

Mixtures of flame protection means containing flame protection means and aluminium phosphites, method for production and use thereof

- 5 The present invention relates to flame retardant mixtures comprising flame retardant and aluminum phosphites, to processes for preparation thereof and to the use thereof.

The prior art discloses flame retardants which are used alone or together with
10 other components, especially synergists, in a wide variety of different polymers. These synergists, also called flame retardant synergists, need not themselves be flame-retardant, but may significantly enhance the efficacy of flame retardants. Typically, the various components, for example flame retardant, flame retardant synergist, additives and fillers, are mixed by kneading and extrusion with the
15 polymer to be rendered flame-retardant. This is done at temperatures at which the polymer is in molten form and which can distinctly exceed 320°C for a brief period. All components, especially the flame retardants and the flame retardant synergists, must be able to withstand these temperatures without decomposition, in order to maintain their efficacy, i.e. the flame retardancy here, and to obtain a
20 flame-retardant polymer mixture.

It has been found that, surprisingly, the inventive mixtures of flame retardants with aluminum phosphites are much more thermally stable than when flame retardant alone or aluminum phosphites alone are used. A synergistic effect of the mixtures
25 claimed is also found when they display their action as flame retardants.

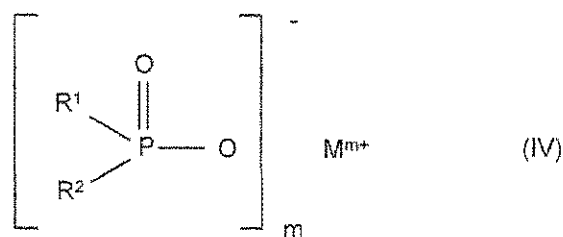
The invention therefore relates to flame retardant mixtures comprising flame retardant and aluminum phosphites.

- 30 The flame retardant preferably comprises dialkylphosphinic acids and/or salts thereof; condensation products of melamine and/or reaction products of melamine with phosphoric acid and/or reaction products of condensation products of

melamine with polyphosphoric acid or mixtures thereof; nitrogen-containing phosphates of the formulae $(\text{NH}_4)_y \text{H}_{3-y} \text{PO}_4$ or $(\text{NH}_4 \text{PO}_3)_z$, where y is 1 to 3 and z is 1 to 10 000; benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine, melamine cyanurate, dicyandiamide and/or guanidine;

- 5 magnesium oxide, calcium oxide, aluminum oxide, zinc oxide, manganese oxide, tin oxide, aluminum hydroxide, boehmite, dihydrotalcite, hydrocalumite, magnesium hydroxide, calcium hydroxide, zinc hydroxide, tin oxide hydrate, manganese hydroxide, zinc borate, basic zinc silicate and/or zinc stannate.

- 10 The dialkylphosphinic acids or salts thereof preferably correspond to the formula (IV)



- 15 in which

R^1, R^2 are the same or different and are each linear or branched $\text{C}_1\text{-C}_6$ -alkyl;

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

m is 1 to 4.

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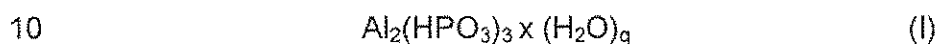
The flame retardant preferably also comprises melam, melem, melon, dimelamine pyrophosphate, melamine polyphosphate, melam polyphosphate, melon polyphosphate and/or melem polyphosphate and/or mixed poly salts thereof and/or ammonium hydrogenphosphate, ammonium dihydrogenphosphate and/or

- 25 ammonium polyphosphate.

The flame retardant preferably also comprises aluminum hypophosphite, zinc hypophosphite, calcium hypophosphite, sodium phosphite, monophenylphosphinic

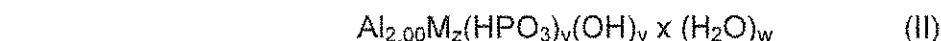
acid and salts thereof, mixtures of dialkylphosphinic acids and salts thereof and monoalkylphosphinic acids and salts thereof, 2-carboxyethylalkylphosphinic acid and salts thereof, 2-carboxyethylmethylphosphinic acid and salts thereof, 2-carboxyethylarylphosphinic acid and salts thereof, 2-carboxyethylphenylphosphinic acid and salts thereof, oxa-10-phosphaphenanthrene (DOPO) and salts thereof and adducts onto para-benzoquinone, or itaconic acid and/or salts thereof.

The aluminum phosphites are preferably those of the formulae (I), (II) and/or (III)



in which

q is 0 to 4,



in which

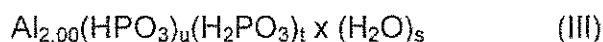
M represents alkali metal ions

z is 0.01 to 1.5

y is 2.63 to 3.5

v is 0 to 2 and w is 0 to 4,

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in which

u is 2 to 2.99,

25 t is 2 to 0.01 and

s is 0 to 4,

and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions, mixtures of aluminum phosphite of the formula (III) with aluminum salts, aluminum phosphite $[\text{Al}(\text{H}_2\text{PO}_3)_3]$, secondary aluminum phosphite $[\text{Al}_2(\text{HPO}_3)_3]$, basic aluminum phosphite $[\text{Al}(\text{OH})(\text{H}_2\text{PO}_3)_2 \cdot 2\text{aq}]$, aluminum phosphite tetrahydrate

$[\text{Al}_2(\text{HPO}_3)_3 \cdot 4\text{aq}]$, aluminum phosphonate, $\text{Al}_7(\text{HPO}_3)_9(\text{OH})_6(1,6\text{-hexanediamine})_{1.5} \cdot 12\text{H}_2\text{O}$, $\text{Al}_2(\text{HPO}_3)^3 \cdot x\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ where $x = 2.27 - 1$ and/or $\text{Al}_4\text{H}_6\text{P}_{16}\text{O}_{18}$.

- 5 Preferably, in the aluminum phosphite of the formula (I),
 q is 0.01 to 0.1.

Preferably, in the aluminum phosphite of the formula (II),

- z is 0.15 to 0.4
 10 y is 2.80 to 3
 v is 0.1 to 0.4 and
 w is 0.01 to 0.1.

Preferably, in the aluminum phosphite of the formula (III),

- 15 u is 2.834 to 2.99
 t is 0.332 to 0.03 and
 s is 0.01 to 0.1.

- The invention also relates to flame retardant mixtures as defined herein,
 20 comprising 0.1 to 99.9% by weight of flame retardant and 0.1 to 99.9% by weight
 of aluminum phosphites of the formulae (I), (II) and/or (III) and/or mixtures of
 aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and
 nitrogen-free extraneous ions and/or mixtures of aluminum phosphite of the
 formula (III) with aluminum salts.

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- The flame retardant mixtures preferably comprise 50 to 99.9% by weight of flame
 retardant and 0.1 to 50% by weight of aluminum phosphites of the formulae (I), (II)
 and/or (III) and/or mixtures of aluminum phosphite of the formula (I) with sparingly
 soluble aluminum salts and nitrogen-free extraneous ions and/or mixtures of
 30 aluminum phosphite of the formula (III) with aluminum salts.

The invention also relates to a process for preparing flame retardant mixtures as defined herein, which comprises mixing pulverulent flame retardants with pulverulent aluminum phosphites of the formulae (I), (II) and/or (III) and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions and/or mixtures of aluminum phosphite of the formula (III) with aluminum salts.

The invention also relates to the use of flame retardant mixtures as defined herein as an intermediate for further syntheses, as a binder, as a crosslinker or accelerator in the curing of epoxy resins, polyurethanes, 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, in electronics applications.

Preference is given to the use of flame retardant mixtures as defined herein in or as a flame retardant, especially in or as a flame retardant for clearcoats and intumescent coatings, in or as a flame retardant for wood and other cellulosic products, in or as a reactive and/or nonreactive flame retardants for polymers, for production of flame-retardant polymer molding compositions, for production of flame-retardant polymer moldings and/or for rendering polyester and pure and blended cellulose fabrics flame-retardant by impregnation, and/or as a synergist and/or as a synergist in further flame retardant mixtures.

The invention also encompasses flame-retardant thermoplastic or thermoset polymer molding compositions or polymer moldings, films, filaments and/or fibers comprising 0.1 to 45% by weight of flame retardant mixtures as defined herein, 55 to 99.9% 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 relates to preferably flame-retardant thermoplastic or thermoset polymer molding compositions or polymer moldings, films, filaments and/or fibers comprising 1 to 30% by weight of flame retardant mixtures as defined herein, 10 to 97% by weight of thermoplastic or thermoset polymer or mixtures thereof, 1 to 30% by weight of additives and 1 to 30% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.

The polymer in the flame-retardant thermoplastic or thermoset polymer molding composition or polymer moldings, films, filaments and/or fibers preferably 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.

The inventive mixtures preferably have a particle size of 0.1 to 1000 μm .

The inventive mixtures preferably have a bulk density of 80 to 800 g/l, more preferably of 200 to 700 g/l.

The inventive mixtures preferably have an L color value of 85 to 99.9, more preferably of 90 to 98.

The inventive mixtures preferably have an a color value of -4 to +9, more preferably of -2 to +6.

The inventive mixtures preferably have a b color value of -2 to +6, more preferably of -1 to +3.

The color values are reported in the Hunter system (CIE-LAB system, Commission Internationale d'Eclairage). L values range from 0 (black) to 100 (white), a values from -a (green) to +a (red), and b values from -b (blue) to +b (yellow).

- 5 Preferred dialkylphosphinic salts are aluminum trisdiethylphosphinate, aluminum trimethylethylphosphinate, titanyl bisdiethylphosphinate, titanium tetrakisdiethylphosphinate, titanyl bismethylethylphosphinate, titanium tetrakisbismethylethylphosphinate, zinc bisdiethylphosphinate, zinc bismethylethylphosphinate and mixtures thereof.

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The inventive mixtures in principle also include mixtures of one or more flame retardants with one or more aluminum phosphites, i.e. three-, four- or multicomponent mixtures are possible.

- 15 Preferred polymer additives for flame-retardant polymer molding compositions and flame-retardant polymer moldings are UV absorbers, light stabilizers, lubricants, colorants, antistats, nucleating agents, fillers, reinforcing agents and/or synergists.

- Preference is given in accordance with the invention to the use of the inventive
20 flame-retardant polymer moldings as lamp components such as lamp fittings and holders, plugs and multisocket extensions, bobbins, housing for capacitors and contactors, and circuit breakers, relay housing and reflectors.

- The invention also relates to intumescent flame-retardant coating comprising 1 to
25 50% of the inventive flame retardant mixtures comprising flame retardant and aluminum phosphites, 0 to 60% ammonium polyphosphate and 0 to 80% by weight of binder, foam former, fillers and/or polymer additives.

- In the mixtures of aluminum phosphite of the formula (I) with sparingly soluble
30 aluminum salts and nitrogen-free extraneous ions, the sparingly soluble aluminum salts are preferably aluminum hydroxide, aluminum hydroxychloride, polyaluminum hydroxyl compounds, aluminum carbonates, hydrotalcites

($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot n\text{H}_2\text{O}$), dihydroxyaluminum sodium carbonate ($\text{NaAl}(\text{OH})_2\text{CO}_3$), aluminum oxides, aluminum oxide hydrate, mixed aluminum oxide hydroxides, basic aluminum sulfate and/or alunite, and the extraneous ions are preferably chlorides, complex chlorides, bromides; hydroxides, peroxides, peroxide hydrates, sulfites, sulfates, sulfate hydrates, acidic sulfates, hydrogensulfates, peroxosulfates, peroxodisulfates; nitrates; carbonates, percarbonates, stannates; borates, perborates, perborate hydrates; formates, acetates, propionates, lactates and/or ascorbates and/or cations of the elements Li, Na, K, Mg, Ca, Ba, Pb, Sn, Cu, Zn, La, Ce, Ti, Zr, V, Cr, Mn, Fe, Co and/or Ni.

The aluminum salts in the mixtures of aluminum phosphite of the formula (III) with aluminum salts are preferably aluminum metal, aluminum alloys, oxides, hydroxides, peroxides, peroxide hydrates, carbonates, percarbonates, mixed carbonates/hydrates, formates, acetates, propionates, stearates, lactates, ascorbates, oxalates, or aluminum salts with anions of acids having a higher vapor pressure than phosphorous acid.

The polymers preferably originate from the group of the thermoplastic polymers such as polyester, polystyrene or polyamide, and/or the thermoset polymers.

The polymers are preferably polymers of mono- and diolefins, for example polypropylene, polyisobutylene, polybutene-1, poly-4-methylpentene-1, polyisoprene or polybutadiene, and addition polymers of cycloolefins, for example of cyclopentene or norbornene; and also polyethylene (which may optionally be crosslinked), e.g. high-density polyethylene (HDPE), high-density high-molar mass polyethylene (HDPE-HMW), high-density ultrahigh-molar mass polyethylene (HDPE-UHMW), medium-density polyethylene (MDPE), low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), branched low-density polyethylene (BLDPE), and mixtures thereof.

The polymers are preferably copolymers of mono- and diolefins with one another or with other vinyl monomers, for example ethylene-propylene copolymers, linear

low-density polyethylene (LLDPE) and mixtures thereof with low-density polyethylene (LDPE), propylene-butene-1 copolymers, propylene-isobutylene copolymers, ethylene-butene-1 copolymers, ethylene-hexene copolymers, ethylene-methylpentene copolymers, ethylene-heptene copolymers, ethylene-octene copolymers, propylene-butadiene copolymers, isobutylene-isoprene copolymers, ethylene-alkyl acrylate copolymers, ethylene-alkyl methacrylate copolymers, ethylene-vinyl acetate copolymers and copolymers thereof with carbon monoxide, or ethylene-acrylic acid copolymers and salts thereof (ionomers), and also terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidenenorbornene; and also mixtures of such copolymers with one another, e.g. polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers, LDPE/ethylene-acrylic acid copolymers, LLDPE/ethylene-vinyl acetate copolymers, LLDPE/ethylene-acrylic acid copolymers and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

The polymers are preferably hydrocarbon resins (e.g. C₅-C₉), including hydrogenated modifications thereof (e.g. tackifier resins) and mixtures of polyalkylenes and starch.

The polymers are preferably polystyrene (Polystyrol® 143E (BASF)), poly(p-methylstyrene), poly(alpha-methylstyrene).

The polymers are preferably copolymers of styrene or alpha-methylstyrene with dienes or acrylic derivatives, for example styrene-butadiene, styrene-acrylonitrile, styrene-alkyl methacrylate, styrene-butadiene-alkyl acrylate and methacrylate, styrene-maleic anhydride, styrene-acrylonitrile-methyl acrylate; more impact-resistant mixtures of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene-propylene-diene terpolymer; and block copolymers of styrene, for example styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene/butylene-styrene or styrene-ethylene/propylene-styrene.

The polymers are preferably graft copolymers of styrene or alpha-methylstyrene, for example styrene onto polybutadiene, styrene onto polybutadiene-styrene or polybutadiene-acrylonitrile copolymers, styrene and acrylonitrile (or methacrylonitrile) onto polybutadiene; styrene, acrylonitrile and methyl

- 5 methacrylate onto polybutadiene; styrene and maleic anhydride onto polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide onto polybutadiene; styrene and maleimide onto polybutadiene, styrene and alkyl acrylates or alkyl methacrylates onto polybutadiene, styrene and acrylonitrile onto ethylene-propylene-diene terpolymers, styrene and acrylonitrile onto polyalkyl
10 acrylates or polyalkyl methacrylates, styrene and acrylonitrile onto acrylate-butadiene copolymers, and mixtures thereof, as known, for example, as ABS, MBS, ASA or AES polymers.

The styrene polymers are preferably comparatively coarse-pore foam such as
15 EPS (expanded polystyrene), e.g. Styropor (BASF) and/or foam with relatively fine pores such as XPS (extruded rigid polystyrene foam), e.g. Styrodur® (BASF). Preference is given to polystyrene foams, for example Austrotherm® XPS, Styrofoam® (Dow Chemical), Floormate®, Jackodur®, Lustron®, Roofmate®, Styropor, Styrodur®, Styrofoam®, Sagex® and Telgopor®.

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The polymers are preferably halogenated polymers, for example polychloroprene, chlorine rubber, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or chlorosulfonated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers,
25 especially polymers of halogenated vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride; and copolymers thereof, such as vinyl chloride-vinylidene chloride, vinyl chloride-vinyl acetate or vinylidene chloride-vinyl acetate.

- 30 The polymers are preferably polymers which derive from alpha,beta-unsaturated acids and derivatives thereof, such as polyacrylates and polymethacrylates, polymethyl methacrylates, polyacrylamides and polyacrylonitriles impact-modified

with butyl acrylate, and copolymers of the monomers mentioned with one another or with other unsaturated monomers, for example acrylonitrile-butadiene copolymers, acrylonitrile-alkyl acrylate copolymers, acrylonitrile-alkoxyalkyl acrylate copolymers, acrylonitrile-vinyl halide copolymers or acrylonitrile-alkyl methacrylate-butadiene terpolymers.

The polymers are preferably polymers which derive from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, such as polyvinyl alcohol, polyvinyl acetate, stearate, benzoate or maleate, polyvinyl butyral, polyallyl phthalate, polyallylimelamine; and copolymers thereof with olefins.

The polymers are preferably homo- and copolymers of cyclic ethers, such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.

The polymers are preferably polyacetals such as polyoxymethylene, and those polyoxymethylenes which contain comonomers, for example ethylene oxide; polyacetals which have been modified with thermoplastic polyurethanes, acrylates or MBS.

The polymers are preferably polyphenylene oxides and sulfides and mixtures thereof with styrene polymers or polyamides.

The polymers are preferably polyurethanes which derive from polyethers, polyesters and polybutadienes having both terminal hydroxyl groups and aliphatic or aromatic polyisocyanates, and the precursors thereof.

The polymers are preferably polyamides and copolyamides which derive from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as nylon 2/12, nylon 4 (poly-4-aminobutyric acid, Nylon[®] 4, from DuPont), nylon 4/6 (poly(tetramethyleneadipamide), Nylon[®] 4/6, from DuPont), nylon 6 (polycaprolactam, poly-6-aminohexanoic acid, Nylon[®] 6,

from DuPont, Akulon K122, from DSM; Zytel® 7301, from DuPont; Durethan® B 29, from Bayer), nylon 6/6 ((poly(N,N'-hexamethylenedipamide), Nylon® 6/6, from DuPont, Zytel® 101, from DuPont; Durethan A30, Durethan® AKV, Durethan® AM, from Bayer; Ultramid® A3, from BASF), nylon 6/9

- 5 (poly(hexamethylenenonanamide), Nylon® 6/9, from DuPont), nylon 6/10 (poly(hexamethylenesebacamide), Nylon® 6/10, from DuPont), nylon 6/12 (poly(hexamethylenedodecanediamide), Nylon® 6/12, from DuPont), nylon 6/66 (poly(hexamethylenedipamide-co-caprolactam), Nylon® 6/66, from DuPont), nylon 7 (poly-7-aminoheptanoic acid, Nylon® 7, from DuPont), nylon 7,7
- 10 (polyheptamethylenepimelamide, Nylon® 7,7, from DuPont), nylon 8 (poly-8-aminooctanoic acid, Nylon® 8, from DuPont), nylon 8,8 (polyoctamethylenesuberamide, Nylon® 8,8, from DuPont), nylon 9 (poly-9-aminononanoic acid, Nylon® 9, from DuPont), nylon 9,9 (polynonamethyleneazelaamide, Nylon® 9,9, from DuPont), nylon 10 (poly-10-aminodecanoic acid, Nylon® 10, from DuPont), nylon 10,9 (poly(decamethyleneazelaamide), Nylon® 10,9, from DuPont), nylon 10,10 (polydecamethylenesebacamide, Nylon® 10,10, from DuPont), nylon 11 (poly-11-aminoundecanoic acid, Nylon® 11, from DuPont), nylon 12 (polylauryllactam, Nylon® 12, from DuPont, Grilamid® L20, from Ems Chemie), aromatic polyamides
- 20 proceeding from m-xylene, diamine and adipic acid; polyamides prepared from hexamethylenediamine and iso- and/or terephthalic acid (polyhexamethyleneisophthalamide, polyhexamethyleneterephthalamide) and optionally an elastomer as a modifier, e.g. poly-2,4,4-trimethylhexamethyleneterephthalamide or poly-m-phenyleneisophthalamide.
- 25 Block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol. In addition, EPDM- or ABS-modified polyamides or copolyamides; and polyamides condensed during processing ("RIM polyamide
- 30 systems").

The polymers are preferably polyureas, polyimides, polyamidimides, polyetherimides, polyesterimides, polyhydantoins and polybenzimidazoles.

5 The polymers are preferably polyesters which derive from dicarboxylic acids and dialcohols and/or from hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate (Celanex[®] 2500, Celanex[®] 2002, from Celanese; Ultradur[®], from BASF), poly-1,4-dimethylolcyclohexane terephthalate, polyhydroxybenzoates, and block polyether esters which derive from polyethers with hydroxyl end groups; and also polyesters
10 modified with polycarbonates or MBS.

The polymers are preferably polycarbonates and polyester carbonates.

15 The polymers are preferably polysulfones, polyether sulfones and polyether ketones.

Preferably, the polymers are crosslinked polymers which derive from aldehydes on the one hand, and phenols, urea or melamine on the other hand, such as phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins.

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The polymers are preferably drying and nondrying alkyd resins.

The polymers are preferably unsaturated polyester resins which derive from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric
25 alcohols, and vinyl compounds as crosslinking agents, and also the halogenated, flame-retardant modifications thereof.

The polymers preferably comprise crosslinkable acrylic resins which derive from substituted acrylic esters, for example from epoxy acrylates, urethane acrylates or
30 polyester acrylates.

Preferably, the polymers are alkyd resins, polyester resins and acrylate resins which have been crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins.

- 5 The polymers are preferably crosslinked epoxy resins which derive from aliphatic, cycloaliphatic, heterocyclic or aromatic glycidyl compounds, for example products of bisphenol A diglycidyl ethers, bisphenol F diglycidyl ethers, which are crosslinked by means of customary hardeners, for example anhydrides or amines, with or without accelerators.

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- The polymers are preferably mixtures (polyblends) of the abovementioned polymers, for example PP/EPDM (polypropylene/ethylene-propylene-diene rubber), polyamide/EPDM or ABS (polyamide/ethylene-propylene-diene rubber or acrylonitrile-butadiene-styrene), PVC/EVA (polyvinyl chloride/ethylene-vinyl acetate), PVC/ABS (polyvinyl chloride/acrylonitrile-butadiene-styrene), PVC/MBS (polyvinyl chloride/methacrylate-butadiene-styrene), PC/ABS (polycarbonate/acrylonitrile-butadiene-styrene), PBTP/ABS (polybutylene terephthalate/acrylonitrile-butadiene-styrene), PC/ASA (polycarbonate/acrylic ester-styrene-acrylonitrile), PC/PBT (polycarbonate/polybutylene terephthalate), 15 PVC/CPE (polyvinyl chloride/chlorinated polyethylene), PVC/acrylate (polyvinyl chloride/acrylate, POM/thermoplastic PUR (polyoxymethylene/thermoplastic polyurethane), PC/thermoplastic PUR (polycarbonate/thermoplastic polyurethane), 20 POM/acrylate (polyoxymethylene/acrylate), POM/MBS (polyoxymethylene/methacrylate-butadiene-styrene), PPO/HIPS (polyphenylene oxide/high-impact polystyrene), PPO/PA 6,6 (polyphenylene oxide/nylon 6,6) and 25 copolymers, PA/HDPE (polyamide/high-density polyethylene), PA/PP (polyamide/polyethylene), PA/PPO (polyamide/polyphenylene oxide), PBT/PC/ABS (polybutylene terephthalate/polycarbonate/acrylonitrile-butadiene-styrene) and/or PBT/PET/PC (polybutylene terephthalate/polyethylene 30 terephthalate/polycarbonate).

Suitable compounding units for production of polymer molding compositions are single-shaft extruders or single-screw extruders, for example from Berstorff GmbH, Hanover and/or from Leistritz, Nuremberg.

- 5 Suitable compounding units are multizone screw extruders with three-zone screws and/or short compression screws.

Suitable compounding units are also co-kneaders, for example from Coperion Buss Compounding Systems, Pratteln, Switzerland, e.g. MDK/E46-11D and/or
10 laboratory kneaders (MDK 46 from Buss, Switzerland with L=11D).

Suitable compounding units are twin-screw extruders, for example from Coperion Werner & Pfleiderer GmbH & Co. KG, Stuttgart (ZSK 25, ZSK 30, ZSK 40, ZSK 58, ZSK MEGAcoupler 40, 50, 58, 70, 92, 119, 177, 250, 320, 350, 380)
15 and/or from Berstorff GmbH, Hanover, Leistritz Extrusionstechnik GmbH, Nuremberg.

Usable compounding units are also ring extruders, for example from 3+Extruder GmbH, Laufen, with a ring of three to twelve small screws which rotate about a
20 static core, and/or planetary gear extruders, for example from Entex, Bochum, and/or vented extruders and/or cascade extruders and/or Maillefer screws.

Suitable compounding units are compounders with a contrarotatory twin screw, for example Compex 37 and 70 models from Krauss-Maffei Berstorff.

25 Effective screw lengths (L) in the case of single-shaft extruders or single-screw extruders are 20 to 40D, and in the case of multizone screw extruders, for example, 25D with intake zone (L=10D), transition zone (L=6D), ejection zone (L=9D); in the case of twin-screw extruders 8 to 48D.

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Production, processing and testing of flame-retardant polymer molding compositions and polymer moldings

The flame-retardant components were mixed with the polymer pellets and any additives and incorporated in a twin-screw extruder (model: Leistritz LSM 30/34) at temperatures of 230 to 260°C (PBT-GR) or of 260 to 280°C (PA 66-GR). The homogenized polymer strand was drawn off, cooled in a water bath and then pelletized.

After sufficient drying, the molding compositions were processed on an injection molding machine (model: Aarburg Allrounder) at melt temperatures of 240 to 270°C (PBT-GR) or of 260 to 290°C (PA 66-GR) to give test specimens.

Test specimens of each mixture were used to determine the UL 94 fire class (Underwriter Laboratories) on specimens of thickness 1.5 mm.

The UL 94 fire classifications are as follows:

V-0: afterflame time never longer than 10 sec, total of afterflame times for 10 flame applications not more than 50 sec, no flaming drops, no complete consumption of the specimen, afterglow time for specimens never longer than 30 sec after end of flame application

V-1: afterflame time never longer than 30 sec after end of flame application, total of afterflame times for 10 flame applications not more than 250 sec, afterglow time for specimens never longer than 60 sec after end of flame application, other criteria as for V-0

V-2: cotton indicator ignited by flaming drops, other criteria as for V-1

Not classifiable (ncf): does not comply with fire class V-2.

Test of thermal stability and phosphine formation

An important criterion for the thermal stability of the inventive flame retardant mixtures comprising flame retardant and aluminum phosphites is the temperature at which decomposition occurs and toxic PH_3 is formed. The release thereof in the course of production of flame-retardant polymers must be avoided. For the determination, a material sample is heated in a tubular oven under flowing nitrogen (30 l/g), by raising the temperature stepwise. The decomposition

temperature has been attained when a Dräger detection tube can detect more than 1 ppm PH_3 (short-term tube for hydrogen phosphide).

Determination of the content of water of crystallization (residual moisture content)

- 5 A sample is heated to constant weight in a Nabertherm muffle furnace heated to 300°C . This typically takes 15 minutes. The mass of the residue based on the starting weight, calculated in percent and subtracted from 100, gives the weight loss.

- 10 The invention is illustrated by the examples which follow.

Example 1 aluminum phosphite of the formula (I)

- 573 g of aluminum hydroxide, 1284 g of 70% by weight phosphorous acid, 307 g of 25% by weight sulfuric acid and 9400 g of demineralized water are initially
15 charged in a 16 l high-pressure stirred vessel, heated to 150°C and stirred for 2.5 h. The resulting suspension is discharged, filtered at 80°C and washed repeatedly with demineralized water, then dried at 220°C . In a very high yield (99%), aluminum phosphite of the formula (I) is obtained with very high thermal stability (PH_3 formation from 360°C).

20

Example 2 aluminum phosphite of the formula (I)

- As in example 1, 593 g of aluminum hydroxide, 1330 g of 70% by weight phosphorous acid, 318 g of 25% by weight sulfuric acid and 9 liters of demineralized water are initially charged, heated to 145°C and stirred for 3 h, then
25 605 g of 25% by weight sodium hydroxide solution are added and the mixture is stirred for 1.5 h. As in example 1, the suspension is discharged, filtered, washed and dried. In a very high yield (99%), aluminum phosphite of the formula (I) is obtained with very high thermal stability (PH_3 formation from 380°C).

- 30 Example 3 aluminum phosphite of the formula (II)

2958 g of water are initially charged in a 16 l high-pressure stirred vessel, heated to 155°C and stirred. Over the course of 3 h, 3362 g of aluminum sulfate solution

and 2780 g of sodium phosphite solution are metered in simultaneously. The suspension is discharged and filtered at 80°C, washed with hot water, redispersed and washed once again. The filtercake is dried in a Reaktotherm drier at 220°C. In a very high yield, an inventive mixed alkali metal/aluminum phosphite is obtained
 5 with very high thermal stability (PH_3 formation from 380°C).

Example 4 aluminum phosphite of the formula (II)

Analogously to example 3, water is initially charged at 155°C and aluminum sulfate solution and sodium phosphite solution are metered in within 0.5 h. The yield is
 10 85% and the thermal stability (PH_3 formation from 360°C) of the product is very high.

Example 5 aluminum phosphite of the formula (III)

1644 g of aluminum hydroxide (Hydral® 710; ALCOA; 99.6%) are initially charged
 15 in a kneader. While mixing, 2635 g of phosphorous acid (98%) are added in portions. A reaction occurs spontaneously with evolution of heat. The mixture is left to react at 145°C for a further 5 h. This gives, in 99.5% yield, aluminum hydrogenphosphite of the composition $\text{Al}_2(\text{HPO}_3)_{2.89}(\text{H}_2\text{PO}_3)_{0.22}$. The thermal stability is very high (PH_3 formation from 360°C).

20

Example 6 aluminum phosphite of the formula (III)

As in example 5, 1537 g of aluminum hydroxide and 2463 g of phosphorous acid are reacted. The product contains aluminum hydrogenphosphite of the composition $\text{Al}_2(\text{HPO}_3)_2(\text{H}_2\text{PO}_3)_2$, and 0.45% phosphorous acid. The yield is
 25 90.5%. The thermal stability is very high (PH_3 formation from 360°C).

Example 7 mixture of aluminum phosphite of the formula (III) with aluminum salt

1600 g of aluminum hydroxide (Hydral® 710; ALCOA; 99.6%) are initially charged in a kneader. While mixing, 2570 g of phosphorous acid (98%) are added in
 30 portions. A reaction occurs spontaneously with evolution of heat. The mixture is left to react at 148°C for a further 160 minutes. The product contains 98.1% by weight of aluminum phosphite of the composition $\text{Al}_2(\text{HPO}_3)_{2.89}(\text{H}_2\text{PO}_3)_{0.22}$, 1.5%

by weight of aluminum hydroxide and 0.25% by weight of unconverted phosphorous acid.

Example 8 mixture of aluminum phosphite of the formula (III) with aluminum salt

- 5 As in example 7, 1600 g of aluminum hydroxide and 2570 g of phosphorous acid are reacted. The product contains 90.8% by weight of aluminum phosphite of the composition $\text{Al}_2(\text{HPO}_3)_2 (\text{H}_2\text{PO}_3)_2$, 8.7% by weight of aluminum hydroxide and 0.4% by weight of phosphorous acid.

- 10 Example 9 mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions

- 606 g of aluminum hydroxide, 1360 g of 70% by weight phosphorous acid, 325 g of 25% by weight sulfuric acid and 10 liters of demineralized water are initially charged in a 16 l high-pressure stirred vessel from Pfaudler, heated to 155°C and
15 stirred for 170 minutes. The resulting suspension is discharged, filtered at 80°C by means of a Seitz pressure filter and repeatedly washed with demineralized water and redispersed, then dried at 150°C. In a very high yield (99%), an inventive mixture of aluminum phosphite of the formula (II) with sparingly soluble aluminum salts (1.3% by weight of aluminum hydroxide) and nitrogen-free extraneous ions
20 (0.1% by weight of sulfate) is obtained with very high thermal stability (PH_3 formation from 360°C).

Example 10 mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions

- 25 As in example 9, 634 g of aluminum hydroxide, 1420 g of 70% by weight phosphorous acid, 340 g of 25% by weight sulfuric acid and 10 liters of demineralized water are initially charged, heated to 125°C and stirred for 3 h, then 646 g of 25% by weight sodium hydroxide solution are added and the mixture is stirred for 80 minutes. As in example 9, the suspension is discharged, filtered,
30 washed and dried. In a very high yield (98.9%), an inventive mixture of aluminum phosphite of the formula (III) with sparingly soluble aluminum salts (3% by weight of aluminum hydroxide) and nitrogen-free extraneous ions (0.3% by weight of

sodium, 0.1% by weight of sulfate) is obtained with very high thermal stability (PH_3 formation from 380°C).

Example 11 (comparative)

- 5 Noninventive, commercially available aluminum phosphite shows a lower thermal stability in comparison (PH_3 formation from 320°C).

Example 12 aluminum phosphite of the formula (I) in polyamide

- 10 52% by weight of nylon 6,6 polymer, 28% by weight of glass fibers, 3.9% by weight of aluminum phosphite according to example 1 and 16.1% by weight of Exolit® OP1230 aluminum diethylphosphinate (from Clariant) are used in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

15

Example 13 aluminum phosphite of the formula (I) in polyester

- 52% by weight of polybutylene terephthalate polymer, 28% by weight of glass fibers, 3.9% by weight of aluminum phosphite according to example 1 and 16.1% by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) are used
20 in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 14 aluminum phosphite of the formula (II) in polyamide

- 25 52% by weight of nylon 6,6 polymer, 28% by weight of glass fibers, 3.9% by weight of aluminum phosphite according to example 3 and 16.1% by weight of Exolit® OP1230 aluminum diethylphosphinate (from Clariant) are used in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form
30 of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 15 aluminum phosphite of the formula (II) in polyester
52% by weight of polybutylene terephthalate polymer, 28% by weight of glass
fibers, 3.9% by weight of aluminum phosphite according to example 3 and 16.1%
by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) are used
5 in accordance with the general methods specified to produce flame-retardant
polymer molding compositions and flame-retardant polymer moldings in the form
of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 16 aluminum phosphite of the formula (III) in polyamide
10 52% by weight of nylon 6,6 polymer, 28% by weight of glass fibers, 3.9% by
weight of aluminum phosphite according to example 5 and 16.1% by weight of
Exolit® OP1230 aluminum diethylphosphinate (from Clariant) are used in
accordance with the general methods specified to produce flame-retardant
polymer molding compositions and flame-retardant polymer moldings in the form
15 of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 17 aluminum phosphite of the formula (II) in polyester
52% by weight of polybutylene terephthalate polymer, 28% by weight of glass
fibers, 3.9% by weight of aluminum phosphite according to example 5 and 16.1%
20 by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) are used
in accordance with the general methods specified to produce flame-retardant
polymer molding compositions and flame-retardant polymer moldings in the form
of UL-94 test specimens. The UL-94 test gives V-0 classification.

25 Example 18 mixture of aluminum salt and aluminum hydrogenphosphite of the
formula (III) in polyamide
52% by weight of nylon 6,6 polymer, 28% by weight of glass fibers, 3.9% by
weight of a mixture of aluminum salt and aluminum hydrogenphosphite of the
formula (III) according to example 7 and 16.1% by weight of Exolit® OP1230
30 aluminum diethylphosphinate (from Clariant) are used in accordance with the
general methods specified to produce flame-retardant polymer molding

compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 19 mixture of aluminum salt and aluminum hydrogenphosphite of the formula (III) in polyester

52% by weight of polybutylene terephthalate polymer, 28% by weight of glass fibers, 3.9% by weight of a mixture of aluminum salt and aluminum phosphite of the formula (III) according to example 7 and 16.1% by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) are used in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 20

52% by weight of nylon 6,6 polymer, 28% by weight of glass fibers, 3.9% by weight of inventive mixture of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions according to example 9 and 16.1% by weight of Exolit® OP1230 aluminum diethylphosphinate (from Clariant) are used in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 21

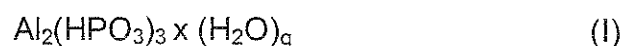
52% by weight of polybutylene terephthalate polymer, 28% by weight of glass fibers, 3.9% by weight of inventive mixture of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions according to example 10 and 16.1% by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) are used in accordance with the general methods specified to produce flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens. The UL-94 test gives V-0 classification.

Example 22 (comparative)

52% by weight of polybutylene terephthalate polymer, 28% by weight of glass fibers, 3.9% by weight of aluminum phosphite from example 11 and 16.1% by weight of Exolit® OP1240 aluminum diethylphosphinate (from Clariant) cannot be processed to give flame-retardant polymer molding compositions and flame-retardant polymer moldings in the form of UL-94 test specimens, due to the formation of toxic phosphine.

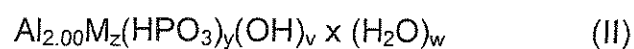
Claims

1. A flame retardant mixture comprising flame retardant and aluminum phosphites, wherein the aluminum phosphites comprise those of the formulae (I), (II) and/or (III):



in which

q is 0 to 4,



in which

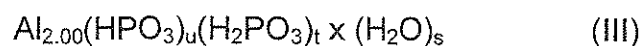
M represents alkali metal ions

z is 0.01 to 1.5

y is 2.63 to 3.5

v is 0 to 2 and

w is 0 to 4,



in which

u is 2 to 2.99,

t is 2 to 0.01 and

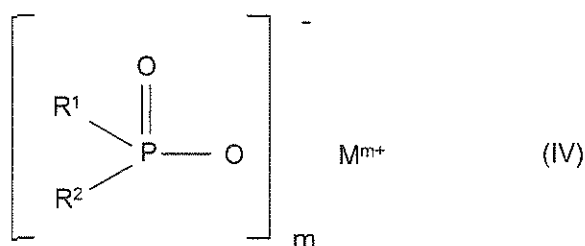
s is 0 to 4,

and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions, mixtures of aluminum phosphite of the formula (III) with aluminum salts, aluminum phosphite $[\text{Al}(\text{H}_2\text{PO}_3)_3]$, secondary aluminum phosphite $[\text{Al}_2(\text{HPO}_3)_3]$, basic aluminum phosphite $[\text{Al}(\text{OH})(\text{H}_2\text{PO}_3)_2 \cdot 2\text{aq}]$, aluminum phosphite tetrahydrate $[\text{Al}_2(\text{HPO}_3)_3 \cdot 4\text{aq}]$, aluminum phosphonate,

$\text{Al}_7(\text{HPO}_3)_9(\text{OH})_6(1,6\text{-hexanediamine})_{1.5} \cdot 12\text{H}_2\text{O}$, $\text{Al}_2(\text{HPO}_3)^3 \cdot x\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ where $x = 2.27 - 1$ and/or $\text{Al}_4\text{H}_6\text{P}_{16}\text{O}_{18}$.

2. The flame retardant mixture as claimed in claim 1, wherein the flame retardant comprises dialkylphosphinic acids and/or salts thereof; condensation products of melamine and/or reaction products of melamine with phosphoric acid and/or reaction products of condensation products of melamine with polyphosphoric acid or mixtures thereof; nitrogen-containing phosphates of the formulae $(\text{NH}_4)_y \text{H}_{3-y} \text{PO}_4$ and $(\text{NH}_4)_z \text{PO}_3$, where y is 1 to 3 and z is 1 to 10 000; benzoguanamine, tris(hydroxyethyl) isocyanurate, allantoin, glycoluril, melamine, melamine cyanurate, dicyandiamide and/or guanidine; magnesium oxide, calcium oxide, aluminum oxide, zinc oxide, manganese oxide, tin oxide, aluminum hydroxide, boehmite, dihydrotalcite, hydrocalumite, magnesium hydroxide, calcium hydroxide, zinc hydroxide, tin oxide hydrate, manganese hydroxide, zinc borate, basic zinc silicate and/or zinc stannate.

3. The flame retardant mixture as claimed in claim 1 or 2, wherein the dialkylphosphinic acids or salts thereof correspond to the formula (IV)



in which

R^1, R^2 are the same or different and are each linear or branched $\text{C}_1\text{-C}_6$ -alkyl;

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

m is 1 to 4.

4. The flame retardant mixture as claimed in one or more of claims 1 to 3, wherein the flame retardant comprises melam, melem, melon, dimelamine pyrophosphate, melamine polyphosphate, melam polyphosphate, melon

polyphosphate and/or melem polyphosphate and/or mixed poly salts thereof and/or ammonium hydrogenphosphate, ammonium dihydrogenphosphate and/or ammonium polyphosphate.

5. The flame retardant mixture as claimed in one or more of claims 1 to 3, wherein the flame retardant comprises aluminum hypophosphite, zinc hypophosphite, calcium hypophosphite, sodium phosphite, monophenylphosphinic acid and salts thereof, mixtures of dialkylphosphinic acids and salts thereof and monoalkylphosphinic acids and salts thereof, 2-carboxyethylalkylphosphinic acid and salts thereof, 2-carboxyethylmethylphosphinic acid and salts thereof, 2-carboxyethylarylphosphinic acid and salts thereof, 2-carboxyethylphenylphosphinic acid and salts thereof, oxa-10-phosphaphenanthrene (DOPO) and salts thereof and adducts onto para-benzoquinone, or itaconic acid and/or salts thereof.

6. The flame retardant mixture as claimed in one or more of claims 1 to 5, wherein q in the aluminum phosphite of the formula (I) is 0.01 to 0.1.

7. The flame retardant mixture as claimed in one or more of claims 1 to 5, wherein z in the aluminum phosphite of the formula (II) is 0.15 to 0.4, y is 2.80 to 3, v is 0.1 to 0.4 and w is 0.01 to 0.1.

8. The flame retardant mixture as claimed in one or more of claims 1 to 5, wherein u in the aluminum phosphite of the formula (III) is 2.834 to 2.99, t is 0.332 to 0.03 and s is 0.01 to 0.1.

9. The flame retardant mixture as claimed in one or more of claims 1 to 8, comprising 0.1 to 99.9% by weight of flame retardant and 0.1 to 99.9% by weight of aluminum phosphites of the formulae (I), (II) and/or (III) and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions and/or mixtures of aluminum phosphite of the formula (III) with aluminum salts.

10. The flame retardant mixture as claimed in one or more of claims 1 to 9, comprising 50 to 99.9% by weight of flame retardant and 0.1 to 50% by weight of aluminum phosphites of the formulae (I), (II) and/or (III) and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions and/or mixtures of aluminum phosphite of the formula (III) with aluminum salts.
11. A process for preparing flame retardant mixtures as claimed in one or more of claims 1 to 10, which comprises mixing pulverulent flame retardants with pulverulent aluminum phosphites of the formulae (I), (II) and/or (III) and/or mixtures of aluminum phosphite of the formula (I) with sparingly soluble aluminum salts and nitrogen-free extraneous ions and/or mixtures of aluminum phosphite of the formula (III) with aluminum salts.
12. The use of flame retardant mixtures as claimed in one or more of claims 1 to 10 as an intermediate for further syntheses, as a binder, as a crosslinker or accelerator in the curing of epoxy resins, polyurethanes, 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, in electronics applications.
13. The use of flame retardant mixtures as claimed in one or more of claims 1 to 10 in or as a flame retardant, especially in or as a flame retardant for clearcoats and intumescent coatings, in or as a flame retardant for wood and other cellulosic products, in or as a reactive and/or nonreactive flame retardants for polymers, for production of flame-retardant polymer molding compositions, for production of flame-retardant polymer moldings and/or for rendering polyester and pure and blended cellulose fabrics flame-retardant by impregnation, and/or as a synergist and/or as a synergist in further flame retardant mixtures.
14. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising 0.1 to 45% by weight of flame retardant mixtures as claimed in one or more of claims 1 to 10, 55 to 99.9% 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.

15. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising 1 to 30% by weight of flame retardant mixtures as claimed in one or more of claims 1 to 10, 10 to 97% by weight of thermoplastic or thermoset polymer or mixtures thereof, 1 to 30% by weight of additives and 1 to 30% by weight of filler or reinforcing materials, where the sum of the components is 100% by weight.

16. A flame-retardant thermoplastic or thermoset polymer molding composition or polymer molding, film, filament or fiber comprising flame retardant mixtures as claimed in one or more of claims 1 to 10, 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.