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(54) Title: FLAME RETARDANT POLYAMIDE COMPOSITION

(57) Abstract: The present invention relates to a flame retardant polyamide composition comprising (A) a semi-crystalline semi-aromatic polyamide having a melting temperature (TmA) and having a number average molecular weight in the range between 7,500 and 30,000 g/mol; (B) a semi-crystalline aliphatic polyamide having a melting temperature (TmB); and having a number average molecular weight in the range between 7,500 and 50,000 g/mol; and (C) a halogen free flame retardant system comprising a metal salt of a phosphinic acid and/or a diphosphinic acid, wherein TmA is higher than TmB and weight ratio of (A): (B) is in the range between 0: 50 and 75: 25. The invention also relates to a process for moulding the flame retardant polyamide composition, and moulded parts made of the flame retardant polyamide composition.

FLAME RETARDANT POLYAMIDE COMPOSITION

The invention relates to a flame retardant polyamide composition, a process for moulding the flame retardant polyamide composition, and moulded parts
5 made of the flame retardant polyamide composition.

The invention in particular relates to halogen free flame retardant moulding compositions for high performance applications. For high performance applications often semi-crystalline polyamides with high melting temperatures are used, if not excluded or prohibited by even higher temperature requirements. For the flame
10 retardancy halogen free flame retardants can be used, although with such flame retardants it is more difficult to achieve the required flame retardancy level, compared to halogen containing flame retardants used in the past. Because of the high temperatures involved in either the processing and/or the applications of these moulding compositions, the selection of flame retardants that can be used is limited,
15 and even the better performing flame retardants commercially available have their limitations and problems. This becomes even more pronounced in more critical applications involving large production series of precision parts with small dimensions.

A lot of attention is paid to the properties of the moulding compositions and the products produced thereof. First of all these moulding
20 compositions should have high flow, the products should preferably have a good weld line strength, a good surface appearance, e.g. high gloss, staining free and blooming free, and have a good flame retardancy rating, such as according to UL94 test methods. The processing should preferably not induce corrosion of the injection moulding equipment.

25 But an important aspect that should not be overlooked for large scale production series is a smoothly running if not flawless injection moulding process that does not have to be regularly interrupted for clean-up of the mould, as this would drastically reduce the throughput of the injection moulding process and the economic utilisation of the equipment. An important aspect herein is the occurrence of what is
30 called plate-out. Plate-out is the outgassing of solid material from the moulding composition and deposition thereof inside the mould. Accumulation of such deposition can block the outgassing openings of the mould. This becomes apparent from burning spots on the moulded parts : through fast injection of the moulding material in the mould, the gas comprised by the mould cannot escape and gets compressed quickly,

resulting in heating up of the gas to such high temperatures that the parts can get burned.

Plate out is different from blooming or staining. Blooming is the migration of solid material from the composition to the surface after exposure of a 5 moulded part to hot and humid conditions. Staining is the migration of solid material from a composition to the surface upon contacting of a moulded part with a liquid.

The aim of the present invention is to provide a halogen free flame retardant moulding composition that has a good balance in properties, and has a good plate out performance. Preferably, the moulded parts made of the composition also 10 have a good surface appearance and low tendency for blooming and staining.

This aim has been achieved with the composition according to the invention comprising

- (A) a semi-crystalline semi-aromatic polyamide (referred to as polyamide (A), or 15 (A)) having a melting temperature (referred to as TmA) and having a number average molecular weight (referred to as Mn-B) in the range between 7,500 and 30,000 g/mol;
- (B) a semi-crystalline aliphatic polyamide (referred to as polyamide (B), or (B)) having a melting temperature (referred to as TmB); and having a number 20 average molecular weight (referred to as Mn-B) in the range between 7,500 and 50,000 g/mol; and
- (C) a halogen free flame retardant system comprising a metal salt of a phosphinic acid and/or a diphosphinic acid (together referred to as metal (di)phosphinate), wherein
 - the TmA is higher than TmB and
 - the weight ratio of (A) : (B) is in the range between 50 : 50 and 75 : 25.

The effect of the composition according to the invention, comprising the above combination of components with the said features is that the composition can be moulded at less severe moulding conditions than corresponding compositions based on a semi-aromatic polyamide only, while still having a good flow at those 30 moulding conditions and resulting in moulded parts with good flame retardancy properties, weld strength and surface appearance, and most importantly reduced plate out, when compared with the corresponding compositions only based on a semi-aromatic polyamide, or when compared with corresponding compositions only based on an aliphatic polyamide composition even though said composition would still not 35 have a comparable flame retardancy level. The flow of the semi-aromatic polyamide

based composition could be improved by using aliphatic polyamides with lower Mn, which can be used in lower amounts, but this results in loss of flame retardancy properties. Alternatively the flow of the semi-aromatic polyamide based composition could be increased by using higher processing temperatures but this would result in even more extensive plate out. Combining an aromatic polyamide and an aliphatic polyamide in a ratio beyond the above range, and/or with number average molecular weights beyond the ranges indicated above for the invention does not solve the problem of plating and/or introduces other problems, such as loss in flame retardancy properties and/or insufficient flow and surface appearance.

Preferably, the semi-crystalline semi-aromatic polyamide (A) has a number average molecular weight (Mn-A) of in the range of 10,000 – 25,000 g/mol, more preferably in the range of 12,500 – 20,000 g/mol. Also preferably, the semi-crystalline aliphatic polyamide (B) has a number average molecular weight (Mn-B) in the range of 10,000 – 40,000 g/mol, more preferably in the range of 15,000 – 30,000 g/mol. A higher Mn has the advantage that the flame retardancy is better retained, while the advantage of a lower Mn is that plate out is further reduced.

The number average molecular weight (Mn) as referred to herein is determined by measuring the molecular weight distribution by gel permeation chromatography (GPC), more particular with Size Exclusion Chromatography (SEC) combined with triple detection method. Herefor a GPC apparatus is coupled to viscometry, refractive index and light scattering detection (90 degrees). The measurements are performed using hexafluoroisopropanol comprising 0.1 wt% potassium trifluoro acetate, relative to the weight of the hexafluoroisopropanol, as solvent, and employing a Size Exclusion Chromatograph equipped with 3 PFG linear XL silica columns; The weight average molecular weight is calculated from the measured molecular weight distribution using TriSEC 3.0 software of the company Viscotek. The Mn and Mw are expressed in g/mol. The triple detection method has the advantage in that this method gives absolute values and does not need an external reference.

For the semi-crystalline semi-aromatic polyamide (A) in principle any semi-crystalline semi-aromatic polyamide used for making moulding compositions can be used. Suitably (A) comprises repeat units derived from terephthalic acid, and optionally another aromatic dicarboxylic acid and/or aliphatic dicarboxylic acid, and aliphatic diamines selected from aliphatic linear or branched diamines comprising 4-12 carbon atoms. An aromatic dicarboxylic acid that suitably is combined with terephthalic

acid is, for example, isophthalic acid. An example of an aliphatic dicarboxylic acid, that can be combined with terephthalic acid, and optionally with the other aromatic dicarboxylic acid, in the semi-crystalline semi-aromatic polyamide (A) is adipic acid.

The semi-crystalline semi-aromatic polyamide (A) suitably has a high 5 melting temperature. Preferably Tm-A is at least 270°C, more preferably at least 280°C. Still more preferably Tm-A is in the range of 290-350 °C, or even better at least 300 – 340 °C. A higher melting temperature for polyamide (A) results in a product with better retention of mechanical and other properties at high temperature. The product can nevertheless be processed at such process conditions that a good flame retardancy 10 and low plate out is achieved.

With the term melting temperature is herein understood the melting temperature (Tm) as determined by the method according to ISO-11357-3.2, 2009, in an N2 atmosphere with a heating and cooling rate of 10°C/min, from the peak value of the melting peak in the second heating cycle. In case there are multiple melting peaks, 15 the peak value is to be taken from the highest melting peak.

A semi-crystalline semi-aromatic polyamide with a higher melting temperature can generally be achieved by using a higher content in terephthalic acid and/or shorter chain diamines in the polyamide. The person skilled in the art of making polyamide moulding compositions will be capable of making and selecting such 20 polyamides. Suitable examples include PA8T, PA9T, PA10T, PA12T, PA6T/6I, PA6T/66, PA6T/46, and copolyamides thereof.

The semi-crystalline aliphatic polyamide (B) also suitably has a high melting temperature, though always remaining below that of (A). Suitably, Tm-B is at least 220 °C. Preferably Tm-B is in the range of 250-300 °C.

25 For the semi-crystalline aliphatic polyamide (B) also a wide variety of polyamides can be used. To obtain a product with good high temperature properties, preferably a polyamide with a high melting point is used such as either polyamide 4,6, polyamide 4,8, polyamide 4,10, or polyamide 6,6 or any mixture or copolymer thereof.

In a preferred embodiment of the flame retardant polyamide 30 composition according to the invention, the weight ratio of (A) : (B) is in the range of 55 : 45 – 72.5 : 27.5.

Most favourably the semi-crystalline semi-aromatic polyamide (A) and the semi-crystalline aliphatic polyamide (B) used in the composition according to the invention are at least miscible with each other to a certain extent. In that respect it is 35 preferred that (A) and (B) have a negative X parameter. Herein X is the miscibility

parameter X_{blend} calculated for (A) and (B) following the method according to T.S. Ellis in Macromolecules 1991, 24, 3845-3852, using the following formula (III)

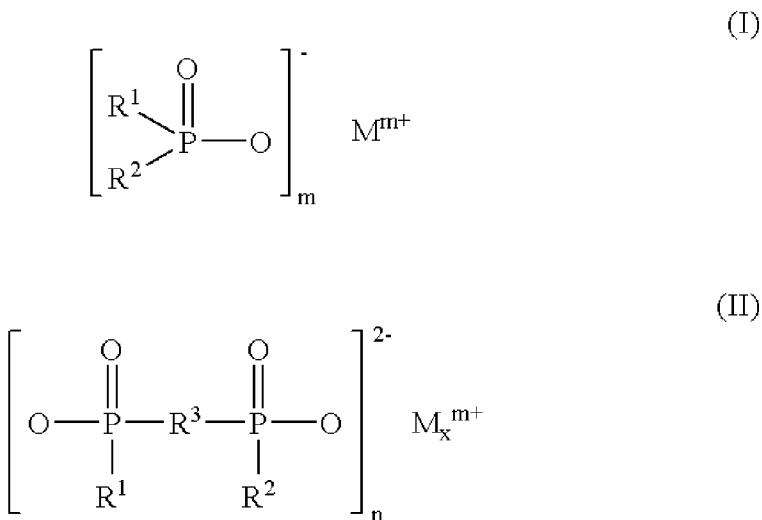
$$\begin{aligned} X_{blend} = & [(1-x)(y-x) + z(x-y)] X_{AB} \\ 5 & + (1-y-z)(1-x-z) X_{BC} \\ & + (1-y-z)(x-y) X_{AC} \end{aligned} \quad \text{Formula (III)}$$

The formula as used by Ellis is applicable for blends of aliphatic and semi-aromatic polyamides, defined as $A_xB_{1-x}/A_yB_zC_{1-y-z}$, where A_xB_{1-x} represents the 10 aliphatic polyamide and $A_yB_zC_{1-y-z}$ represents the aromatic polyamide, and wherein A, B and C represent the methylene, amide, and phenyl repeat units, x, 1-x, y, z and 1-y-z represent the relative amounts of these repeat units in the polyamides. For the 15 calculations of X_{blend} , the parameters X_{AB} , X_{AC} and X_{BC} , representing the interaction between methylene and amide, methylene and phenyl units, and amide and phenyl units respectively, were taken equal to respectively 7.982, -0.288 and 7.46, as determined by Ellis in above article.

Applying these values Formula III reduces to the following formula (IV)

$$\begin{aligned} X_{blend} = & [(1-x)(y-x) + z(x-y)] * 7.982 \\ 20 & + (1-y-z)(1-x-z) * 7.46 \\ & - (1-y-z)(x-y) * 0.288 \end{aligned} \quad \text{Formula (IV)}$$

Suitable salts of (di)phosphinic acids that can be used in the 25 composition according to the present invention are, for example, a phosphinate of the formula (I), a disphosphinate of the formula (II),



or polymers of these wherein R^1 and R^2 are identical or different or are $\text{C}_1 - \text{C}_6$ alkyl, linear or branched, and/or aryl; R^3 is $\text{C}_1 - \text{C}_{10}$ -alkylene, linear or branched, $\text{C}_6 - \text{C}_{10}$ -arylene, -alkylarylene or -arylalkylene; M is one or more of calcium ions, magnesium ions, aluminum ions and zinc ions, m is 2 to 3; n is 1 or 3; x is 1 or 2. R^1 and R^2 may be identical or different and are preferably methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, n-pentyl and/or phenyl. R^3 is preferably methylene, ethylene, n-propylene, isopropylene, n-butylene, tert-butylene, n-pentylene, n-octylene, n-dodecylene, or phenylene or naphthylene, or methylphenylene, ethylphenylene, tert-butylphenylene, methylnaphthylene, ethylnaphthylene or tert-butylnaphthylene, or phenylmethylene, phenylethylene, phenylpropylene or phenylbutylene. M is preferably aluminum ions or zinc ions. These compounds are disclosed in U.S. Pat. No. 6,255,371, which is hereby incorporated herein by reference.

15 Preferably the flame retardant system (C) comprises an aluminum (di)phosphinate. Suitable examples thereof are methylethyl(di)phosphinate and/or aluminum diethyl(di)phosphinate.

20 Suitably, flame retardant system (C) is present in an amount of 1 – 100 parts by weight (pbw) relative to 100 pbw of (A) + (B). Preferably, the amount of (C) is in the range of 5 – 50 parts by weight (pbw) relative to 100 pbw of (A) + (B).

25 The flame retardant system (C) is also suitably present in an amount in the range of at least 5 wt.% and/or at most 30 wt.%, more particular at least 5 wt.% and/or at most 25 wt.%. Herein the weight percentages (wt.%) are relative to the total weight of the flame retardant polyamide composition. Preferably, the amount of the metal (di)phosphinate comprised by the flame retardant polyamide composition is

preferably in the range of 5 -25 wt.%, more preferably 7.5 – 20 wt.%, relative to the total weight of the composition.

The composition may comprise one or more other flame retardants than the metal (di)phosphinates, and/or one or more flame retardant synergists. Flame retardant synergists generally used in combination with metal (di)phosphinate flame retardants include metal borates, such as Znborate and BaBorate.

In a preferred embodiment, the composition comprises at most 1 wt.%, more preferably at most 0.5 wt.%, and even better 0 – 0.1 wt.% ZnBorate. The advantage of a lower content or even absence of ZnBorate is that the staining of the composition is improved, compared to the corresponding composition comprising a higher ZnBorate content.

The polyamide composition of the present invention may optionally comprise further components, such as inorganic fillers, fibrous reinforcing agents, other polymers, as well as additives selected from, for example, acid scavengers, impact modifiers, plasticizers, stabilizers (such as, for example, thermal stabilizers, oxidative stabilizers, UV light stabilizers and chemical stabilizers), processing aids (such as, for example, mould release agents and nucleating agents), solid lubricants, colorants (such as carbon black, other pigments, dyes), nanoclays, etc. An impact modifier is advantageously included to further improve impact resistance for e.g. housings for electronic devices.

Examples of inorganic reinforcing agents and/or fillers, that the composition may optionally comprise, include one or more of glass fibres, which may be flat glass fibres, glass flakes, kaolin, clay, talc, mica, wollastonite, calcium carbonate, silica, carbon fibres, potassium titanate, etc. Glass fibres and carbon fibres are preferred.

The inorganic reinforcing agent and/or filler used in the present invention, if used at all, is suitably present in amount from, for example, about 5 wt.% up to about 60 wt.%, based on the total weight of the composition.

In a particular embodiment of the invention, the flame retardant polyamide composition comprises 5 – 25 wt.% of flame retardant (C), and 5 – 60 wt.% of glass or carbon fibre reinforcement, wherein the wt.% are relative to the total weight of the composition.

In a preferred embodiment, the total amount of fibrous reinforcing agents and fillers in the composition is in the range of 45-60 wt.%, for example about 50 wt.% or about 55 wt.%. Such a high amount is preferred in case a high stiffness is

required, such as for example, for use in housings for electronic devices such as for notebooks, mobile phones and PC tablets.

In case a high flow is required, such as for connectors with a high aspect ratio, i.e. thin but relatively long as in DDR connectors, the amount of the 5 inorganic reinforcing agents and/or fillers is suitably up to about 45 wt.%, or more preferably up to about 40 wt.%, based on the total weight of the composition.

In a particular embodiment of the invention, the flame retardant polyamide composition consists of

(A)/(B) 30 – 90 wt.% of polyamide (A) and polyamide (B) in a weight ratio in the 10 range between 50 : 50 and 75 : 25;

(C) 5 – 25 wt.% of metal(di)phosphinate;

(D) 0 – 60 wt.% of inorganic fillers and/or fibrous reinforcing agents;

(E) 0 – 40 wt.% of other components

In a preferred embodiment thereof, the flame retardant polyamide 15 composition consists of

(A)/(B) 30 – 87 wt.% of polyamide (A) and polyamide (B) in a weight ratio in the range between 50 : 50 and 75 : 25.

(C) 7.5 – 20 wt.% of metal(di)phosphinate

(D) 5 – 55 wt.% of inorganic fillers and/or fibrous reinforcing agents;

20 (E) 0.5 – 20 wt.% of other components

Herein the weight percentages (wt.%) are relative to the total weight of the composition, and the sum of (A)-(E) is 100 %.

The compositions according to the invention can be prepared by a process, wherein the semi-aromatic polyamide, the aliphatic polyamide, the flame 25 retardant system and optional additional ingredients are melt-blended. Part of the materials may be mixed in a melt-mixer, and the rest of the materials may then be added and further melt-mixed until uniform. Melt-blending may be carried out using any appropriate method known to those skilled in the art. Suitable methods may include using a single or twin-screw extruder, blender, kneader, Banbury mixer, moulding 30 machine, etc. Twin-screw extrusion is preferred, particularly when the process is used to prepare compositions that contain additives such as flame retardants, and reinforcing agents. The compositions of the present invention have a high melt flow and may be conveniently formed into a variety of articles using injection moulding, rotomoulding and other melt-processing techniques. The articles are useful in SMT 35 applications among others and include connectors, such as memory cards, (CPU)

sockets, I/O, FPC, motherboard and automotive connectors, and housings and stiffener frames for electronic devices, for example housings and stiffener frames for notebooks, mobile phones, stiffeners and PC tablets.

The invention also relates to a process for the production of moulded parts from the flame retardant polyamide composition according to the invention, or any embodiment thereof, as described above, by injection moulding, comprising a step wherein the composition is heated in an injection moulding machine to form a polymer melt. In said process, the melt is heated to a temperature of at most 10°C above TmA, i.e. above the melting temperature of the semi-crystalline semi-aromatic polyamide comprised by the composition. The effect thereof is that the plate out is reduced, while simultaneously achieving the other properties as described above

In a preferred embodiment of the said process, the polymer melt is injected into a mould with a mould temperature of at least 100°C. Preferably the temperature of the mould is in the range of 110 – 150°C. A mould temperature of 100°C and higher has the advantage that the resulting product has an improved gloss.

The invention also relates to an article or moulded product made from a composition according to the present invention, or any specific embodiment thereof. Suitably, the article is a plastic part of a connector or a housing or stiffener frame for an electronic device.

The invention is further illustrated with the following examples and comparative experiments.

Materials

PPA	PA4T/66 based semi-aromatic polyamide according to the invention with a melting temperature of 325°C
PA-46	PA-46 based aliphatic polyamide according to the invention with a melting temperature of 290°C
PA-66	PA-66 based aliphatic polyamide according to the invention with a melting temperature of 260°C
Flame retardant	Exolit OP1230, Clariant GmbH
Synergist	ZnBorate
Glass Fibres	Standard grade for thermoplastic polyamide compositions

Compounding

Flame retardant polyamide compositions were prepared on a twin screw extruder. For the compositions of Examples I-III and Comparative Experiments A, B and D, the temperature of the extruded melt was typically about 340 °C, so well 5 above 325 °C. For Comparative Experiments the melt temperature was about 310 °C. After the melt compounding the resulting melt was extruded into strands, cooled and cut into granules.

Injection moulding

10 The flame retardant polyamide compositions were injection moulded into appropriate test moulds using a standard injection moulding machine. For the compositions of Examples I-III and Comparative Experiments C the settings were such that the melts of the compositions reached a temperature of about 310 °C. For Comparative Experiments A, B and D, the settings were such that the melts of the 15 compositions reached a temperature of about 340 °C.

The compositions and test results have been summarized in Table 1.

It is noted that Comparative Experiments A, B and D could not be processed in a proper manner with a melt temperature much lower than 340 °C, and certainly not below 325 °C. The Examples I-III and Comparative Experiments C could 20 be processed with a melt temperature above 325 °C, but when processed at the conditions used for Comparative Experiments A, B and D this resulted in deteriorated products with bad properties.

Table1 : compositions and test results for Examples I-III and Comparative experiments A-D.

	Ex-I	EX-II	EX-III	CE-A	CE-B	CE-C	CE_D
Polyamides / weight ratio							
PPA	70	60	60	90	80	-	100
PA-46	30	40	-	10	20	100	-
PA-66	-	-	40	-	-	-	-
X-parameter	< 0	< 0	< 0	-	-	-	-
Composition (wt.%)							
Polyamide polymer	48	48	48	48	48	42	48
Glass Fibres	30	30	30	30	30	30	30
Exolit	12	12	12	12	12	18	12
ZnBorate	-	-	-	-	-	4	-
Performance rating *)							
Flow	+	+	+/-	+/-	+/-	+/-	=
Corrosion	+/-	+/-	+/-	+/-	+/-	+/-	-
Plate out	+	+	+	+/-	+/-	-	-
Weld strength	+	+	+/-	+	+	+/-	+
Flame retardancy (V0)	+	+	+	+	+	#)	++
Gloss (@ 120°C mould temperature)	++	++	+/-	+/-	+/-	+/-	-

*) ++ = very good, + = good, +/- = moderate; - = bad, = = very bad.

#) despite high loading of flame retardants, only V2 rating was obtained.

CLAIMS

1. Flame retardant polyamide composition comprising
 - (A) a semi-crystalline semi-aromatic polyamide having a melting temperature (TmA);
 - (B) a semi-crystalline aliphatic polyamide having a melting temperature (TmB); and
 - (C) a halogen free flame retardant system comprising a metal salt of a phosphinic acid and/or a diphosphinic acid
- 10 wherein
 - the weight ratio of (A) : (B) is in the range between 50 : 50 and 75 : 25;
 - (A) has a number average molecular weight (Mn-A) in the range between 7,500 and 30,000 g/mol;
 - (B) has a number average molecular weight (Mn-B) in the range between 7,500 and 50,000 g/mol;
 - TmA is higher than TmB.
2. Flame retardant polyamide composition according to claim 1 or 2, wherein Mn-A is in the range of 10,000 – 25,000 g/mol, and/or wherein Mn-B in the range of 10,000 – 40,000 g/mol.
- 20 3. Flame retardant polyamide composition according to any one of claims 1 -3 , wherein Tm-A is in the range of 290-350 °C, and/or wherein Tm-B is in the range of 250-300 °C.
4. Flame retardant polyamide composition according to claim 1, wherein the weight ratio of (A) : (B) is in the range of 55 : 45 – 72.5 : 27.5.
- 25 5. Composition according to any one of claims 1 – 4, wherein (A) and (B) have a negative X parameter, the X parameter being calculated for (A) and (B) by applying the method according to T.S. Ellis in Macromolecules 1991,24, 3845-3852 and using the following formula

$$X_{\text{blend}} = [(1 - x)(y - x) + z(x - y)] * 7.982 \\ + (1 - y - z)(1 - x - z) * 7.46 \\ - (1 - y - z)(x - y) * 0.288$$

wherein x and 1-x represent the relative amounts of methylene and amide phenyl repeat units in (A), and y, z and 1-y-z represent the relative amounts of methylene, amide and phenyl repeat units in (B).

6. Flame retardant polyamide composition according to any of claims 1 – 5, wherein the flame retardant system (C) comprises an aluminium (di)phosphinate.
7. Flame retardant polyamide composition according to any of claims 1 – 7, 5 wherein (C) is present in an amount of at least 5 wt.% and at most 30 wt.%, relative to the total weight of the composition.
8. Composition according to any one of claims 1 – 6, wherein the composition comprises at most 1 wt.% ZnBorate.
9. Flame retardant polyamide composition according to any of claims 1 – 8, 10 wherein the composition comprises inorganic fillers and/or fibrous reinforcement agents (D) in a total amount of at least 5 wt.%, relative to the total weight of the composition.
10. Flame retardant polyamide composition according to any of claims 1 – 9, comprising 5 – 25 wt.% of flame retardant (C), and 5 – 60 wt.% of glass or 15 carbon fibre reinforcement, wherein the wt.% are relative to the total weight of the composition.
11. Process for the production of moulded parts from a flame retardant polyamide composition by injection moulding, comprising a step wherein the composition is heated in an injection moulding machine to form a polymer melt, 20 characterized in that the composition is a the flame retardant polyamide composition according to any one of claims 1 – 10, comprising a semi-crystalline semi-aromatic polyamide (A) having a melting temperature (TmA); and a semi-crystalline aliphatic polyamide (B) having a melting temperature (TmB); and wherein the melt is heated to a temperature of at most 10°C 25 above TmA.
12. Process according to claim 11, wherein the polymer melt is injected into a mould with a mould temperature of at least 100°C, preferably in the range of 110 – 150°C.
13. Article made from a composition according to any of claims 1-10.
- 30 14. Article according to claim 13, being a plastic part for a connector.
15. Article according to claim 13, being a housing or a stiffener frame for an electronic device.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/064467

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08L77/02 C08L77/06
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>GOTO S ET AL: "Polyamide resin composition for electrical and electronic components, consists of polyamide resin, melamine-phosphoric acid addition product, specific phosphinic and/or diphosphine acid salt, and inorganic filler", WPI / THOMSON,, vol. 2005, no. 2, 28 October 2004 (2004-10-28), XP002648553, abstract -& JP 2004 300189 A (ASAHI CHEMICAL CORP) 28 October 2004 (2004-10-28) paragraph [0014] examples 4,5; table 1</p> <p style="text-align: center;">-----</p> <p style="text-align: center;">-/-</p>	1-15

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
17 August 2012	29/08/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Russell, Graham

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/064467

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2011/105655 A1 (HARDER PHILIPP [CH] ET AL) 5 May 2011 (2011-05-05) paragraph [0011] - paragraph [0012] examples 1,3; table 1 claims 1,3.10 paragraph [0045] - paragraph [0051] -----	1-15
A	US 2010/249292 A1 (SAGA YUJI [JP] ET AL) 30 September 2010 (2010-09-30) paragraph [0023] paragraph [0025] example 3; table 2 claims 1-5 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/064467

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
JP 2004300189	A	28-10-2004	NONE		
US 2011105655	A1	05-05-2011	CN	101910259 A	08-12-2010
			EP	2060596 A1	20-05-2009
			JP	2011503306 A	27-01-2011
			KR	20100098370 A	06-09-2010
			US	2011105655 A1	05-05-2011
			WO	2009062691 A1	22-05-2009
US 2010249292	A1	30-09-2010	CN	102378784 A	14-03-2012
			EP	2414446 A1	08-02-2012
			KR	20110137381 A	22-12-2011
			US	2010249292 A1	30-09-2010
			WO	2010117708 A1	14-10-2010