- and/or iron(III) tris(diethylphosphinate), -(dipropylphosphinate), -(butylethylphosphinate), -(n-butylethylphosphinate), -(sec-butylethylphosphinate), -(hexylethylphosphinate), -(dibutylphosphinate), -(hexylbutylphosphinate), -(octylethylphosphinate), -(ethyl(cyclopentylethyl)phosphinate), -(butyl(cyclopentylethyl)phosphinate), -(ethyl(cyclohexylethyl)phosphinate), -(butyl(cyclohexylethyl)phosphinate), -(ethyl(phenylethyl)phosphinate), -(butyl(phenylethyl)phosphinate), -(ethyl(4-methylphenylethyl)phosphinate), -(butyl(4-methylphenylethyl)phosphinate), -(butylcyclopentylphosphinate), -(butylcyclohexylethylphosphinate), -(butylphenylphosphinate), -(ethyl(4-methylphenyl)phosphinate) and/or -(butyl(4-methylphenyl)phosphinate);
iron(II) mono- and/or iron(III) mono(ethylphosphinate), -(propylphosphinate),

-(butylphosphinate), -(n-butylphosphinate), -(sec-butylphosphinate), -(hexylphosphinate) and/or -(octylphosphinate); or of iron(II) and/or iron(III) ethylphosphonate, propylphosphonate, butylphosphonate, n-butylphosphonate, sec-butylphosphonate, hexylphosphonate, octylphosphonate, iron(II) and/or iron(III) salts of 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, ethylphenylphosphinic acid, butyl(4-methylphenylethyl)phosphinic acid, butylcyclopentylphosphinic acid, butylcyclohexylethylphosphinic acid, butylphenylphosphinic acid, ethyl(4-methylphenyl)phosphinic acid, butyl(4-methylphenyl)phosphinic acid, ethylphosphinylacetic acid and/or ethylphosphinylbutyric acid, of hydroxymethyl(ethyl)ethylphosphinic acid, 1-hydroxy-1-methylpropylethylphosphinic acid, butyl ethylphosphonate, acylethylphosphonic anhydride, butylethylphosphonic acid, butylethylphosphinic acid, ethylphosphinylisobutyronitrile (1-cyano-1-methylethylethylphosphinic acid), propylethylphosphinic acid, t-butyl ethylphosphonate, t-butylethylphosphinic acid, hydroxymethyl(butyl)ethylphosphinic acid, 3-hydroxy-3-methylpentylethylphosphinic acid, propoxyethylethylphosphinic acid, phenylethylethylphosphinic acid, 2-ethylphosphinylethyl laurate, ethylpentylphosphinic acid, t-butoxyethylethylphosphinic acid, ethylphosphinylisohexanonitrile, hexylethylphosphinic acid and/or ethylphosphinylethyl sulfate.

4. The flame retardant mixture as claimed in one or more of claims 1 to 3, wherein, in formula (III), w and x are each 2 or 3 and k and l are each 1 to 3 and M is Al, Ti, Fe or Zn.

5. The flame retardant mixture as claimed in one or more of claims 1 to 4, wherein the telomers are 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, ethylphosphinylisobutyronitrile (1-cyano-1-methylethylethylphosphinic acid), propylethylphosphinic acid, hydroxymethyl(butyl)ethylphosphinic acid, 3-hydroxy-3-methylpentylethylphosphinic acid, propoxyethylethylphosphinic acid, phenylethylethylphosphinic acid, ethylpentylphosphinic acid, t-butoxyethylethylphosphinic acid, ethylphosphinylisohexanonitrile, hexylethylphosphinic acid and/or ethylphosphinylethyl sulfate, where 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.

6. The flame retardant mixture as claimed in one or more of claims 1 to 5, 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 and/or calcium magnesium carbonate.

7. The flame retardant mixture as claimed in one or more of claims 1 to 6, wherein components A) and B1) are in the form of a physical mixture.

8. The flame retardant mixture as claimed in one or more of claims 1 to 6, wherein components A), B1) and C) are in the form of a physical mixture with one another.

9. The flame retardant mixture as claimed in one or more of claims 1 to 6, wherein components A) and C) form a homogeneous mixture with one another and they are in the form of a physical mixture with component B1).

10. The flame retardant mixture as claimed in one or more of claims 1 to 9, which comprises
a particle size of 0.01 to 1000 µm,
a bulk density of 50 to 1500 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,
b color values of -2 to +6.

11. The flame retardant mixture as claimed in one or more of claims 1 to 10, which comprises
a particle size of 0.5 to 800 µm,
a bulk density of 80 to 800 g/L,
a tamped density of 600 g/L to 800 g/L,
an angle of repose of 10 to 40 degrees.

12. A process for producing flame retardant mixtures as claimed in one or more of claims 1 to 11, 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 1 to 9 further olefin molecules onto 0% to 20% of the dialkylphosphinate molecules from process stage 1, so as to form telomers, with conversion of dialkylphosphinic acid, if it is formed, to a corresponding salt,

d) in a process stage 4 conducting a crystallization of the intermediate from b) and/or c) and a metal salt,

e) in a process stage 5 mixing in an iron compound/component B1).

13. A process for producing flame retardant mixtures as claimed in one or more of claims 1 to 11, 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 1 to 9 further olefin molecules onto 0.1% to 20% of the dialkylphosphinate molecules from process stage 1, so as to form telomers, with conversion of dialkylphosphinic acid, if it is formed, to a corresponding salt,

d) in a process stage 4 conducting a coprecipitation of the intermediate from c) and a metal salt, and

e) in a process stage 5 mixing in an iron compound/component B1).

14. A process for producing flame retardant mixtures as claimed in one or more of claims 1 to 11, 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, with conversion of dialkylphosphinic acid, if it is formed, to a corresponding salt,

c) in a process stage 3 conducting a coprecipitation of the intermediate from b) and an iron salt, and

d) in a process stage 4 mixing in the telomers/component C).

15. A process for producing flame retardant mixtures as claimed in one or more of claims 1 to 11, 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, with conversion of dialkylphosphinic acid, if it is formed, to a corresponding salt,

c) in a process stage 3 conducting a crystallization of the intermediate from b) and a metal salt,

e) in a process stage 4 optionally mixing in telomers and

f) in a process stage 5 mixing in an iron compound/component B1).

16. The process as claimed in one or more of claims 12 to 15, wherein the iron compounds and/or iron salts used are those with anions of the seventh main group; with anions of the oxo acids of the seventh main group; with anions of the sixth main group; with anions of the oxo acids of the sixth main group; with anions of the fifth main group; with anions of the oxo acids of the fifth main group; with anions of the oxo acids of the fourth main group; with anions of the oxo acids of the third main group; with anions of the pseudohalides; with anions of the oxo acids of the transition metals; with organic anions from the group of the mono-, di-, oligo- and polycarboxylic acids, of acetic acid, of trifluoroacetic acid, propionates, butyrates, valerates, caprylates, oleates, stearates, of oxalic acid, of tartaric acid, citric acid, benzoic acid, salicylates, lactic acid, acrylic acid, maleic acid, succinic acid, of amino acids, of acidic hydroxo functions, para-phenolsulfonates, para-phenolsulfonate hydrates, acetylacetonate hydrates, tannates, dimethyldithiocarbamates, trifluoromethanesulfonate, alkylsulfonates and/or aralkylsulfonates; as elemental iron; as iron compound in the form of the 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, hydroxidecarbonates, 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, acrylic acid, maleic acid, succinic acid, glycine, phenoxides, para-phenolsulfonates, para-phenolsulfonate hydrates, acetylacetonate hydrates, tannates, dimethyldithiocarbamates, trifluoromethanesulfonate, alkylsulfonates and/or aralkylsulfonates; and/or in the form of alloys of iron with copper, tin, nickel, chromium, molybdenum, tungsten, vanadium.

17. The process as claimed in one or more of claims 12 to 16, wherein the following are added in the process stages: initiators, free-radical initiators, photoinitiators, inhibitors, free-radical control auxiliaries, nucleating agents, cocrystallization auxiliaries, crystallization auxiliaries, strong electrolytes, wetting agents, solvents, acids, alkalis, alkaline compounds, strongly alkaline solutions, flow auxiliaries, bleaches, coupling reagents, adhesion promoters, separating agents, plastics additives, coatings additives, and flame retardants ensheathed by the flame retardant mixture as claimed in at least one of claims 1 to 11.

18. The use of flame retardant mixtures as claimed in one or more of claims 1 to 11 as an 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;
as flame retardants, as flame retardants for clearcoats and intumescent coatings, as flame retardants for wood and other cellulosic products, as 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.

19. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising 0.5% to 50% by weight of flame

retardant mixtures as claimed in one or more of claims 1 to 11, 0.5% to 95% by weight of thermoplastic or thermoset polymer or mixtures thereof, 0% to 55% by weight of additives and 0% to 70% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight;

and where 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 formaldehyde-, epoxide- or melamine-phenolic resin polymer, unsaturated polyester, epoxy resin and/or polyurethane type.

20. The thermoplastic or thermoset polymer molding composition, molding, film, filament or fiber as claimed in claim 19, which comprises further additives, which are antioxidants, UV stabilizers, gamma ray stabilizers, hydrolysis stabilizers, antistats, emulsifiers, nucleating agents, plasticizers, processing auxiliaries, impact modifiers, dyes, pigments and others.