

Flame-retardant polyamide compositions having high heat dimensional resistance and use thereof

Description

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The present invention relates to flame-retardant polyamide compositions and to moldings produced therefrom which feature a high heat dimensional resistance temperature (HDT).

10 Combustible plastics generally have to be equipped with flame retardants in order to be able to attain the high flame retardancy demands made by the plastics processors and in some cases by the legislator. Preferably – for environmental reasons as well – nonhalogenated flame retardant systems that form only a low level of smoke gases, if any, are used.

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Among these flame retardants, the salts of phosphinic acid (phosphinates) have been found to be particularly effective for thermoplastic polymers (DE 2 252 258 A and DE 2 447 727 A).

20 In addition, there are known synergistic combinations of phosphinates with particular nitrogen-containing compounds which have been found to be more effective as flame retardants in a whole series of polymers than the phosphinates alone (WO-2002/28953 A1, and also DE 197 34 437 A1 and DE 197 37 727 A1).

25 US 7,420,007 B2 discloses that dialkylphosphinates containing a small amount of selected telomers as flame retardant are suitable for polymers, the polymer being subject only to quite a minor degree of degradation on incorporation of the flame retardant into the polymer matrix.

30 Flame retardants frequently have to be added in high dosages in order to ensure sufficient flame retardancy of the polymer according to international standards. Due to their chemical reactivity, which is required for flame retardancy at high temperatures, flame retardants, particularly at higher dosages, can impair the

processing stability of plastics. This may result in increased polymer degradation, crosslinking reactions, outgassing or discoloration.

5 WO 2014/135256 A1 discloses polyamide molding compounds having distinctly improved thermal stability, reduced tendency to migration and good electrical and mechanical properties.

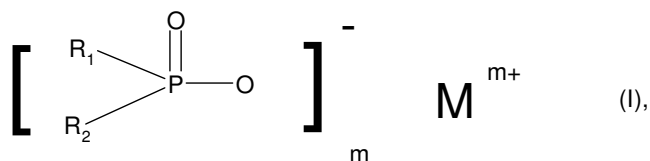
10 However, there has to date been a lack of flame-retardant phosphinate-containing polyamide compositions that achieve all the properties required simultaneously, such as good electrical values, excellent heat dimensional resistance and effective flame retardancy.

15 It was therefore an object of the present invention to provide flame-retardant polyamide compositions based on phosphinate-containing flame retardant systems which have all the aforementioned properties at the same time and which especially have good electrical values (GWFI, CTI), excellent heat dimensional resistance (HDT-A) and effective flame retardancy, characterized by minimum afterflame times (UL-94, time).

20 The invention provides flame-retardant polyamide compositions having a heat dimensional resistance temperature HDT-A of at least 280°C, comprising

- 25 - polyamide having a melting point of not less than 290°C, preferably of not less than 290°C and most preferably of not less than 300°C, as component A,
- fillers and/or reinforcers, preferably glass fibers, as component B,
- phosphinic salt of the formula (I) as component C

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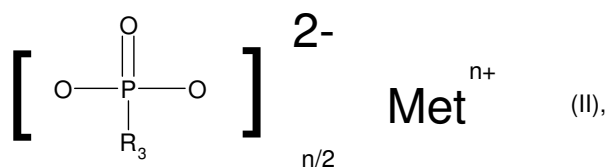
in which R_1 and R_2 are ethyl,

M is Al, Fe, TiO_p or Zn,

5 m is 2 to 3, preferably 2 or 3, and

$p = (4 - m) / 2$

- compound selected from the group of the Al, Fe, TiO_p and Zn salts of ethylbutylphosphinic acid, of dibutylphosphinic acid, of ethylhexylphosphinic acid, of butylhexylphosphinic acid and/or of dihexylphosphinic acid as component D, and
- 10
- phosphonic salt of the formula (II) as component E



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in which R_3 is ethyl,

Met is Al, Fe, TiO_q or Zn,

n is 2 to 3, preferably 2 or 3, and

20 $q = (4 - n) / 2$.

In the polyamide composition of the invention, the proportion of component A is typically 25% to 95% by weight, preferably 25% to 75% by weight.

25 In the polyamide composition of the invention, the proportion of component B is typically 1% to 45% by weight, preferably 20% to 40% by weight.

In the polyamide composition of the invention, the proportion of component C is typically 1% to 35% by weight, preferably 5% to 20% by weight.

5 In the polyamide composition of the invention, the proportion of component D is typically 0.01% to 3% by weight, preferably 0.05% to 1.5% by weight.

In the polyamide composition of the invention, the proportion of component E is typically 0.001% to 1% by weight, preferably 0.01% to 0.6% by weight.

10 These percentages for the proportions of components A to F are based on the total amount of the polyamide composition.

Preference is given to flame-retardant polyamide compositions in which

- the proportion of component A is 25% to 95% by weight,
- 15 - the proportion of component B is 1% to 45% by weight,
- the proportion of component C is 1% to 35% by weight,
- the proportion of component D is 0.01% to 3% by weight, and
- the proportion of component E is 0.001% to 1% by weight, where the percentages are based on the total amount of the polyamide composition.

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Particular preference is given to flame-retardant polyamide compositions in which

- the proportion of component A is 25% to 75% by weight,
- the proportion of component B is 20% to 40% by weight,
- the proportion of component C is 5% to 20% by weight,
- 25 - the proportion of component D is 0.05% to 1.5% by weight, and
- the proportion of component E is 0.01% to 0.6% by weight.

Salts of component C that are used with preference are those in which M^{m+} is Zn^{2+} , Fe^{3+} or especially Al^{3+} .

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Salts of component D that are used with preference are zinc, iron or especially aluminum salts.

Salts of component E that are used with preference are those in which Met^{n+} is Zn^{2+} , Fe^{3+} or especially Al^{3+} .

Very particular preference is given to flame-retardant polyamide compositions in which M and Met are Al, m and n are 3, and in which the compounds of component D take the form of aluminum salts.

In a preferred embodiment, the above-described flame-retardant polyamide compositions comprise inorganic phosphonate as a further component F.

The use of the inorganic phosphonates used in accordance with the invention as component F or else of salts of phosphorous acid (phosphites) as flame retardants is known. For instance, WO 2012/045414 A1 discloses flame retardant combinations comprising, as well as phosphinic salts, also salts of phosphorous acid (= phosphites).

Preferably, the inorganic phosphonate (component F) conforms to the formula (IV) or (V)



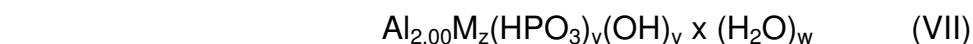
in which Kat is a p-valent cation, especially a cation of an alkali metal or alkaline earth metal, an ammonium cation and/or a cation of Fe, Zn or especially of Al, including the cations $\text{Al}(\text{OH})$ or $\text{Al}(\text{OH})_2$, and p is 1, 2, 3 or 4.

Preferably, the inorganic phosphonate (component F) is 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 $\text{Al}_4\text{H}_6\text{P}_{16}\text{O}_{18}$.

The inorganic phosphonate (component F) preferably also comprises aluminum phosphites of the formulae (VI), (VII) and/or (VIII)



where q is 0 to 4,



where M represents alkali metal cations, z is 0.01 to 1.5 and y is 2.63 to 3.5 and v is 0 to 2 and w is 0 to 4;



where u is 2 to 2.99 and t is 2 to 0.01 and s is 0 to 4, and/or

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, $\text{Al}_7(\text{HPO}_3)_9(\text{OH})_6(1,6\text{-}$

20 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 $\text{Al}_4\text{H}_6\text{P}_{16}\text{O}_{18}$.

Preferred inorganic phosphonates (component F) are salts that are insoluble or sparingly soluble in water.

25 Particularly preferred inorganic phosphonates are aluminum, calcium and zinc salts.

More preferably, component F is a reaction product of phosphorous acid and an
30 aluminum compound.

Particularly preferred components F are aluminum phosphites having CAS numbers 15099-32-8, 119103-85-4, 220689-59-8, 56287-23-1, 156024-71-4 and 71449-76-8.

- 5 The aluminum phosphites used with preference are prepared by reaction of an aluminum source with a phosphorus source and optionally a template in a solvent at 20-200°C over a period of time of up to 4 days. For this purpose, aluminum source and phosphorus source are mixed for 1-4 h, heated under hydrothermal conditions or at reflux, filtered off, washed and dried, for example at 110°C.

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Preferred aluminum sources are aluminum isopropoxide, aluminum nitrate, aluminum chloride, aluminum hydroxide (e.g. pseudoboehmite).

- 15 Preferred phosphorus sources are phosphorous acid, (acidic) ammonium phosphite, alkali metal phosphites or alkaline earth metal phosphites.

Preferred alkali metal phosphites are disodium phosphite, disodium phosphite hydrate, trisodium phosphite, potassium hydrogenphosphite.

- 20 A preferred disodium phosphite hydrate is Brüggolen[®] H10 from Brüggemann.

Preferred templates are 1,6-hexanediamine, guanidine carbonate or ammonia.

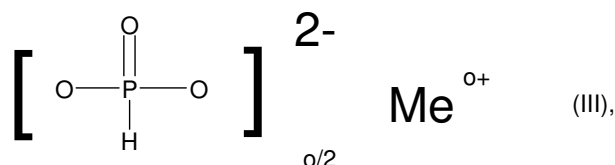
A preferred alkaline earth metal phosphite is calcium phosphite.

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The preferred ratio of aluminum to phosphorus to solvent here is 1:1:3.7 to 1:2.2:100 mol. The ratio of aluminum to template is 1:0 to 1:17 mol. The preferred pH of the reaction solution is 3 to 9. A preferred solvent is water.

- 30 In the application, particular preference is given to using the same salt of phosphinic acid as of phosphorous acid, i.e., for example, aluminum diethylphosphinate together with aluminum phosphite or zinc diethylphosphinate together with zinc phosphite.

In a preferred embodiment, the above-described flame-retardant polyester compositions comprise, as component F, a compound of the formula (III)



in which Me is Fe, TiO_r , Zn or especially Al,
o is 2 to 3, preferably 2 or 3, and
 $r = (4 - o) / 2$.

Compounds of the formula (III) that are used with preference are those in which Me^{o+} is Zn^{2+} , Fe^{3+} or especially Al^{3+} .

Component F is preferably present in an amount of 0.005% to 10% by weight, especially in an amount of 0.02% to 5% by weight, based on the total amount of the polyamide composition.

The flame-retardant polyamide compositions of the invention have a high heat deflection temperature (HDT-A) according to DIN EN ISO 75-3 of at least 280°C, preferably of at least 290°C and more preferably of at least 300°C.

Preference is given to flame-retardant polyamide compositions of the invention that have a comparative tracking index, measured according to International Electrotechnical Commission Standard IEC-60112/3, of not less than 500 volts.

Likewise preferred flame-retardant polyamide compositions of the invention attain a V-0 assessment according to UL-94, especially measured on moldings of thickness 3.2 mm to 0.4 mm.

Further preferred flame-retardant polyamide compositions of the invention have a glow wire flammability index according to IEC-60695-2-12 of not less than 960°C, especially measured on moldings of thickness 0.75-3 mm.

- 5 The polyamide compositions of the invention comprise, as component A, one or more thermoplastic polyamides having a melting point of not less than 290°C. The melting point is determined by means of differential scanning calorimetry (DSC) at a heating rate of 10 K/second.

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According to Hans Domininghaus in "Die Kunststoffe und ihre Eigenschaften" [The Polymers and Their Properties], 5th edition (1998), pages 14, thermoplastic polyamides are polyamides wherein the molecular chains have no side branches or else varying numbers of side branches of greater or lesser length, and which
15 soften when heated and are virtually infinitely shapable.

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The polyamides preferred in accordance with the invention may be prepared by various methods and be synthesized from very different starting materials and, in the specific application case, may be modified alone or in combination with
processing auxiliaries, stabilizers or else polymeric alloy partners, preferably
elastomers, to give materials having specifically established combinations of
properties. Also suitable are blends having proportions of other polymers,
preferably of polyethylene, polypropylene, ABS, in which case it is optionally
possible to use one or more compatibilizers. The properties of the polyamides can
25 be improved by addition of elastomers, for example with regard to impact
resistance, especially when they are reinforced polyamides. The multitude of
possible combinations enables a very large number of products having a wide
variety of different properties.

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A multitude of procedures have become known for preparation of polyamides, using different monomer units, various chain transfer agents for establishment of a desired molecular weight or else monomers having reactive groups for intended later aftertreatments according to the end product desired.

The processes of industrial relevance for preparation of polyamides usually proceed by polycondensation in the melt. This is also understood to include the hydrolytic polymerization of lactams as a polycondensation.

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Polyamides for use with preference as component A are semicrystalline and aromatic or semiaromatic polyamides which can be prepared proceeding from diamines and dicarboxylic acids and/or lactams having at least 5 ring members or corresponding amino acids.

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Useful reactants include mainly aromatic dicarboxylic acids, preferably isophthalic acid and/or terephthalic acid or the polyamide-forming derivatives thereof, such as salts, which are used alone or in combination with aliphatic dicarboxylic acids or the polyamide-forming derivatives thereof, preferably adipic acid, 2,2,4- and

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2,4,4-trimethyladipic acid, azelaic acid and/or sebacic acid, together with aliphatic and/or aromatic diamines, preferably tetramethylenediamine, hexamethylenediamine, nonane-1,9-diamine, 2,2,4- and

2,4,4-trimethylhexamethylenediamine, the isomeric diaminodicyclohexylmethanes, diaminodicyclohexylpropanes, bis(aminomethyl)cyclohexanes, phenylenediamines

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and/or xylylenediamines, and/or aminocarboxylic acids, preferably aminocaproic acid, or the corresponding lactams. Copolyamides formed from two or more of the monomers mentioned are included.

Also particularly suitable are aromatic and semiaromatic polyamides, i.e.

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compounds in which at least some of the repeat units are formed from aromatic structures. These polymers may optionally be used in combination with smaller amounts such as up to 20% by weight, based on the amount of polyamide, of aliphatic polyamides, especially PA6 and/or PA6.6, if a heat deflection temperature of the molding compound or of the molding produced therefrom of at least 290°C

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is attained thereby.

Preferably suitable are aromatic polyamides based on xylylenediamine and adipic acid; or polyamides prepared from hexamethylenediamine and iso- and/or

terephthalic acid and optionally an elastomer as modifier, e.g. poly-2,4,4-trimethylhexamethyleneterephthalamide or poly-m-phenyleneisophthalamide, block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bound or grafted elastomers, or with
 5 polyethers, for example with polyethylene glycol, polypropylene glycol or polytetramethylene glycol. Also EPDM- or ABS-modified polyamides or copolyamides; and polyamides condensed during processing ("RIM polyamide systems").

- 10 In a preferred embodiment, component A is an aromatic or semiaromatic polyamide or a mixture of two or more aromatic or semiaromatic polyamides or a mixture of nylon-6,6 and one or more aromatic or semiaromatic polyamides.

In a preferred embodiment, it is possible to add customary additives, especially
 15 demolding agents, stabilizers and/or flow auxiliaries to the polymers for additional use as well as the thermoplastic polyamide, by mixing them in the melt or applying them to the surface. Starting materials for the thermoplastic polyamides of component A may have been synthesized, for example, from petrochemical raw materials and/or via chemical or biochemical processes from renewable raw
 20 materials.

Fillers and/or preferably reinforcers are used as component B, preferably glass fibers. It is also possible to use mixtures of two or more different fillers and/or
 25 reinforcers.

Preferred fillers are mineral particulate fillers based on talc, mica, silicate, quartz, titanium dioxide, wollastonite, kaolin, amorphous silicas, nanoscale minerals, more preferably montmorillonites or nanoboehmites, magnesium carbonate, chalk, feldspar, glass beads and/or barium sulfate. Particular preference is given to
 30 mineral particulate fillers based on talc, wollastonite and/or kaolin.

Particular preference is further also given to using acicular mineral fillers. Acicular mineral fillers are understood in accordance with the invention to mean a mineral

filler having highly pronounced acicular character. Preference is given to acicular wollastonites. Preferably, the mineral has a length to diameter ratio of 2:1 to 35:1, more preferably of 3:1 to 19:1, especially preferably of 4:1 to 12:1. The average particle size of the acicular mineral fillers used in accordance with the invention as
5 component B is preferably less than 20 μm , more preferably less than 15 μm , especially preferably less than 10 μm , determined with a CILAS granulometer.

Components B used with preference in accordance with the invention are
reinforcers. These may, for example, be reinforcers based on carbon fibers and/or
10 on glass fibers.

The filler and/or reinforcer may, in a preferred embodiment, have been surface-modified, preferably with an adhesion promoter or an adhesion promoter system, more preferably a silane-based adhesion promoter system. Especially in the case
15 of use of glass fibers, in addition to silanes, it is also possible to use polymer dispersions, film formers, branching agents and/or glass fiber processing auxiliaries.

The glass fibers used with preference in accordance with the invention as
20 component B may be short glass fibers and/or long glass fibers. Short or long glass fibers used may be chopped fibers. Short glass fibers may also be used in the form of ground glass fibers. In addition, glass fibers may also be used in the form of continuous fibers, for example in the form of rovings, monofilament, filament yarns or threads, or glass fibers may be used in the form of textile fabrics,
25 for example of a glass weave, a glass braid or a glass mat.

Typical fiber lengths for short glass fibers prior to incorporation into the polyamide matrix are within the range from 0.05 to 10 mm, preferably from 0.1 to 5 mm. After incorporation into the polyamide matrix, the length of the glass fibers has
30 decreased. Typical fiber lengths for short glass fibers after incorporation into the polyamide matrix are within the range from 0.01 to 2 mm, preferably from 0.02 to 1 mm.

The diameters of the individual fibers may vary within wide ranges. Typical diameters of the individual fibers vary within the range from 5 to 20 μm .

5 The glass fibers may have any desired cross-sectional forms, for example round, elliptical, n-gonal or irregular cross sections. It is possible to use glass fibers having mono- or multilobal cross sections.

Glass fibers may be used in the form of continuous fibers or in the form of chopped or ground glass fibers.

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The glass fibers themselves, irrespective of their cross-sectional area and length, may be selected, for example, from the group of the E glass fibers, A glass fibers, C glass fibers, D glass fibers, M glass fibers, S glass fibers, R glass fibers and/or ECR glass fibers, particular preference being given to the E glass fibers, R glass
15 fibers, S glass fibers and ECR glass fibers. The glass fibers have preferably been provided with a size, preferably containing polyurethane as film former and aminosilane as adhesion promoter.

E glass fibers used with particular preference have the following chemical
20 composition: SiO_2 50-56%; Al_2O_3 12-16%; CaO 16-25%; $\text{MgO} \leq 6\%$; B_2O_3 6-13%; $\text{F} \leq 0.7\%$; Na_2O 0.3-2%; K_2O 0.2-0.5%; Fe_2O_3 0.3%.

R glass fibers used with particular preference have the following chemical
25 composition: SiO_2 50-65%; Al_2O_3 20-30%; CaO 6-16%; MgO 5-20%; Na_2O 0.3-0.5%; K_2O 0.05-0.2%; Fe_2O_3 0.2-0.4%, TiO_2 0.1-0.3%.

ECR glass fibers used with particular preference have the following chemical
composition: SiO_2 57.5-58.5%; Al_2O_3 17.5-19.0%; CaO 11.5-13.0%; MgO 9.5-11.5.

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The salts of diethylphosphinic acid used as component C in accordance with the invention are known flame retardants for polymeric molding compounds.

Salts of diethylphosphinic acid with proportions of the phosphinic and phosphonic salts used in accordance with the invention as components D and E are also known flame retardants. The production of this combination of substances is described, for example, in US 7,420,007 B2.

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The salts of diethylphosphinic acid of component C that are used in accordance with the invention may contain small amounts of salts of component D and of salts of component E, for example up to 10% by weight of component D, preferably 0.01% to 6% by weight, and especially 0.2% to 2.5% by weight thereof, and up to 10% by weight of component E, preferably 0.01% to 6% by weight, and especially 0.2% to 2.5% by weight thereof, based on the amount of components C, D and E.

The salts of ethylphosphonic acid used in accordance with the invention as component E are likewise known as additions to diethylphosphinates in flame retardants for polymeric molding compounds, for example from WO 2016/065971 A1.

In a further preferred embodiment, components C, D and E are in particulate form, where the median particle size (d_{50}) is 1 to 100 μm .

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The polyamide compositions of the invention may also comprise further additives as component G. Preferred components I in the context of the present invention are antioxidants, UV stabilizers, gamma ray stabilizers, hydrolysis stabilizers, costabilizers for antioxidants, antistats, emulsifiers, nucleating agents, plasticizers, processing auxiliaries, impact modifiers, dyes, pigments and/or further flame retardants other than components C, D, E and F.

The further additives are known per se as additions to polyamide compositions and can be used alone or in a mixture or in the form of masterbatches.

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The aforementioned components A, B, C, D, E and optionally F and/or G may be processed in a wide variety of different combinations to give the flame-retardant polyamide composition of the invention. For instance, it is possible, at the start or

at the end of the polycondensation or in a subsequent compounding operation, to mix the components into the polyamide melt. In addition, there are processing operations in which individual components are not added until a later stage. This is practiced especially in the case of use of pigment or additive masterbatches.

- 5 There is also the possibility of applying components, particularly those in pulverulent form, to the polymer pellets, which may be warm as a result of the drying operation, by drum application.

- 10 It is also possible to combine two or more of the components of the polyamide compositions of the invention by mixing before they are introduced into the polyamide matrix. It is possible here to use conventional mixing units in which the components are mixed in a suitable mixer, for example at 0 to 300°C for 0.01 to 10 hours.

- 15 It is also possible to use two or more of the components of the polyamide compositions of the invention to produce pellets that can then be introduced into the polyamide matrix.

- 20 For this purpose, two or more components of the polyamide composition of the invention can be processed with pelletizing aids and/or binders in a suitable mixer or a dish pelletizer to give pellets.

- The crude product formed at first can be dried in a suitable drier or heat-treated to further increase the grain size.

- 25 The polyamide composition of the invention or two or more components thereof may, in one embodiment, be produced by roll compaction.

- 30 The polyamide composition of the invention or two or more components thereof may, in one embodiment, be produced by subjecting the ingredients to mixing, extruding, chopping (and optionally crushing and classifying) and drying (and optionally coating).

The polyamide composition of the invention or two or more components thereof may, in one embodiment, be produced by spray granulation.

5 The flame-retardant polymer molding compound of the invention is preferably in pellet form, for example in the form of an extrudate or compound. The pelletized material is preferably in cylindrical form with a circular, elliptical or irregular footprint, in bead form, in cushion form, in cube form, in cuboid form or in prism form.

10 Typical length-to-diameter ratios of the pelletized material are 1:50 to 50:1, preferably 1:5 to 5:1.

The pelletized material preferably has a diameter of 0.5 to 15 mm, more preferably of 2 to 3 mm, and preferably a length of 0.5 to 15 mm, more preferably of 2 to
15 5 mm.

The invention also provides moldings produced from the above-described flame-retardant polyamide composition comprising components A, B, C, D and E and optionally components F and/or G.

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The moldings of the invention may be in any desired shape and form. Examples of these are fibers, films or shaped bodies obtainable from the flame-retardant polyamide molding compounds of the invention by any desired shaping processes, especially by injection molding or extrusion.

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The flame-retardant shaped polyamide bodies of the invention can be produced by any desired shaping methods. Examples of these are injection molding, pressing, foam injection molding, internal gas pressure injection molding, blow molding, film casting, calendering, laminating or coating at relatively high temperatures with the
30 flame-retardant polyamide molding compound.

The moldings are preferably injection moldings or extrudates.

The flame-retardant polyamide compositions of the invention are suitable for production of fibers, films and shaped bodies, especially for applications in the electricals and electronics sector.

- 5 The invention preferably relates to the use of the flame-retardant polyamide compositions of the invention in or for plug connectors, current-bearing components in power distributors (residual current protection), printed circuit boards, potting compounds, power connectors, circuit breakers, lamp housings, LED housings, capacitor housings, coil elements and ventilators, grounding
10 contacts, plugs, in/on printed circuit boards, housings for plugs, cables, flexible circuit boards, charging cables for mobile phones, motor covers or textile coatings.

- The invention likewise preferably relates to the use of the flame-retardant polyamide compositions of the invention for production of shaped bodies in the
15 form of components for the electrics/electronics sector, especially for parts of printed circuit boards, housings, films, wires, switches, distributors, relays, resistors, capacitors, coils, lamps, diodes, LEDs, transistors, connectors, regulators, memory elements and sensors, in the form of large-area components, especially of housing components for switchgear cabinets and in the form of
20 components of complicated configuration with demanding geometry.

- The wall thickness of the shaped bodies of the invention may typically be up to 10 mm. Particularly suitable shaped bodies are those having a wall thickness of less than 1.5 mm, more preferably a wall thickness of less than 1 mm and
25 especially preferably a wall thickness of less than 0.5 mm.

The examples which follow elucidate the invention without restricting it.

1. Components used
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Commercial polyamides (component A):

nylon-6T/6,6 (melting range of 310-320°C): Vestamid[®] HAT plus 1000 (Evonik)

Nylon-6T/6I (amorphous): Grivory[®] G21, (EMS)

Glass fibers (component B):

PPG HP 3610 glass fibers, diameter 10 μm , length 4.5 mm (from PPG, NL)

- 5 Flame retardant FM 1 (components C, D and E):
aluminum salt of diethylphosphinic acid containing 0.9 mol% of aluminum ethylbutylphosphinate and 0.5 mol% of aluminum ethylphosphonate prepared according to example 3 of US 7,420,007 B2
- 10 Flame retardant FM 2 (components C, D and E):
aluminum salt of diethylphosphinic acid containing 2.7 mol% of aluminum ethylbutylphosphinate and 0.8 mol% of aluminum ethylphosphonate prepared according to example 4 of US 7,420,007 B2
- 15 Flame retardant FM 3 (components C, D and E):
aluminum salt of diethylphosphinic acid containing 0.5 mol% of aluminum ethylbutylphosphinate and 0.05 mol% of aluminum ethylphosphonate prepared by the process according to US 7,420,007 B2
- 20 Flame retardant FM 4 (components C, D and E):
aluminum salt of diethylphosphinic acid containing 10 mol% of aluminum ethylbutylphosphinate and 5 mol% of aluminum ethylphosphonate prepared by the process according to US 7,420,007 B2
- 25 Flame retardant FM 5 (component C):
aluminum salt of diethylphosphinic acid prepared in analogy to example 1 of DE 196 07 635 A1
- Flame retardant FM 6 (components C and E):
- 30 aluminum salt of diethylphosphinic acid containing 8.8 mol% of aluminum ethylphosphonate

Flame retardant FM 7 (component F):

aluminum salt of phosphonic acid prepared according to example 1 of
DE 102011120218 A1

- 5 2. Production, processing and testing of flame-retardant polyamide molding
 compounds

10 The flame retardant components were mixed with one another in the ratios
 specified in the tables and incorporated via the side intake of a twin-screw extruder
 (Leistritz ZSE 27/44D) at temperatures of 310 to 330°C. The glass fibers were
 added via a second side intake. The homogenized polymer strand was drawn off,
 cooled in a water bath and then pelletized.

15 After sufficient drying, the molding compounds were processed to test specimens
 on an injection molding machine (Arburg 320 C Allrounder) at melt temperatures of
 300 to 320°C, and tested and classified for flame retardancy using the UL 94 test
 (Underwriter Laboratories). As well as the classification, the afterflame time was
 also reported.

20 The comparative tracking index of the moldings was determined according to
 International Electrotechnical Commission Standard IEC-60112/3.

25 The glow wire flammability index (GWIT index) was determined according to
 standard IEC-60695-2-12.

 The heat deflection temperature (HDT) was determined according to DIN EN ISO
 75-3.

30 In the determination of the HDT, a standard test specimen with rectangular cross
 section is subjected to a three-point bending test at constant load. According to
 specimen height, for achievement of a so-called edge fiber tension σ_f of 1.80
 (method A), 0.45 (method B) or 8.00 N/mm² (method C) a force is applied by
 means of weights and/or springs. Subsequently, the stressed samples are

subjected to heating at a constant heating rate of 120 K/h (or 50 K/h). If the bending of the sample reaches an edge fiber tension of 0.2%, the corresponding temperature corresponds to the HDT value.

- 5 All tests in the respective series, unless stated otherwise, were performed under identical conditions (such as temperature programs, screw geometry and injection molding parameters) for comparability.

Examples 1-5 and comparative examples C1-C3 with PA 6,6

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The results of the experiments with PA 6T/6,6 molding compounds are listed in the examples adduced in the table which follows. All amounts are reported as % by weight and are based on the polyamide molding compound including the flame retardants and reinforcing.

Table 1: PA 6T/6.6 GF 30 test results (1-5 inventive; V1-V3 comparisons)

Example No.	1	2	3	4	5	C1	C2	C3
A: PA 6T/6,6	55	55	55	55	55	55	50	55
B: HP3610 glass fibers	30	30	30	30	30	30	30	30
C+D+E: FM 1	15	-	-	-	-	-	-	-
C+D+E: FM 2	-	15	-	-	13	-	-	-
C+D+E: FM 3	-	-	15	-	-	-	-	-
C+D+E: FM 4	-	-	-	15	-	-	-	-
C: FM 5	-	-	-	-	-	-	-	15
C+E: FM 6	-	-	-	-	-	15	20	-
F: FM 7	-	-	-	-	2	-	-	-
HDT-A [°C]	295	295	295	295	295	285	295	285
UL 94 0.4 mm / time [sec.]	V-0/23	V-0/17	V-0/37	V-0/23	V-0/08	V-0/41	V-0/35	V-0/47
GWFI [°C]	960	960	960	960	960	900	900	900
CTI [volts]	600	600	600	600	600	500	600	500

The inventive polyamide compositions of examples 1 to 5 are molding compounds which attain the UL94 V-0 fire class at 0.4 mm, simultaneously have CTI 600 volts, GWFI 960°C and HDT-A 295°C. The addition of component F in example 5 leads to another improvement in flame retardancy, expressed by a reduced afterflame time.

The omission of component D in comparative example C1 resulted not only in a prolonged afterflame time but also in a reduction in the CTI, GWFI and HDT/A values compared to examples 1-4.

In comparative example C2, it was possible to achieve an improvement in the afterflame time by increasing the concentration of components C and E compared to example C1. However, this polyamide composition still had a lower GWFI value compared to example 2.

The omission of components D and E in comparative example C3 resulted not only in a prolonged afterflame time but also in a reduction in the CTI, GWFI and HDT/A values compared to examples 1-4.

Examples 6-10 and comparative examples C4-C6 with PA 6T/6I

The results of the experiments with PA 6T/6I molding compounds are listed in the examples adduced in the table which follows. All amounts are reported as % by weight and are based on the polyamide molding compound including the flame retardants and reinforcing agents.

Table 2: PA 6T/6I GF 30 test results (6-10 inventive; V4-V6 comparisons)

Example No.	6	7	8	9	10	C4	C5	C6
A: PA 6T/6I	55	55	55	55	55	55	50	55
B: HP3610 glass fibers	30	30	30	30	30	30	30	30
C+D+E: FM 1	15	-	-	-	-	-	-	-
C+D+E: FM 2	-	15	-	-	13	-	-	-
C+D+E: FM 3	-	-	15	-	-	-	-	-
C+D+E: FM 4	-	-	-	15	-	-	-	-
C: FM 5	-	-	-	-	-	-	-	15
C+E: FM 6	-	-	-	-	-	15	20	-
F: FM 7	-	-	-	-	2	-	-	-
HDT-A [°C]	305	305	305	305	305	295	300	295
UL 94 0.4 mm / time [sec.]	V-0/21	V-0/15	V-0/35	V-0/21	V-0/06	V-0/39	V-0/33	V-0/43
GWFI [°C]	960	960	960	960	960	900	950	900
CTI [volts]	600	600	600	600	600	500	600	500

The inventive polyamide compositions of examples 6 to 10 are molding compounds which attain the UL94 V-0 fire class at 0.4 mm, simultaneously have CTI 600 volts, GWFI 960°C and HDT-A 305°C. The addition of component F in example 10 leads to another improvement in flame retardancy, expressed by a reduced afterflame time.

The omission of component D in comparative example C4 resulted not only in a prolonged afterflame time but also in a reduction in the HDT-A, GWFI and CTI values compared to examples 6-9.

In comparative example C5, it was possible to achieve an improvement in the afterflame time by increasing the concentration of components C and E compared to example C4. However, this polyamide composition still had reduced HDT-A and GWFI values compared to example 7.

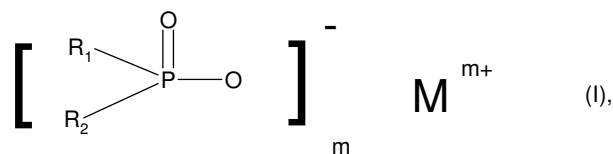
The omission of components D and E in comparative example C6 resulted not only in a prolonged afterflame time but also in a reduction in the HDT-A, GWFI and CTI values compared to examples 6-9.

Patent claims

1. A flame-retardant polyamide composition having a heat deflection temperature HDT-A of not less than 280°C, comprising

- 5 - polyamide having a melting point of not less than 290°C as component A, wherein said component A is an aromatic or semiaromatic polyamide or a mixture of two or more aromatic or semiaromatic polyamides.
- fillers and/or reinforcers as component B,
- phosphinic salt of the formula (I) as component C

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in which R₁ and R₂ are ethyl,

M is Al, Fe, TiO_p or Zn,

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m is 2 to 3, and

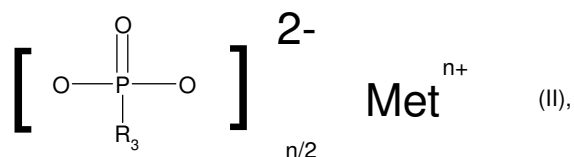
p = (4 - m) / 2

- compound selected from the group of the Al, Fe, TiO_p and Zn salts of ethylbutylphosphinic acid, of dibutylphosphinic acid, of ethylhexylphosphinic acid, of butylhexylphosphinic acid and/or of dihexylphosphinic acid as

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component D, and

- phosphonic salt of the formula (II) as component E



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in which R₃ is ethyl,

Met is Al, Fe, TiO_q or Zn,

n is 2 to 3, and

q = (4 - n) / 2.

2. The flame-retardant polyamide composition as claimed in claim 1 wherein M and Met are Al, m and n are 3, and component D is an aluminum salt.

5 3. The flame-retardant polyamide composition as claimed in at least one of claims 1 and 2, wherein

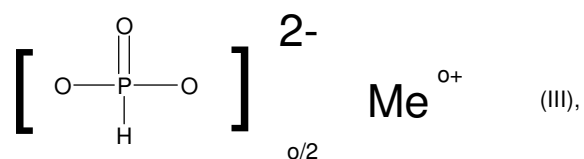
- the proportion of component A is 25% to 95% by weight,
 - the proportion of component B is 1% to 45% by weight,
 - the proportion of component C is 1% to 35% by weight,
 - 10 - the proportion of component D is 0.01% to 3% by weight, and
 - the proportion of component E is 0.001% to 1% by weight,
- where the percentages are based on the total amount of the polyamide composition.

15 4. The flame-retardant polyamide composition as claimed in claim 3, wherein

- the proportion of component A is 25% to 75% by weight,
- the proportion of component B is 20% to 40% by weight,
- the proportion of component C is 5% to 20% by weight,
- the proportion of component D is 0.05% to 1.5% by weight, and
- 20 - the proportion of component E is 0.01% to 0.6% by weight, wherein the sum of each component is less than or equals to 100% by weight.

5. The flame-retardant polyamide composition as claimed in at least one of claims 1 to 4, wherein the polyamide composition comprises inorganic
25 phosphonate as further component F.

6. The flame-retardant polyamide composition as claimed in claim 5, wherein the inorganic phosphonate is a compound of the formula (III)



in which Me is Fe, TiO_r, Zn or especially Al,

o is 2 to 3, and

$r = (4 - o) / 2$, in which

5 the amount of the compound of the formula (III) is 0.005% to 10% by weight, especially 0.02% to 5% by weight, based on the total amount of the polyamide composition.

7. The flame-retardant polyamide composition as claimed in at least one of
10 claims 1 to 6, which has a comparative tracking index measured by International Electrotechnical Commission Standard IEC-60112/3 of not less than 500 volts.

8. The flame-retardant polyamide composition as claimed in at least one of
15 claims 1 to 7, which attains a V-0 assessment according to UL94 from thickness 3.2 mm to 0.4 mm.

9. The flame-retardant polyamide composition as claimed in at least one of
claims 1 to 8, which has a glow wire flammability index according to IEC-60695-2-
12 of not less than 960°C at thickness 0.75-3 mm.

20 10. The flame-retardant polyamide composition as claimed in at least one of claims 1 to 9, which has a heat deflection temperature HDT-A according to DIN EN ISO 75-3 of at least 300°C.

25 11. The flame-retardant polyamide composition as claimed in at least one of claims 1 to 10, wherein glass fibers are used as component B.

30 12. The flame-retardant polyamide composition as claimed in at least one of claims 1 to 11, wherein components C, D, E and optionally F are in particulate form, where the median particle size d_{50} of these components is 1 to 100 μm .

13. The flame-retardant polyamide composition as claimed in at least one of claims 1 to 12, which comprises further additives as component G, where the further additives are selected from the group consisting of antioxidants, UV stabilizers, gamma ray stabilizers, hydrolysis stabilizers, costabilizers for
- 5 antioxidants, antistats, emulsifiers, nucleating agents, plasticizers, processing auxiliaries, impact modifiers, dyes, pigments and/or further flame retardants other than components C, D, E and F.
14. The use of the polyamide compositions as claimed in any of claims 1 to 13
- 10 for production of fibers, films and shaped bodies, especially for applications in the electricals and electronics sector.