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(54) Benævnelse: **Sammensætninger af flammebeskyttelsesmidler indeholdende triazin-interkalerede metalfosfater**

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WO-A2-02/48248
DE-A1-102007 036 465
HIROKAZU NAKAYAMA: "INTERCALATION OF ORGANIC MOLELECULES INTO LAYERED PHOSPHATES", PHOSPHORUS RESEARCH BULLETIN, Bd. 23, 1. Januar 2009 (2009-01-01), Seiten 1-9, XP55017083, ISSN: 0918-4783, DOI: 10.3363/prb.23.1
JENNY ALONGI ET AL: "Flame retardancy properties of [alpha]-zirconium phosphate based composites", POLYMER DEGRADATION AND STABILITY, Bd. 95, Nr. 9, 27. April 2010 (2010-04-27) , Seiten 1928-1933, XP55017029, ISSN: 0141-3910, DOI: 10.1016/j.polymdegradstab.2010.04.007
"Melamine derivatives", SpecialChem S.A. , 28. Juni 2009 (2009-06-28), XP002667710, Gefunden im Internet: URL:http://web.archive.org/web/20090628141703/http://www.specialchem4polymers.com/tc/Melamine-Flame-Retardants/index.aspx?id=4004 [gefunden am 2012-01-20]

Flame retardant compositions containing triazine-intercalated metal phosphates

The present invention relates to flame retardant compositions containing triazine-intercalated metal phosphates with open framework structures (Open Framework), to the use thereof, to such metal phosphates as well as to the production thereof.

Using organophilic phyllosilicates, which, for example, were produced by means of ion exchange, as filling materials for thermoplastic substances and for thermosets is known, wherein nanocomposites are obtained. When using suitable organophilic phyllosilicates as filling materials, the physical and mechanical properties of the thus produced moulded articles are significantly improved. Increasing the stiffness with at least equal toughness is of particular interest. Particularly good properties show nanocomposites, which contain the phyllosilicate in an exfoliated form. These nanocomposites are preferably used as flame retardants or as synergists.

Organophilic phyllosilicates are known from WO-A 00/44669, which are produced by treating a natural or synthetic phyllosilicate or a mixture of such silicates, with a salt of an - optionally quaternary - cyclic melamine compound or a mixture of such salts.

Similar considerations should also apply to organophilic metal phosphate with open framework structures (see definition in "A Review of Open Framework Structures", *Annu. Rev. Mater. Sci.* **1996,** 26, 135-151), in particular for those which are intercalated with melamine (intercalate also known as interstitial compound, see definition in RÖMPP, Chemielexikon, 9th edition, **1995**, G. Thieme, Vol. 3, p. 2005).

In the literature, diverse melamine phosphates are described which do not have open framework structures. For instance, melamine orthophosphate in *Magn. Reson. Chem.* **2007,** 45, p. 231- p. 246., bismelamine di(pyro)phosphate in J. *Phys. Chem.* B **2004,** 108, 15069-15076 and melamine polyphosphate in J. *Phys. Chem.* B **2005,** 109, 13529-13537. The use thereof as flame retardants is specified therein in the cited secondary literature.

Certain melamine metal phosphates are described in WO-A 2009/015772. However, these compounds possess, as shown by the aluminium compound, only a limited (thermal) inherent stability which is insufficient for incorporation into polyamides (see Examples 7 and 8).

Melamine-intercalated (layered) zirconium phosphates are known from *Solid State Sciences* **2009,** 11, 1007-1015. However, the use as plastic additives, in particular as flame retardants, is not described herein. Other melamine-intercalated layered (metal) phosphates are not documented in the literature.

An intercalation of α, ω-alkanediamines into (layered) aluminum triphosphate is published in J. *Inclusion Phenomena and Macrocyclic Chem.* **1999,** 34 401-412.

The layer structure of aluminum triphosphate is documented in Chem. Commun. **2006,** 747-749. An open network structure is known for ethylenediamine-zinc phosphate adducts from *Zeolites and Related Microporous Materials* **1994,** 2229-2236.

Ethylenediaminebis(zinc phosphate) is claimed in US5994435 and US6207735 as a flame retardant. Amine-zinc phosphates are described in JP8269230, which also comprise the anions HPO_4, H_2PO_4, $Zn_2(HPO_4)_3$ und $Zn_4[(PO_4)_2 (HPO_4)_2]$. The applications JP9040686, JP10259275, JP11152373, JP11199708, JP11246754, JP11269187, JP11293155, JP2000063562, JP2000063563, JP2000154283, JP2000154287, JP2000154324 and JP2001031408 describe methods for producing specific application forms and combinations of ethylenediamine-zinc phosphate. However, the methods are uneconomical, since they either work with H_3PO_4 excess or proceed from $Zn(en)_3$ complexes. JP9169784 and JP2001011462 publish diethylenetriamine or piperazine-zinc phosphate complexes as flame retardants.

Inorganic phosphates with open framework structures are described in an article in *Angew. Chem.* **1999,** 111, 3466-3492.

Disadvantages of said compounds from the prior art are the limited intrinsic (thermal) stability and the adverse mechanical properties which result after incorporation into the polymer substrate.

The object is to provide flame retardant compositions which have a high degree of intrinsic (thermal) stability and provide the polymers with excellent mechanical properties after incorporation.

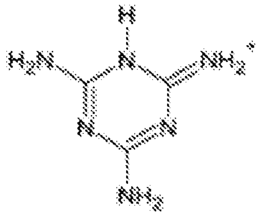
The object was achieved, inter alia, by providing flame retardant compositions containing

(a) at least one triazine-intercalated metal phosphate with at least one monomer unit of the subsequent general formula (I)

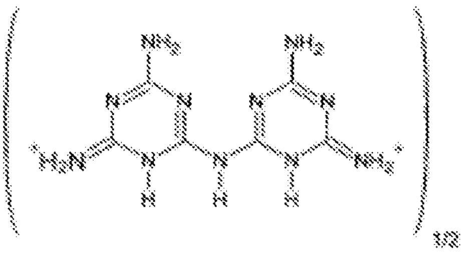
$$(A - H)_a^{(+)} [M_b^{m+} (H_2PO_4)_{x1}^{(-)} (HPO_4)_{x2}^{2(-)} (PO_4)_{x3}^{3(-)} (PO_3)_y^{(-)}]^{(a-)} * pH_2O \quad (I)$$

wherein

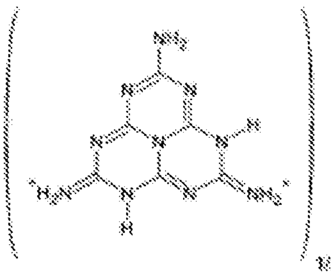
$(A - H)^{(+)}$ is a triazine derivative of the formulae (II-1), (II-2) or (II-3)



Melamine (II-1)



Melame (II-2)



Meleme (II-3)

each **M** = Al;

a is 2,

b is 1,

m = 3,

and

$x_1 = 0$ or 1; $x_2 = 0$ or 2; $x_3 = 1$ or 0; $y = 2$ or 0 and $p = 0$ to 5,

wherein: $a+mb=x_1+2x_2+3x_3+y$

and

(b) at least one further flame retardant component different from (a).

In a preferred embodiment of the invention, the flame retardant compositions containing the triazine-intercalated metal phosphates (a) of the formula (I) have open framework structures. The triazine derivatives, and likewise melon, are known as chemical precursors for carbon nitride $(C_3N_4)_x$.

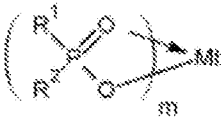
Triazine-intercalated metal phosphates, in particular with open framework structures, which are preferably produced by direct reaction of (aqueous) acidic metal phosphates with melamine and subsequent tempering from the corresponding (precursor) steps, show high thermal stability when processing combined with excellent dispersing action and interfacial adhesion. These systems feature surprisingly good layer separation, combined with excellent adhesion to a plurality of polymers and fillers. Moreover, it is surprising that the inventive triazine-intercalated metal phosphates with open framework structures are not only excellent fillers for improving the mechanical properties of polymers, but also act as flame retardants.

The triazine-intercalated (metal) phosphates with open framework structures can also consist of chain (ribbon) phosphates (catena type), sheet phosphates (ladder or phyllo type - all with 1-D structures), layered phosphates (with 2-D structures) or 3-D phosphates (zeolite type).

In a particularly preferable embodiment of the present invention, the flame retardant compositions contain the components (a), $(A\text{-}H)^{(+)}$= (II-1) and M= Al.

Component (b) is preferably at least one metal compound which is not a metal phosphate of component (a), or/and at least one metal-free phosphorus compound.

This at least one metal compound (b) is preferably a metal oxide, a metal hydroxide, a metal phosphate, a metal pyrophosphate, a hydrotalcite, a cationically or anionically modified organoclay, a stannate or molybdate salt, a metal borate or metal phosphinate of the formula (III):



(III)

wherein R^1 and R^2 are hydrogen or a straight-chain or a branched C_1 - C_6 alkyl radical or a phenyl radical; and Mt = Ca, Mg, Zn or Al and m = 2 or 3 or a hypophosphite salt of the formula $M^{m+}[H_2PO_2]_m^{m-}$ (M = Al, Ca, Mg and Zn and m = 2 and 3).

Organoclays are understood to mean organophilically modified clay minerals (principally montmorillonite) based on caution exchange, such as triethanol-tallow-ammonium montmorillonite and triethanol-tallow ammonium hectorite (Dr. G. Beyer; *Konf. Fire Resistance in Plastics 2007).* Anionic organoclays are organophilically modified hydrotalcites based on anion exchange with alkali rosinates, unsaturated and saturated fatty acid salts, and sulfonates and sulfates substituted by long-chain alkyl.

Particularly preferred metal oxides are diantimony trioxide, diantimony tetroxide, diantimony pentoxide or zinc oxide.

Particularly preferred metal hydroxides are aluminum hydroxide (ATH) or gibbsite (hydrargillite), aluminum oxo hydroxide (boehmite) and magnesium hydroxide (MDH, brucite) and hydromagnesite. In addition to gibbsite and boehmite, the other modifications of aluminum hydroxides, namely bayerite, nordstrandite and disapore, should also be mentioned.

Preferred metal phospahtes are metal pyrophosphates. Particular preference is given to aluminum pyrophosphate and zinc pyrophosphate, and zinc triphosphate and aluminum triphosphate, as well as aluminum metaphosphate and aluminum orthophosphate.

Preferred hydrotalcites are magnesium aluminum hydroxocarbonate and calcium aluminum hydroxocarbonate.

Among the cationically or anionically modified organoclays, particular preference is given to the alkyl sulfate- or fatty acid carboxylate-modified hydrotalcites or long chain quaternary ammonium-modified clay minerals.

Among the stannate and molybdate salts, particular preference is given to zinc stannate, zinc hydroxy stannate, ammonium heptamolybdate and ammonium octamolybdate. Other molybdates (inclding polymolybdates) such as calcium zinc molybdate, basic zinc molybdate and calcium molybdate should also be identified.

Preferred borates are alkali and alkaline earth borates, and zinc borate. Moreover, aluminium borate, barium borate, calcium borate, magnesium borate, manganese borate, melamine borate, potassium borate and zinc borophosphate should also be mentioned.

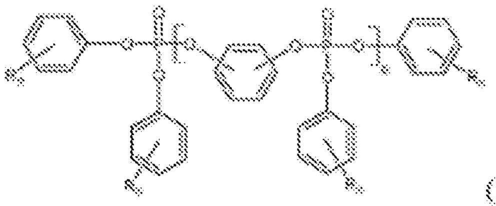
Among the metal phosphinates, preference is given to Ca, Mg, Zn or Al phosphinates. Particularly preferable are Ca, Mg, Zn or Al phenyl(benzene)phosphinate and Ca, Mg, Zn or Al diethyl(ethane)phosphinate.

Among the hypophosphites, particular preference is given to Mg, Ca, Zn and Al salt.

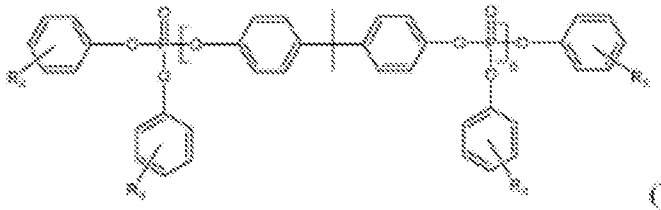
A further preference of the invention relates to flame retardant compositions containing at least one metal-free phosphorus compound as component (b).

This at least one metal-free phosphorus compound (b) is red phosphorus, an oligomeric phosphate ester, an oligomeric phosphonate ester, a cyclic phosphonate ester, a thiopyrophosphoric acid ester, melamine pyrophosphate, melamine polyphosphate, ammonium polyphosphate, melaminium phenylphosphonate and the semi-ester salt thereof (WO2010/063623), melamine benzenephosphinate (WO2010/057851), hydroxyalkylphosphine oxides (WO2009/034023), tetrakis(hydromethyl)phosphonium salts and phospholane or phosphole derivatives, and bisphosphoramidates with piperazine as a bridge member or a phosphonite ester.

Oligomeric phosphate esters are of the formula (IV) or formula (V):



(IV)

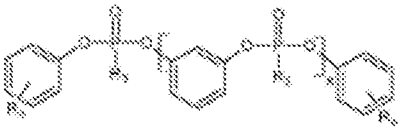


(V)

wherein each R is independently hydrogen, C_1 - C_4 alkyl or hydroxyl, n = 1 to 3 and o is 1 to 10.

Particular preference is given to the oligomer where R_n = H and resorcinol or hydroquinone as a component of the bridge member, and R_n = H and bisphenol A or bisphenol F as a component of the bridge member.

Oligomeric phosphonate esters are preferably characterised by formula (VI):

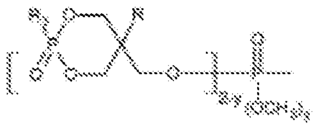


(VI)

wherein R^3 = methyl or phenyl and x is 1 to 20, and R, n possess the meaning specified above.

Particular preference is given to the oligomer where R_n = H and resorcinol or hydroquinone as a component of the bridge member.

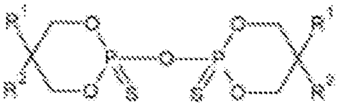
Cyclic phosphonate esters preferably have the following formula (VII):



(VII)

wherein y = 0 or 2. Particular preference is given to bis[5-ethyl-2-methyl-1,3,2-dioxaphosphorinane-5-y1)methyl]methyl phosphonates P,P´-dioxide.

Thiopyrophosphoric acid esters are preferably characterised by the following formula (VIII):



(VIII)

Particular preference is given to 2,2´-oxybis[5,5-dimethyl-1,3,2-dioxaphosphorinane]2,2´-disulfide.

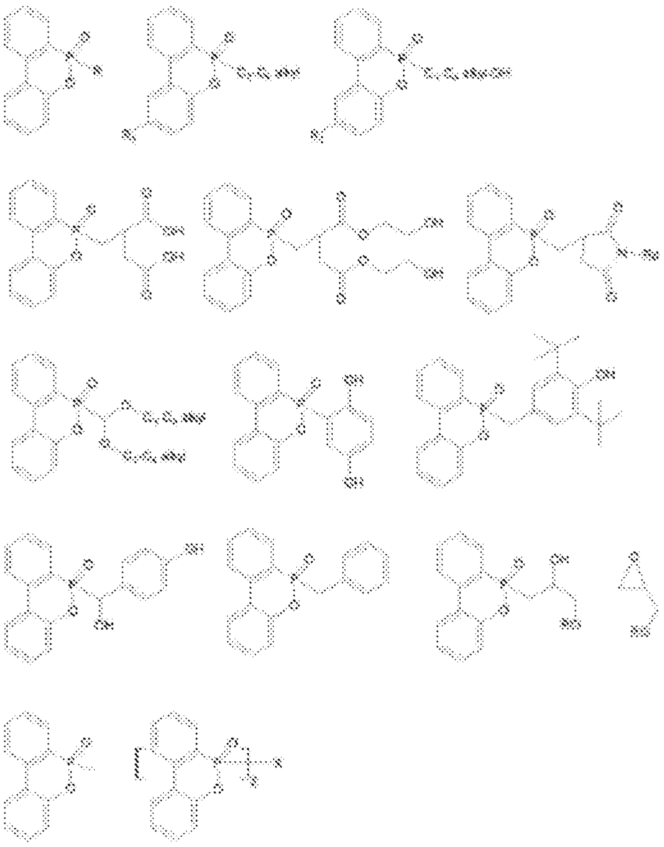
Among the hydroxyalkylphosphine oxides, preference is given to isobutylbis(hydroxymethyl)phosphine oxide and the combination thereof with epoxy resins (WO-A 2009/034023).

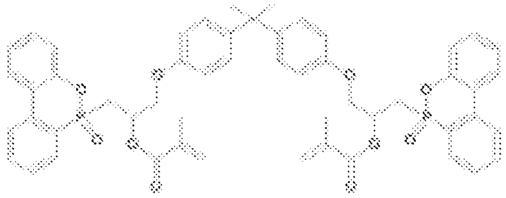
Among the tetrakis(hydroxyalkyl)phosphonium salts, particular preference is given to the tetrakis(hydroxymethyl)phosphonium salts.

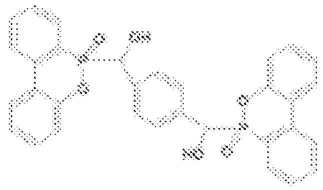
Among the phosphlane or phosphole derivatives, particular preference is given to dihydrophosphol(oxide) derivates and phospholane (oxide) derivates, and the salts thereof (EP 089 296 and EP 1024 166).

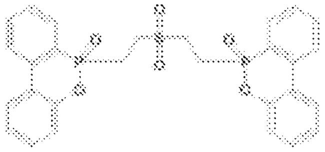
Among the bisphosphoramidates, particular preference is given to the bis(diorthoxylyl) esters with piperazine as a bridge member.

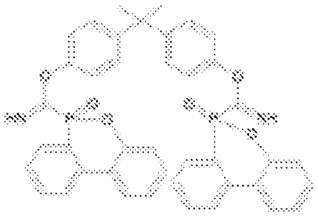
Among the phosphonite esters, preference is given to benzene phosphinic acid phenyl ester and the pH-functionalised derivatives and DOPO derivatives thereof.
DOPO derivatives (9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide derivatives or 6H-dibenzo(c,e)(1,2-oxaphosphorine 6-oxide derivatives (preference being given to PH-functionalised derivatives)) include the following compounds which are structurally depicted (cf. WO-A 2008/119693):

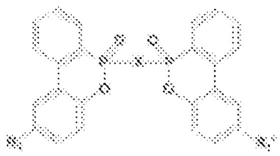


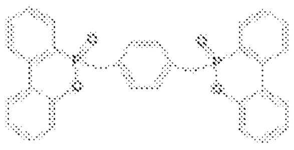


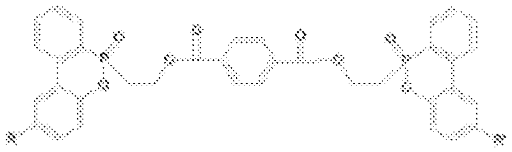


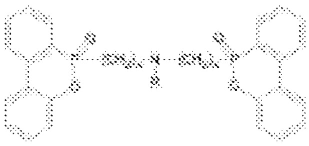


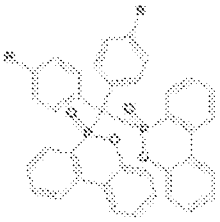


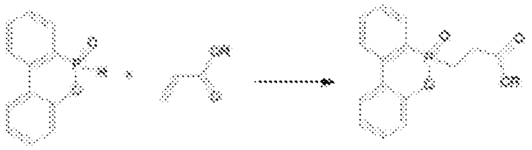


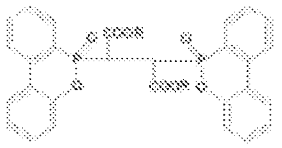


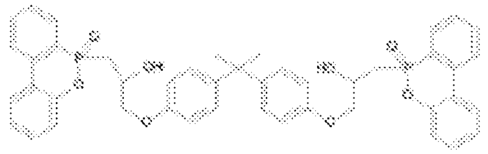




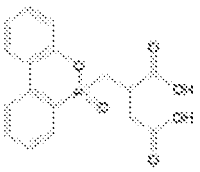


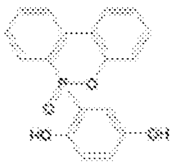






Particular preference is given to:





DOPO can also be replaced with dihydrooxaphospaha anthracene oxid(one)e. An overview thereof can be inferred from WO-A 2008/119693.

Further additives (synergists) include: polyols, aminouracils, tris(hydroxyethyl) isocyanurate

(THEIC), melamine (iso)cyanurate, POSS compounds and expandable graphite.

Among the polyols, particular preference is given to pentaerythritol, dipentaerythritol and tripentaerythritol.

Among the aminouracils, particular preference is given to 1-methyl-6-aminouracil and 1,3-dimethyl-6-aminouracil.

POSS compounds (polyhedral oligomeric silsesquioxanes) and derivatives are described in detail in *POLYMER*, Vol. 46, pp 7855-7866. In this case, preference is given to POSS derivatives based on methyl siloxane.

Furthermore, tris(hydroxyethyl) isocyanurate polyterephthalates as well as triazine polymers with piperazine-1,4-diyl bridge members and morpholine-1-y1 end groups can also be present.

Moreover, the following additives may be present: bisazine pentaerythritoldiphosphate salts, hexaaryloxytriphosphazenes, poly(aryloxy)phosphazenes and siloxanes $(R_2SiO)_r$ or $(RSiO_{1,5})_r$.

Metal oxides such as titanium dioxide, silicon dioxide; clay minerals such as kaolinite, muscovite, pyrophyllite, bentonite and talc, or other minerals such as wollastonite, quartz, mica, feldspar.

Furthermore, polymers can additionally contain dolomite, bentonite, huntite, or silicas and the natural or synthetic silicate minerals thereof.

Moreover, in addition to the at least one inventive metal phosphate, foaming agents can be added to a polymer. Foaming agents include: melamine, melamine formaldehyde resins, urea derivatives such as urea, thiourea, guanamines, benzoguanamine, acetoguanamine and succinylguanamine, dicyandiamide, guanidine and guanidine sulfamate and other guanidine salts or allantoins and glycolurils.

Furthermore, a polymer containing the at least one inventive metal phosphate can also contain antidripping agents, in particular based on polytetrafluoroethylene. The concentration of such antidripping agents is 0.01 to 15% by weight based on the polymer to be processed.

In addition, further components can also be added to polymers containing the at least one inventive metal phosphate, for example fillers and reinforcing agents such as glass fibres, glass beads or mineral additives such as chalk. Antioxidants, light stabilisers, lubricants, pigments, nucleating agents and antistatics can serve as further additives.

The present invention also relates to the use of the inventive triazine-intercalated metal phosphates with open framework structures as flame retardants in a polymer, paper, textiles or wood plastic composites (WPC).

The inventive flame retardants are ideal for providing synthetic, in particular thermoplastic, polymers with flame-retardant properties.

A particular embodiment of the invention relates to the use of the at least one inventive metal phosphate in a polymer as a flame retardant, said polymer being a thermoplastic which is preferably selected from the group which consists of polyamide, polycarbonate, polyolefin, polystyrene, polyester, polyvinyl chloride, polyvinyl alcohol, ABS and polyurethane, or being a thermoset which is preferably selected from the group which consists of epoxy resin (with hardener), phenol resin and melamine resin.

If the polymer in which the at least one inventive metal phosphate is used as a flame retardant is a thermoplastic, preference is given to polyamide, polyurethane, polystyrene, polyolefin or polyester.

If the polymer in which the at least one inventive metal phosphate is used as a flame retardant is a thermoset, preference is given to epoxy resin.

Mixtures of one or more polymers, in particular thermoplastics and/or thermosets, in which the inventive metal phosphate is used as a flame retardant, can also be used.

Examples of such polymers are:

1) Polymers from mono- and diolefins, for example polypropylene, polyisobutylene, polybutene-1, poly-4-methylpentene-1, polyvinylcyclohexane, polyisoprene or polybutadiene and polymerisates of cycloolefins, for example of cyclopentene or norbornene and polyethylene (also crosslinked), for example High Density Polyethylene (HDPE) or High Molecular Weight (HDPE-HMW), High Density Polyethylene with Ultra-High Molecular Weight (HDPE-UHMW), Medium Density Polyethylene (MDPE), Low Density Polyethylene (LDPE) and Linear Low Density Polyethylene (LLDPE), (VLDPE) and (ULDPE) and copolymeres of ethylene and vinyl acetate (EVA);

2) Polystyrene, poly(p-methylstyrene), poly(α-methylstyrene);
3) Copolymers and graft copolymers of polybutadiene-styrene or polybutadiene and (meth)acrylonitrile such as ABS and MBS;
4) Halogenated polymers, for example polychloroprene, polyvinyl chloride (PVC); polyvinylidene chloride (PVDC), copolymers of vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinyl chloride/vinyl acetate;
5) Poly(meth)acrylates, polymethyl methacrylates (PMMA), polyacrylamide and polyacrylonitrile (PAN);
6) Polymers of unsaturated alcohols and amines or acyl derivatives or acetals thereof, such as polyvinyl alcohol (PVA), polyvinyl acetates, stearates, benzoates or maleates, polyvinyl butyral, polyallyl phthalates and polyallylmelamines;
7) Homo- and copolymers of cyclic ethers, such as polyalkylene glycols, polyethylene oxides, polypropylene oxides and copolymers thereof with bisglycidyl ethers;
8) Polyacetals, such as polyoxymethylenes (POM) and polyurethane- and acrylate-modified polyacetals;
9) Polyphenylene oxides and sulfides and the mixtures thereof with styrene polymers or polyamides;
10) Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 12/12, polyamide 11, polyamide 12, aromatic polyamides derived from m-xylylenediamine and adipic acid and copolyamides modified with EPDM or ABS. Examples of polyamides and copolyamides are derived from ε-caprolactam, adipic acid, sebacic acid, dodecanoic acid, isophthalic acid, terephthalic acid, hexamethylenediamine, tetramethylenediamine, 2-methylpentamethylenediamine, 2,2,4-trimethylhexamethylenediamine, 2,4,4-trimethylhexamethylenediamine, m-xylylenediamine or bis(3-methyl-4-aminocyclohexyl)methane;
11) Polyureas, polymides, polyamideimides, polyetherimides, polyesterimides, polyhydantoins and polybenzimidazoles;
12) Polyesters derived from dicarboxylic acids and dialcohols and/or hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylcyclohexane terephthalate, polyalkylene naphthalate (PAN) and polyhydroxybenzoates, polylactic acid esters and polyglycolic acid esters;
13) Polycarbonates and polyester carbonates;
14) Polyketones;
15) Mixtures or alloys of the abovementioned polymers, for example PP/EPDM, PA/EPDM or ABS, PVC/EVA, PVC/ABS, PBC/MBS, PC/ABS, PBTP/ABS, PC/AS, PC/PBT,

PVC/CPE, PVC/acrylate, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA6.6 and copolymers, PA/HDPE, PA/PP, PAPPO, PBT/PC/ABS or PBT/PET/PC, such as TPE-O, TPE-S and TPE-E;

16) Thermosets such as PF, MF or UF or mixtures thereof;
17) Epoxy resins - thermoplastics and thermosets;
18) Phenol resins;
19) Wood-plastic composites (WPC) and polymers based on PLA, PHB and starch.

The concentration of the at least one claimed triazine-intercalated metal phosphate (a) and component (b) in a polymer or a polymer mixture is preferably 0.1 to 60% by weight based on the polymer to be processed.

The material thus rendered flame-retardant by the addition of the at least one inventive metal phosphate can be processed into fibres, films, cast articles, and can be used for treating surfaces.

The at least one inventive metal phosphate can also be used for surface treatment (impregnation) of fibres, films, textiles or other industrial materials.

Consequently, the present invention relates to the use of an inventive composition as a flame retardant in a polymer, textile or wood plastic composite (WPC). In particular, the polymer is a thermoplastic, preferably selected from the group consisting of polyamide, polycarbonate, polyolefin, polystyrene, polyester, polyvinyl chloride, polyvinyl alcohol, ABS and polyurethane or is a thermoset, preferably selected from the group consisting of epoxy resin, phenolic resin and melamine resin.

The present invention further relates to the use of the inventive triazine-intercalated metal phosphates with open framework structures for the production of paints, adhesives, casting resins, coatings, thixotropic agents and flame retardants for polymers.

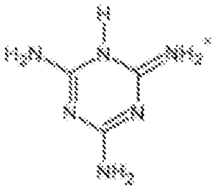
The present invention further relates to the use of the at least one inventive metal phosphate as a filler in polymers.

A further subject-matter of the present invention relates to the compounds of the general formula (I)

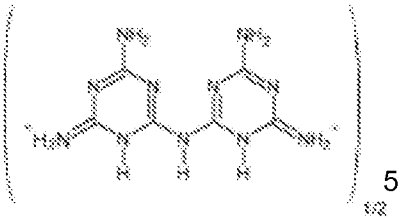
$(A - H)_a^{(+)} [M_b^{m+} (H_2PO_4)_{x1}^{(-)} (HPO_4)_{x2}^{2(-)} (PO_4)_{x3}^{3(-)} (PO_3)_y^{(-)}]^{(a-)} * pH_2O$ (I)

wherein

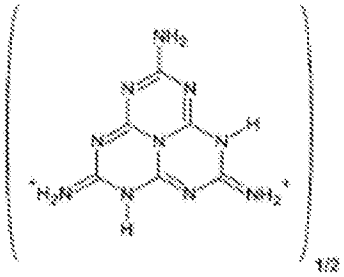
$(A - H)^{(+)}$ is a triazine derivative of the formulae (II-1, II-2 or II-3)



Melamine (II-1)



Melame (II-2)



Meleme (II-3)

each **M** = Al,

a 2,

b 1,

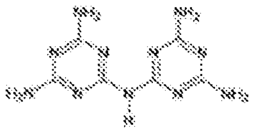
m 3,

x_1= 0 or 1, **x_2** = 0 or 2, **x_3** = 1 or 0, **y** = 2 or 0 and **p** is 0 to 5 and wherein:

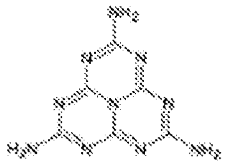
$a+mb=x_1+2x_2+3x_3+y$.

Furthermore, the invention relates to a method of producing the abovementioned compounds comprising the step of reacting a compound (A), wherein (A) is a triazine of the formulae (II-4), (II-5) or (II-6)

(II-4) Melamine



(II-5) Melame



(II-6) Meleme

with an acidic metal phosphate of the formula $H_a^{(+)}[M_b^{m+} (H_2PO_4)_{x1}^{(-)} (HPO_4)_{x2}^{2(-)} (PO_4)_{x3}^{3(-)} (PO_3)_y^{((-)}]^{(a-)}{*}pH_2O$, wherein each M = Al.

In an inventive method of producing the inventive metal phosphate, the reaction can take place in water and preferably between 20 and 90 °C, particularly preferably between 20 and 60 °C and most preferably between 20 and 40 °C.

A further subject-matter of the present invention is a compound which is obtainable according to the above-described inventive method.

In particular, such compounds are characterised in that the overall composition is a melamine aluminum phosphate $[(\text{melamine-H})_2^{+}\ [AlP_3O_{10}]^{2(-)}]_Z$, has the following ^{31}P-MAS NMR shifts (□ values): -10.6ppm, -22.0ppm, -24.5ppm and -27.6ppm and exhibits a single shift around 40 ppm in the ^{27}Al NMR spectrum. In particular, the overall composition is a melamine zinc phosphate $[(\text{melamine-H})_2^{+}\ [ZnP_2O_7]^{2(-)}]_z$ with the following ^{31}P MAS NMR shifts (□ values): +6.2ppm, +3.7ppm, +2.0ppm, -2.5ppm, -5.5ppm, -8.2ppm, -10.7ppm, -12.1ppm, -22.2ppm and -24.7ppm.

The respective metal phosphate can be produced, for example, by premixing in the form of powder and/or granules in a mixer and then by homogenising in a polymer melt by compounding (inter alia in a twin screw extruder). The metal phosphate can possibly also be added directly during the process.

In particular, sheet phosphates of the formulae $M(H_2PO_4)_3$ and $M(H_2PO_4)_2$ (M = Al) and condensed phosphates such as triphosphates or pyrophosphates of the formulae $H_2AlP_3O_{10}$ are considered as metal phosphates for producing triazine-intercalated metal phosphates with open framework structures.

However, the systems are best produced via a reaction with melamine as a template in aqueous acidic metal salt solution. An alternative method consists in the reaction of triazine phosphates with aqueous metal salt solutions (in line with *Angew. Chem.*, **1999,** 111, 3688-3692).

The metal phosphates with open framework structures which are thus produced have orthophosphate (H_XPO_4 type where x = 2, 1 or 0), pyrophosphate or triphosphate as complex ligands, melamine being intercalated in protonated form (melamine cation) between the lattice layers or into the cavities and a widening of the layer spacings taking place in the case of layer structures.

In further processing, the inventive triazine-intercalated metal phosphates are incorporated into a suitable polymer matrix. Suitable polymers which can be used as a substrate are known per se. For the incorporation, preference is given to thermoplastic polymers and thermoset polymer systems, rubbers and textiles.

Melamine is preferred as an intercalate.

With orthophosphate as ligands, the new intercalates can be depicted by way of example as follows, wherein **(A - H)**$^{(+)}$ (mel-H) $^{(+)}$ (melamine cation):

1. $(\mathrm{Mel\text{-}H})^{(+)}[\mathrm{Al}^{3(+)}(\mathrm{HPO_4})_2^{2(-)}]^{(-)}$
2. $(\mathrm{Mel\text{-}H})^{(+)}[\mathrm{Al}^{3(+)}(\mathrm{HPO_4})_2^{2(-)}\ \mathrm{H_2O}]^{(-)}$
3. $(\mathrm{Mel\text{-}H})_2^{(+)}[\mathrm{Al}^{3(+)}(\mathrm{H_2PO_4})^{(-)}\ (\mathrm{HPO_4})_2^{2(-)}]^{2(-)}$
4. $(\mathrm{Mel\text{-}H})_2^{(+)}[\mathrm{Al}^{3(+)}\ (\mathrm{PO_4})^{3(-)}\ (\mathrm{PO_3})_2^{(-)}]^{2(-)}$ (triphosphate type)

it being possible to remove aquo (complex) water by thermal treatment.

Particular preference is given to 3 and 4.

A further subject-matter of the present invention is a method of producing a flame-retardant, deformable polymer, wherein the at least one inventive triazine-intercalated metal phosphate is exfoliated in the polymer.

A further subject-matter of the invention is the achievement of an anticorrosive protective effect by coating metal surfaces.

Fig. 1 shows, by way of example, a lattice section from an intercalation model of melamine in aluminum triphosphate ($\mathrm{AlH_2P_3O_{10}}$) layers ($\oplus$= melaminium cation).

The invention is explained in greater detail by means of the subsequent examples.

Substances used: melamine (DSM); aluminum tris(dihydrogen phosphate (50% solution in water) (PRAYON Deutschland), zinc oxide, orthophosphoric acid (ALDRICH)

Example 1: Synthesis of bismelamine aluminium dihydrogen phosphate bis(hydrogen phosphate)

(**Product A**) - Precursor compound

$(\mathrm{C_3H_7N_6})_2{}^{(+)}[\mathrm{Al(H_2PO_4)(HPO_4)_2}]^{2(-)}$

(**a** = 2, **M** = Al, **b** = 1, **m** = 3, $\mathbf{x_1}$ = 1, $\mathbf{x_2}$ = 2, $\mathbf{x_3}$ = 0, **y** = 0, **p** = 0)

100.9 g (0.8 mol) of melamine are dissolved in 2.4 l of water while stirring at an elevated temperature (40 to 60 °C). In this solution, 254.4 g (0.4 mol) of aluminum tris(dihydrogen phosphate) (50% solution in water) are added dropwise, forming a thick paste. Subsequently,

it is stirred for 30 minutes, cooled to room temperature, the white precipitate which has formed is removed by suction, it is washed with water and dried to constant weight at 120 °C. Yield: 211.7 g corresponds to 92.8% of theory.
Elemental analysis: C: **12.7 %** (12.6 %); H: **3.3%** (3.2 %); N: **29.9%** (29.5 %); Al: **4.7%** (4.7 %); P: **16.4 %** (16.3 %) (theoretical values)

Example 2: Synthesis of bismelamine aluminium triphosphate
(Product B)
$(C_3H_7N_6)_2{}^{(+)} [Al^{3(+)(}PO_4)^{3(-)} (PO_3)_2{}^{(-)}]^{2(-)}$
(**a** = 2, **M** = Al, **b** = 1, **m** = 3, $\mathbf{x}_1$ = 0, $\mathbf{x}_2$ = 0, $\mathbf{x}_3$=1, **y** =2, **p** = 0)

Product (A) is tempered to a virtually constant weight at 280 °C with frequent mixing for 5 h. The resulting white product possesses the following composition:

Elemental analysis: C: **13.5 %** (13.5 %); H: **2.6 %** (2.6 %); N: **30.1 %** (31.5); Al: **5.1 %** (5.1 %); P: **17.5 %** (17.4 %) (theoretical values)

^{31}P MAS NMR shifts (δ values): -10.6ppm, -22.0ppm, -24.5ppm and -27.6ppm (see Fig. 2). In this case, Fig. 2 shows the quantitative ^{31}P NMR spectrum of bismelamine aluminium triphosphate (product B) ($_{VMAS}$=20KHz, ^{1}H decoupled)).

^{27}Al NMR spectrum: sole shift by 40ppm (see Fig. 4, $_{VMAS}$=20KHz).

Comparative Example 3: Synthesis of trismelamine aluminium tris(hydrogen phosphate)dihydrate
(Product C)-Precursor compound
$(C_3H_7N_6)_3{}^{(+)}[Al(HPO_4)_3]^{3(-)}\cdot 2H_2O$
(**a** = 3, **M** = Al, **b** = 1, **m** = 3, $\mathbf{x}_1$ = 0, $\mathbf{x}_2$ = 3, $\mathbf{x}_3$ = 0, **y** = 0, **p** = 2).

94.6 g (0.75 mol) of melamine are dissolved in 2.3 l of water while stirring under heat. Into this solution, 159.0 g (0.25 mol) of aluminum tris(dihydrogen phosphate) (50% solution in water) are added dropwise, forming a voluminous paste. Subsequently, it is stirred for 30 minutes, cooled to room temperature, the white precipitate which has formed is removed by suction, it is washed twice with water and dried to constant weight at 120 °C. Yield: 174.0 g corresponds to 95.0% of theory.

Elemental analysis: C: **14.8 %** (14.8 %); H: **3.5 %** (3.9 %); N: **33.8** % (34.4 %) (theoretical values)

Example 4: Synthesis of **Product B** preceding from **Product C**.

Production of **Product C** as in Example 3, but with subsequent tempering at 210 °C for 5 h. This results in trismelamine aluminium tris(dihydrogen phosphate)monohydrate as a precursor.

$(C_3H_7N_6)_3^{(+)}[Al(HPO_4)_3]^{3(-)} * H_2O$.

Yield: 165.7 g corresponds to 92.8% of theory.

Elemental analysis: C: **15.1 %** (15.1 %); H: **4.3 %** (3.7 %); N: **35.1 %** (35.3 %); (theoretical values)

Product B is obtained from this precursor by renewed tempering at 280 °C for 6 h, a decrease in weight of 25% taking place. The result is bismelamine aluminium triphosphate $(C_3H_7N_6)_2^{(+)}[Al^{3(+)}(PO_4)^{3(-)}(PO_3)_2^{(-)}]^{2(-)}$ (quantity yield)

Elemental analysis: **C: 13.4 %** (13.5 %); **H: 4.0 %** (2.6 %); **N: 29.7** % (31.5 %); (theoretical values)

It is evident therefrom that an alternative route to **Product B** is also possible by using **Product C**. However, this method is uneconomical in practice, since approximately a third of the melamine used must be removed again by tempering.

However, if the tempering is dispensed with, incorporation into the polyamides, polycarbonates and polyesters is much more difficult since significant amounts of melamine sublime. However, these difficulties do not occur when using Product B produced according to Example 2.

Example 5: Synthesis of bismelamine zinc diphosphate
(Product D)
$(C_3H_7N_6)_2^{(+)}[Zn^{2(+)}(PO_4)^{3(-)}(PO_3)^{(-)}]^{2(-)}$
(**a** = 2, **M** = Zn, **b** = 1, **m** = 2, $\mathbf{x_1}$ = 0, $\mathbf{x_2}$ = 0, $\mathbf{x_3}$ = 1, **y** = 1, **p** = 0)

Product D obtained by the above specification is dried at 280 °C for 5 h, a decrease in weight of approximately 6.0% taking place.

Elemental analysis: C: **15.1 %** (14.6 %); H: **2.8 %** (2.9 %); N: **34.0 %** (34.1 %); Zn: 12.6% (13.3 %); P: 12.2 % (12.2 %). (theoretical values)

^{31}P MAS NMR shifts (□ values): +6.2ppm, +3.7ppm, +2.0ppm, -2.5ppm, - 5.5ppm, -8.2ppm, -10.7ppm, -12.1ppm, -22.2ppm and -24.7ppm. (see Fig. 3). In this case, Fig. 3 shows the quantitative ^{31}P NMR spectrum of bismelamine zinc diphosphate (Product D) ($_{VMAS}$=20KHz).

Example 6: Static thermal treatment of precursor products **A** and **C**:

The results are summarised in Tab. 1.

Table 1: Thermal treatment of precursor products

	Product A (%)	Product C (%)
	100	100
200 °C / 2h	94.9	93.9
240 °C / 2h	91.4	86.0
280 °C / 2h	89.5	82.4
300 °C /2h	85.9	77.7
300 °C/ 4h	82.7	76.0

As is evident from Table 1, the inventive **Product A** is substantially more thermally stable than the prior art **Product C** (WO-A 2009/015772). This behaviour was surprising as it was unforeseeable.

Example 7: Static thermal treatment of the temper products **B**, **D** and MPP (Melamine polyphosphate, prior art)

The results are summarised in Tab. 2.

Table 2: Thermal treatment of temper products

	Product B(%)	Product D (%)	Product MMP (%)
	100	100	100
200 °C / 2h	99.8	99.2	99.1
240 °C / 2h	99.5	98.9	98.9
280 °C / 2h	98.3	97.4	98.0

300 °C /2h	94.3	94.1	91.3
300 °C/ 4h	89.7	92.7	83.7

As is evident from Table 2, the inventive **Products B** and **D** are substantially more thermally stable than the prior art **MPP**. This behaviour was surprising as it was unforeseeable.

Performance testing in PVC

I. Producing the rolled sheets:

The dry mixtures prepared according to Table 1 **(R-1, R-2)** are each plasticised on a Collin analytical laboratory roll mill (model: W100E, manufactured: 2005, from COLLIN) for 5 minutes (roll diameter: 110 mm, 15 rpm, friction: -15 %) at the specified temperature. The thus obtained films (thickness 0.3mm) are thus applied to further tests.

II. Carrying out the static heat test (SHT)

Test strips (15 mm x 15 mm) are cut out of the rolled sheets produced according to I. These are stressed in a METRASTAT IR 700 test oven (DR. STAPFER GmbH, Düsseldorf) at the specified temperature until significant discolouration. Subsequently, the YI value (yellowness index) is determined according to DIN 53381 with a Spectro-Guide colourimeter (from BYK-GARDNER) and compared with the YI value of the unstressed rolled sheet (zero minute value). The results are summarised in table form. The smaller the YI value at a specified time, the better the colour characteristics.

III. Carrying out the flame retardant testing:

The rolled sheets produced above are processed to pressure plates (120x100x3mm) and subjected to flame retardant testing in line with UL94. The UL94 test is described in *„Flammability of Plastic Materials for Parts in Devices and Appliances",* 5th edition, October, 1996.

IV. Determining the mechanical properties:

The mechanical properties were determined by means of *Instron 5569* (5kN side action grips) according to ASTM D412.

V. Carrying out the NMR measurements:

All measurements were carried out on a Bruker Avance II 200 solid state MAS spectrometer with 4.7 T magnet and a double resonance sample head for 2.5 mm rotors under *magic angle spinning* (MAS) conditions. The rotation frequencies ν_{MAS} used are specified for the corresponding measurements. Chemical shifts are specified relative to the reference substances currently recommended by IUPAC (^{27}Al: 1.1 M $Al(NO_3)_3$ in D_2O; ^{31}P: 85% phosphoric acid), the spectrometer calibration being performed with the help of the unified shift scale from the proton resonance of TMS.

The following formulations were tested:

Example 8: Testing in flexible PVC:

The following dry mixtures are produced (Table 3) - Initial weight in parts by weight:

Tab. 3: Formulations

Components	**(R-1)**	**(R-2)**
PVC (Evipol SH 7020) K value = 70	100	100
Plasticizer (DINP)$^{1)}$	50	50
Zinc stearate	0.6	0.6
Hydrotalcite$^{2)}$	2.9	2.9
Antioxidant (bisphenol A)	0.5	0.5
Flame retardant 1 (ATH)$^{3)}$	60	25
Flame retardant 2 (Product B)	--	5
Flame retardant effect (burn time in sec. after 3 ignitions)	0/1/1	0/1/1

1) diisononyl phthalate, ex BASF

2) sorbacid 911, ex SÜD CHEMIE

3) aluminium trihydroxide, APYRAL 40CD, ex NABALTEC

As is evident from Table 3, the inventive formulation **(R-2)** is comparable to the prior art example **(R-1)**

Table 4: SHT (200 °C) according to II

Time [min]	**(R-1)**	**(R-2)**
3	10.3	5.8
6	10.0	5.5
9	11.0	5.7
12	11.5	6.4
15	12.9	7.4
18	13.9	8.6
21	15.5	10.3
24	18.8	12.7
27	22.0	15.8
30	25.8	19.3
33	31.7	24.9
36	40.3	33.3
39	52.9	44.5
42	70.5	62.7
45	95.3	76.7
48	110.8	85.5
51	117.2	89.2
54	118.4	90.9
57	117.6	91.3
60	115.72	92.4

As is evident from Table 4, the inventive formulation **(R-2)** shows significantly better colour characteristics, in particular in relation to the initial colour, than the non-inventive formulation **(R-1)**.

Tab. 5.: Mechanical properties

	Tensile strength [MPa]	Strain at break [%]	Young's modulus [MPa]
(R-1)	13.64	331.38	33.59
(R-2)	15.24	368.45	25.27

Table 5 shows that the mechanical properties of the inventive formulation **(R-2)** are even improved in comparison to the prior art **(R-1)**.

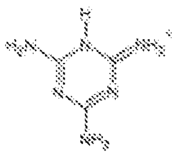
Patentkrav

1. Den generelle formels (I) forbindelser

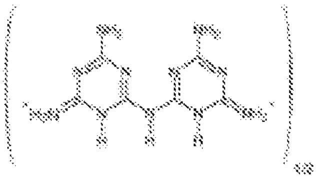
$(A\text{-}H)_a^{(+)}[M_b^{m+}(H_2PO_4)_{x1}^{(-)}(HPO_4)_{x2}^{2(-)}(PO_4)_{x3}^{3(-)}(PO_3)_y^{(-)}]^{(a-)}*pH_2O$ (I)

hvor

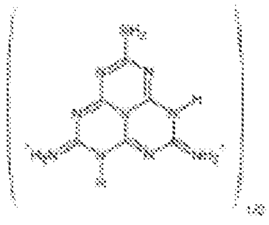
$(A - H)^{(+)}$ er et triazin-derivat af formlerne (II- 1, II-2 eller II-3)



Melamin (II- 1)



Melam (II-2)



Melem (II-3)

for hvert **M** = Al,

a er 2,

b er 1,

m = 3,

og

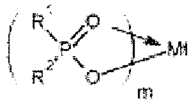
x_1 = 0 eller 1; **x_2** = 0 eller 2; **x_3** = 1 eller 0; **y** = 2 eller 0 og p = 0 til 5, hvor: $a + mb = x_1 + 2x_2 + 3x_3 + y$.

2. Sammensætning af flammebeskyttelsesmidler indeholdende
   - (a) mindst en forbindelse ifølge krav 1 som et triazin-interkaleret metal-fosfat med mindst en monomerenhed af den generelle formel (I), og
   - (b) mindst en yderligere flammebeskyttelsesmiddelkomponent, som er forskellig fra (a).

3. Sammensætning ifølge krav 2, kendetegnet ved, at denne mindst ene yderligere komponent (b) er en metalforbindelse, som ikke er et metal-fosfat i komponenten (a), eller/og mindst en metalfri fosfatforbindelse.

4. Sammensætning ifølge krav 3, kendetegnet ved, at den mindst ene metalforbindelse (b)

er et metaloxid, et metalhydroxid, et metalfosfat, et metalpyrofosfat, et hydrotalcit, et kationisk- eller anionisk-modificeret organoclay, et stannat eller molybdat-salt, et metalborat eller metal-fosfinat af formlen (III):



(III)

hvor R^1 og R^2 er hydrogen eller en ligekædet eller en forgrenet C_1 - C_6-alkylrest eller en phenylrest; og Mt = Ca, Mg, Zn eller Al og m = 2 eller 3.

5. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er diantimontrioxid, diantimontetroxid, diantimonpentoxid eller zinkoxid.

6. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er magnesiumhydroxid (Brucit), aluminiumtrihydroxid (ATH, Gibbsit) eller aluminiummonohydroxid (Boehmit).

7. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er magnesium- aluminium-hydroxo-karbonat eller kalcium-aluminium-hydroxo-karbonat.

8. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er et alkylsulfat- eller fedtsyrecarboxylat-modificeret hydrotalcit eller et langkædet kvaternært ammonium-modificeret lermineral.

9. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er ammoniumheptamolybdat, ammoniumoctamolybdat, zinkstannat eller zinkhydroxystannat.

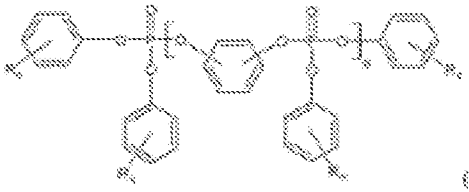
10. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er et alkali-, jordalkali- eller zinkborat.

11. Sammensætning ifølge krav 3 eller 4, kendetegnet ved, at den mindst ene metalforbindelse (b) er Ca-, Mg-, Zn- eller Al-fosfinat (hypofosfit), Ca-, Mg-, Zn- eller Al-phenyl(benzol)fosfinat eller Ca-, Mg-, Zn- eller Al-diethyl(ethan)fosfinat.

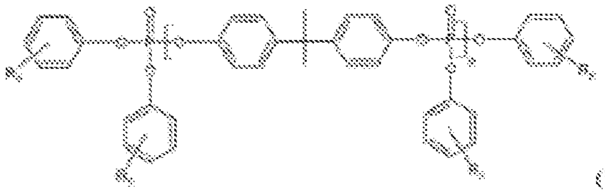
12. Sammensætning ifølge ethvert af kravene 3 til 11, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse (b) er rød fosfor, et oligomert fosfasestere, et oligomert fosfonatestere, et cyklisk fosfonatestere, et thiopyrofosforsyreestere, et

melaminpolyfosfat eller ammoniumpolyfosfat, et hydroxyalkyl-fosfinoxid, et tetrakis-hydroxyalkyl-fosfoniumsalt, et phospholan(oxid)-derivat eller dihydrophopshol(oxid)-derivat eller et phosphonitestere.

13. Sammensætning ifølge ethvert af kravene 3 til 12, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse er et oligomert fosfatestere af formlen (IV) eller formlen (V):



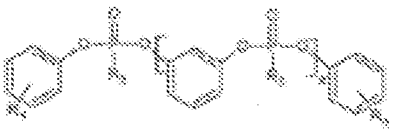
(IV)



(V)

hvor hvert R hhv. er uafhængigt hydrogen, C_1 - C_4alkyl eller hydroxy, n = 1 til 3 og o 1 til 10.

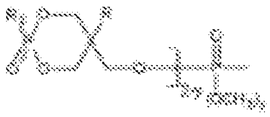
14. Sammensætning ifølge ethvert af kravene 3 til 12, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse er et oligomert fosfonatestere af formlen (VI):



(VI)

hvor R^3 = methyl eller phenyl og x 1 til 20 og R, n har betydningen som i krav 13.

15. Sammensætning ifølge ethvert af kravene 3 til 12, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse er et cyklisk fosfonatestere af formlen (VII):



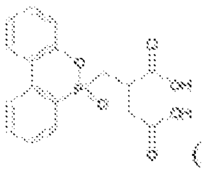
(VII)

hvor y = 0 eller 2.

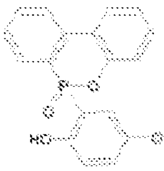
16. Sammensætning ifølge ethvert af kravene 3 til 12, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse er et thiopyrofosforsyreestere af formlen (VIII):

(VIII)

17. Sammensætning ifølge ethvert af kravene 3 til 12, kendetegnet ved, at den mindst ene metalfrie fosforforbindelse foreligger som et fosfonitestere i form af et benzolmonophenylesterederivat eller som et DOPO-derivat (9,10-dihydro-9-0xa-10-phosphaphenanthren-10-oxid eller 6H-dibenzo(c,e) (1,2)-oxaphosphorin-6-on)-derivat af formlen (IX) eller (X):



(IX),



(X)

18. Sammensætning ifølge ethvert af kravene 3 til 17, kendetegnet ved, at der er indeholdt ekstra polyoler og/eller aminouracile og/eller PO SS-forbindelser og/eller trishydroxyethylisocyanurat og/eller melamincyanurat og/eller grafitsyre.

19. Sammensætning ifølge krav 18, kendetegnet ved, at polyol pentaerythrit, dipentaerythrit eller tripentaerythrit, aminouracil 1,3-dimethyl-6-aminouracil POSS-forbindelsen er methylsiloxan-baseret.

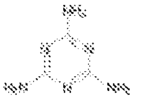
20. Sammensætning ifølge ethvert af kravene 2 til 19, kendetegnet ved, at koncentrationen af mindst et triazin-interkaleret metal-fosfat (a) og af komponenten (b) i et polymer eller en polymerblanding fortrinsvist er 0,1 til 60 vægt-% refererende til polymeret, som skal forarbejdes.

21. Anvendelse af en sammensætning ifølge ethvert af kravene 2 til 20 som flammebeskyttelsesmiddel i et polymer, papir, tekstiler eller Wood Plastic Composites (WPC = kompositmaterialer af træ og plastik).

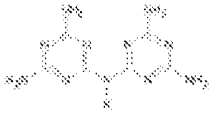
22. Anvendelse ifølge krav 21, kendetegnet ved, at polymeret er et termoplast, fortrinsvist udvalgt blandt gruppen bestående af polyamid, polykarbonat, polyolefin, polystyrol, polyester, polyvinylklorid, polyvinylalkohol, ABS og polyuretan eller et duroplast, fortrinsvist udvalgt blandt gruppen bestående af epoxidharpiks, phenolharpiks og melaminharpiks.

23. Metode til fremstilling af en forbindelse ifølge krav 1, indeholdende skridtet at omsætte

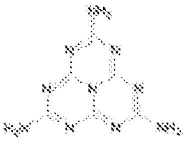
en forbindelse (A), hvor (A) er triazin af formlen (II-4), (II-5) eller (II-6)



(II-4) Melamin



(II-5) Melam



(II-6) Melem

med et acid metal-fosfat af formlen $H_a^{(+)}[M_b^{m+}(H_2PO_4)_{x1}^{(-)}(HPO_4)_{x2}^{2(-)} (PO_4)_{x3}^{3(-)}(PO_3)_y^{((-)}]^{(a-)}*pH_2O$, hvor hvert M = Al.

24. Metode ifølge krav 23, kendetegnet ved, at en omsætning finder sted i vand og fortrinsvist imellem 20 og 90 °C, især helst imellem 20 og 60 °C og aller helst imellem 20 og 40 °C.

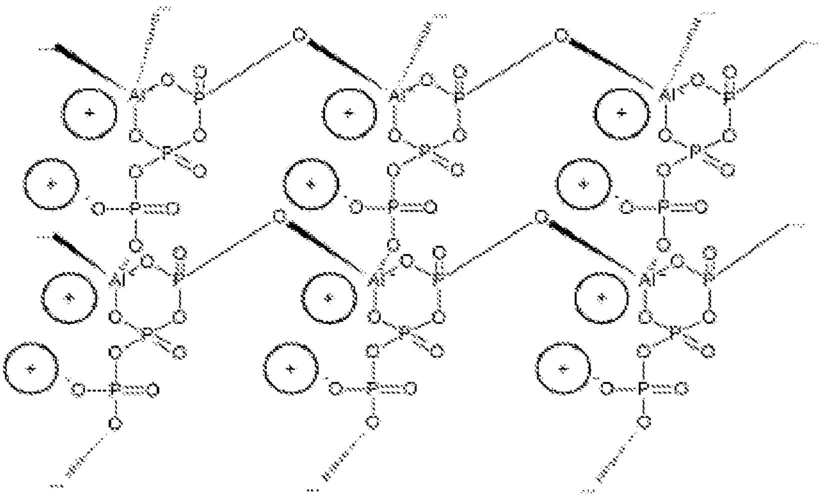


Fig. 1

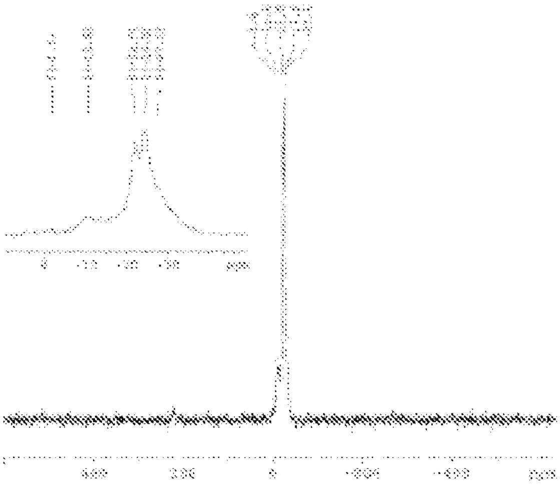


Fig. 2

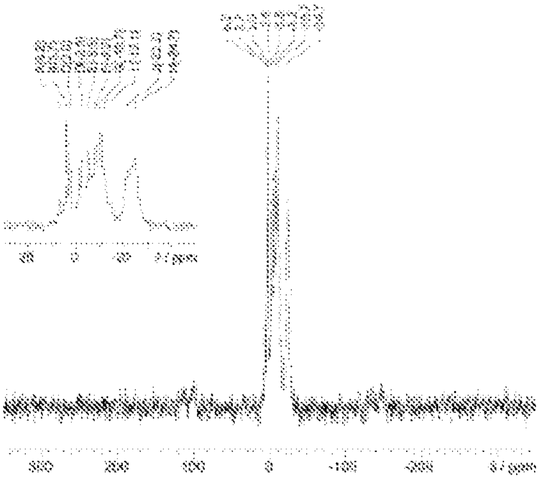


Fig. 3

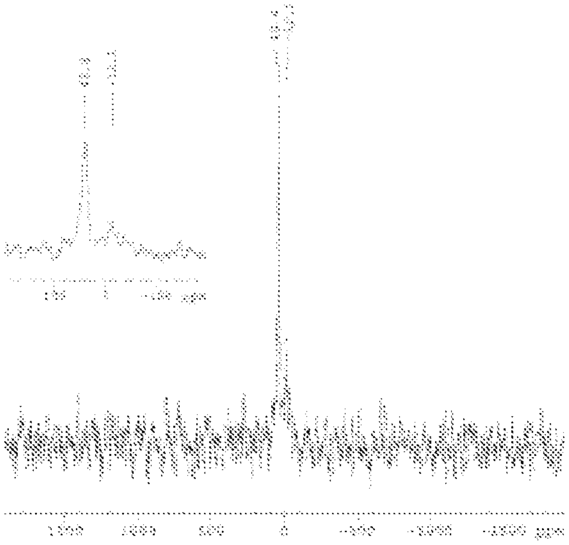


Fig. 4