

COMPOSITIONS BASED ON FLAME-RETARDED POLYAMIDE

The present invention relates to new compositions based on polyamide flame-retarded by means of red phosphorus, which compositions are intended in particular for the production of articles for the electrical and electronics industries. More particularly, it relates to compositions leading to flame-retarded articles which offer a good compromise of properties, in particular with regard to fire resistance, resilience, resistance to arc tracking and surface appearance, and low corrosiveness.

It is known that the addition of red phosphorus to compositions based on polyamide makes it possible to obtain a high degree of flame retardancy.

In US Patent No. 3,883,475, compositions based on flame-retarded polyamide were described in which the aim was to prevent the evolution of highly toxic phosphine, which forms following a disproportionation reaction of red phosphorus under the action of the traces of water present in the polymer and of the high heat necessary for its conversion, by adding to the composition a metal compound which advantageously consists of cupric oxide.

An improvement, consisting in making use of cadmium oxide instead of CuO , was proposed in French Patent No. 2,367,100; in addition to its effectiveness (at least equal to that of CuO) in preventing the evolution of phosphine, cadmium oxide leads to articles



which have a particularly high resistance to arc tracking (within the meaning of French Standard NF C 26220), which is equal to or greater than 400 volts in the case of compositions containing no fillers
5 and equal to or greater than 375 volts in the case of compositions filled with more than 25 % by weight of glass fibres.

A replacement product for cadmium oxide (which has some toxicity), consisting of a compound
10 based on lanthanide, was proposed in French Patents Nos. 2,553,783 and 2,621,594. With this adjuvant, the compositions based on flame-retarded polyamide which are obtained lead to articles which offer a compromise of properties, in particular with regard to flame
15 retardancy, resilience and resistance to arc tracking, which is better than that associated with the use of cadmium oxide.

However, these compositions flame-retarded by means of red phosphorus and optionally comprising other
20 components to prevent the evolution of phosphine have a certain corrosiveness with respect to parts based on metal material which are in contact with the polymer or inserted, for example by moulding, in an article moulded with these compositions. This phenomenon is
25 observed in particular with moulded parts used in the electrical or electronics field to support metal contacts, for example copper contacts.

One of the aims of the present invention is,

in particular, to overcome these disadvantages by providing a composition based on flame-retarded polyamide which has good mechanical properties as well as good resistance to electric arc tracking and low
5 corrosiveness to metals.

To this end, the invention provides a composition which is based on polyamide and contains red phosphorus as flame retardant, characterised in that it comprises an additive consisting of a zinc
10 compound chosen from the group comprising zinc oxide, oxygen-containing zinc salts and zinc sulphide. A mixture of at least two of these compounds may be used.

According to a preferred embodiment of the invention, the zinc compound content, expressed as
15 weight of zinc with respect to the weight of red phosphorus, is between about 10 % and about 100 %. Preferably this content is between 20 % and 80 % and advantageously between 40 and 80 %.

The polyamide composition may comprise a
20 filler such as an inorganic filler.

Inorganic fillers which may be mentioned by way of example are mineral fibres, such as glass or asbestos fibres, glass microbeads, silica, micas, kaolin, bentonites or a mixture of these.

25 According to another preferred characteristic of the invention, the zinc compound is a zinc borate or a mixture of zinc borate and zinc oxide. When it is used in a polyamide composition filled with glass

fibres, this compound has, in particular, the advantage of not substantially affecting the mechanical properties of the composition. Thus, the impact strength of the polyamide composition filled with glass fibres is not substantially affected by the incorporation of zinc borate.

According to a preferred embodiment of the invention, the composition comprises a mixture of zinc borate and zinc oxide in concentrations by weight expressed as metallic Zn with respect to phosphorus of between 15 and 60 % for zinc oxide and 15 to 40 % for zinc borate. Of course, the total concentration of zinc compounds is within the ranges given above.

The polyamides to be flame-retarded which are suitable for the present invention comprise, in particular: the polyamides obtained by a polycondensation reaction of saturated aliphatic dicarboxylic acids having from 6 to 12 carbon atoms with saturated aliphatic diprimary diamines having from 6 to 12 carbon atoms; the polyaminoacids obtained either by a direct homopolycondensation reaction of ω -aminoalkanoic acid containing a hydrocarbon chain having from 4 to 12 carbon atoms or by hydrolytic opening and polymerisation of the lactams derived from said acids; the copolyamides obtained from the starting monomers of the abovementioned polyamides, it being possible for the acid component of said copolyamides also to consist in part of terephthalic acid and/or

isophthalic acid; and the mixtures of such polyamides.

The following may be mentioned, for example, by way of illustration of the polyamides obtained by a polycondensation reaction of diacids and diamines:

5 nylon 6,6 (polymer of hexamethylenediamine and adipic acid), nylon 6,9 (polymer of hexamethylenediamine and azelaic acid), nylon 6,10 (polymer of hexamethylene-diamine and sebacic acid) and nylon 6,12 (polymer of hexamethylenediamine and dodecanedioic acid).

10 The following may be mentioned by way of illustration of the polyamino acids which may be suitable: nylon 4 (polymer of 4-aminobutanoic acid or of γ -butyrolactam), nylon 5 (polymer of 5-aminopentanoic acid or of δ -amylolactam) nylon 6
15 (polymer of ϵ -caprolactam), nylon 7 (polymer of 7-aminoheptanoic acid), nylon 8 (polymer of capryllactam), nylon 9 (polymer of 9-aminononanoic acid), nylon 10 (polymer of 10-aminodecanoic acid), nylon 11 (polymer of 11-aminoundecanoic acid) and nylon
20 12 (polymer of 12-aminododecanoic acid or of lauryllactam).

The following may be mentioned, for example, by way of illustration of copolyamides: nylon 6,6/6,10 (copolymer of hexamethylenediamine, adipic acid and
25 sebacic acid) and nylon 6,6/6 (copolymer of hexamethylenediamine, adipic acid and caprolactam).

The polyamides to be flame-retarded which are preferred for the present invention are nylon 6,6,

nylon 6,10, nylon 6, nylon 6,6/6,10 and nylon 6,6/6.

The term "red phosphorus" within the meaning of the present invention denotes the diverse coloured allotropic varieties of phosphorus (red, violet or
5 black phosphorus) marketed under the name red phosphorus.

The amount of red phosphorus is generally between 1 and 30 % by weight with respect to the weight of the polyamide to be flame-retarded. Preferably, this
10 amount is between 2 and 15 % by weight. Still more preferentially, this amount is between 4 and 10 %. In general, it is desirable to use red phosphorus in finely divided form, for example in the form of particles having an average diameter not exceeding
15 200 μm and preferably of between 1 and 100 μm .

The red phosphorus may be used either as such or in the form of red phosphorus particles coated by means of a polymer skin. Amongst these polymers, the following may be mentioned in particular: epoxy resins
20 (cf. French Patent No. 2,314,221), polymers having maleic, fumaric or allyl unsaturated bonds (cf. French Patent No. 2,314,219), saturated polyesters with a melting point of between 50° and 90°C and a molecular mass of less than 10,000 (cf. French Patent
25 No. 2,373,575), thermoplastic phenol-formaldehyde polycondensation products of the novolac type (cf. French Patent No. 2,344,615) and thermoplastic phenol-isobutyraldehyde polycondensation products (cf.

European Patent Application No. 82.106329.4, published under the No. 0,071,788); the use of thermoplastic phenol-formaldehyde polycondensation products is a particularly preferred measure for implementation of the present invention. The amount of polymer used, if necessary, to coat the phosphorus particles may vary within wide limits. Generally this amount represents 5 to 50 % of the total weight of the red phosphorus/coating polymer mixture. It should be pointed out that larger amounts of coating polymer, which can range up to 90 % of the total weight of the red phosphorus/coating polymer mixture, may be used without disadvantage.

The zinc compounds are added to the composition of the invention in diverse forms, such as, for example, in powder form. They may also be in crystalline form or in anhydrous or amorphous form. Advantageously, the zinc compounds must be stable or substantially stable at the temperature at which the composition is converted and at the normal use temperatures of said compositions. The characteristics of this powder are not critical. Thus, the shape, the size and the methods for introducing and mixing the zinc compound in the polyamide composition are determined as a function of the usual criteria for the production of a thermoplastic polymer composition intended to be converted by any process, for example by moulding, extrusion or injection moulding. Thus, it is

preferred to use a powder or a material having a fine particle size, the effect being generally better when the particle size of the powder is finer.

The suitable processes for the preparation of these compositions are those conventionally used in the production of polyamide-based compositions.

Thus, the compositions according to the present invention may be prepared by simple mixing of the various constituents in any appropriate ways enabling a homogeneous composition to be obtained. Preferentially, mixing of the diverse constituents in powder or granule form is performed by first carrying out premixing in the cold in a conventional mixer and then homogenizing the whole by hot blending in a single-screw or multiple-screw extruder, the extrusion preferably being carried out under an inert atmosphere such as, for example, nitrogen or argon. At the end of this treatment, rods are obtained which are cooled in water and then cut into granules, it being possible for the latter then to be subjected to drying, if appropriate. The compositions according to the invention may also be prepared by making up a master mix, prepared in the form of granules based on a portion of the polyamide to be flame-retarded, red phosphorus and the zinc compound, which will then be mixed, before use, with granules of the remainder of the polyamide to be flame-retarded.

These compositions have been defined above by

their essential constituents. It goes without saying that it would not depart from the scope of the invention to modify these compositions in the indicated manner.

5 By way of examples, when they are intended for the production of shaped articles, the compositions according to the invention may contain diverse additives: they may thus contain, as described above, reinforcing or gelling fillers, such as glass or
10 asbestos fibres, glass microbeads, kaolin, silica, micas, bentonites, bentones or mixtures of these species. Amongst the abovementioned fillers, glass fibres are most commonly used; these fibres in general have an average diameter of between 1 and 15 μ m and a
15 length of between 2 and 8 mm. In order to obtain articles endowed with optimum mechanical properties, it is advantageous to use fibres sized, for example, using epoxy resins, polyester resins, polyurethane resins or vinyl resins, these resins generally being combined
20 with coupling agents of the aminosilane type. The proportions of fillers may vary between, for example, 10 % and 60 % by weight with respect to the weight of the polyamide in the composition.

 It is also possible to make use of other
25 additives, such as lubricants, stabilizers, impact modifiers, pigments or dyes, antistatic agents, crystallizing agents and agents which stabilize red phosphorus: these additives and their use are

extensively described in the literature.

The compositions according to the invention may be converted into finished or semifinished articles by use of the customary injection or extrusion techniques, for example.

The compositions of the invention have the advantages of compositions flame-retarded with red phosphorus, that is to say a fire resistance and combustibility according to "Underwriters Laboratories" UL 94 vertical test (for test pieces 1.6 mm thick) within the classification range V0 to V1. This property is even improved compared with that of compositions without zinc compounds.

However, the presence of the zinc compound improves the resistance to electric arc tracking (the property being designated IRC). This resistance may be greater than 600 volts in the case of the compositions filled with at least 25 % by weight of glass fibre.

In addition, the compositions of the invention has a much lower corrosiveness towards metal materials, such as copper, than do compositions without zinc compounds. These improvements are observed to a high degree when the composition contains a black colorant. The aggressive nature of the compositions is illustrated by the following test:

150 g of compound, in the form of granules, containing the composition to be tested are added to a leaktight vessel.

Metal test pieces made of copper, brass, silver and bronze are suspended in the vessel above the compound.

The whole is heated at 125°C for 336 hours.

5 The degree of corrosion is determined by determining the change (generally the increase) in the weight of the test pieces.

The other properties are determined in accordance with the methods below:

10 - Arc propagation resistance (IRC) in volts:

method termed the "KC technique" described in DIN standard 53480/1972.

- Behaviour on combustion (UL 94):

15 method for determining the vertical combustion in accordance with the standard UL 94 using test pieces 1.6 mm thick, which are assessed:

- after conditioning for 48 hours under 50 % relative humidity, and
20 - after conditioning for one week at 70°C.

- Migration:

25 Plates of compound 100 mm x 100 mm in size and 3.2 mm thick are arranged in a chamber containing a sulphuric acid solution in order to obtain a degree of humidity of 93 %.

The plates are subjected to 17 24-hour cycles comprising 8 hours at 70°C and 16 h at 23°C. Each plate is then washed with 400 ml of

water for 4 hours at 40°C. The conductivity of the wash water is determined.

- Charpy impact strength: determined in accordance with ISO standard 179

5 The flame-retarded compositions according to the present invention are particularly suitable for the production of shaped articles which can be used in the electricity industries (for example the electrical and electronics, electric household appliances, radio and
10 automotive industries). The characteristics of these compositions also make it possible to manufacture articles by extrusion and film-forming.

 The invention will be illustrated by the examples below which are given solely by way of
15 nonlimiting example.

 The compositions of the invention are obtained by mixing the constituents of the composition in a Werner Pfleiderer type ZSK 40 extruder, the glass fibres being fed by a Werner ZSB twin feed screw.

20 The extruder has a screw rotating at a speed of 250 revolutions per minute at a temperature of 280°C and with a throughput of 70 kg/h. The degassing pressure is 56×10^2 Pa.

 The starting materials used are:

- 25 - nylon 6,6 (polymer of hexamethylenediamine and adipic acid): this is a product which has a viscosity index of 133 ml/g (determined in accordance with ISO standard R 307, 1977 edition,

- on the soluble fraction in 90 % formic acid);
- R 23 Dxl glass fibres marketed by Owens Corning Fiberglass; these are present in a concentration of 25 % by weight,
 - 5 - a lubricant: aluminium stearate in a concentration of 0.4 % by weight,
 - a colorant marketed by Williams under the name Nigrosine Oisol Black N in a concentration of 1.16 % by weight,
 - 10 - a flame retardant consisting of red phosphorus marketed under the name CPC 400 by Wilbright and Wilson, and
 - a zinc compound chosen from the group comprising zinc borate, zinc sulphide and zinc oxide. These
 - 15 compounds may be either anhydrous or in crystalline form.

The various compositions and their properties are collated in Table 1 below. The concentrations are expressed as percentage by weight of compound with

20 respect to the mass of final composition. The zinc oxide is an anhydrous oxide and the zinc borate is a hydrate.

Ex.	PA %	Phosphorus %	Zn compounds %	Viscosity	UL 94	Migration μ siemens	Charpy impact strength kJ/m^2	IRC (V)
1 Ref.	62.34	4.2	---	150	V1	41.1	63.2	425
2	59.14	5.1	ZnO : 1.2	159	V1	29.3	42.2	475
3	59.16	4.5	Zn borate : 2.6	161	V0	24.3	49.3	500
4	59.74	4.2	Zn borate : 2.6	147	V1	18.5	51.1	550
5	56.80	4.0	ZnO : 1.2 Zn borate : 2.6	153	V1	7	43.8	575
6	58.54	4.2	ZnO : 1.2 Zn borate : 2.6	139	V2	13	40.1	≥ 600
7	61.18	4.8	ZnO : 2 Zn borate : 3	137	V1	5	38	600

TABLE 1

Another series of compositions was produced using as flame retardant a red phosphorus coated with a phenol-formaldehyde resin. This composition contains 60 % by weight of red phosphorus which has an average 5 particle size of 20 to 30 μm and is coated with 40 % by weight of the phenol-formaldehyde polycondensation product which has a melting point of 80°C and a molecular weight of 800. The results obtained are collated in Table 2 below.

Ex.	PA % by weight	Phosphorus % by weight	Zn compounds % by weight	Viscosity	UL 94	Migration μ siemens	Charpy impact strength kJ/m^2	IRC (V)
8	64.42	7.6	Zns : 0.32	148	V1	16.5	40	425
9	63.34	7.6	ZnS : 0.5	143	V0	16.5	38	475
10	61.24	8.5	Zn borate : 2.6	129	V1	6.5	38.4	350

TABLE 2

The results of the corrosion test are given below (increase in the weight of the test pieces in mg):

Ex.	Test pieces				
	Copper	Brass	Bronze	Silver	
5	1	5.3	1.3	10	2.2
	2	6.5	2	12	1.1
	3	4	0.6	2.7	0.1
	4	1.5	0.6	1.5	0.4
	5	4.6	0.6	1.3	0.1
10	6	2.3	0.2	10.5	0.2
	7	1.1	0.4	1.1	0.1
	8	18.2	15.4	12	2.5
	9	14	4.3	14.7	2.2
	10	8.3	0.8	4	0.2

15 These results clearly show the effect of the addition of the zinc compounds on the corrosiveness of the polyamide compositions towards metals, as well as the reduction in migration phenomena.

CLAIMS

1. Composition based on polyamide and containing red phosphorus as a flame retardant, characterized in that it comprises a zinc oxide and/or
5 a zinc salt chosen from the group comprising the oxygen-containing zinc salts and the sulphides.
2. Composition according to Claim 1, characterized in that the oxygen-containing zinc salt is a zinc borate.
- 10 3. Composition according to Claim 1, characterized in that it comprises, as additive, a mixture of zinc borate and zinc oxide.
4. Composition according to one of the preceding claims, characterized in that it comprises
15 from 10 % to 100 % of zinc compounds (expressed as mass of metal) with respect to the mass of red phosphorus, preferably between 20 % and 80 %.
5. Composition according to Claim 4, characterized in that it comprises from 40 to 80 % by
20 weight of zinc compounds (expressed as mass of metal) with respect to the mass of red phosphorus.
6. Composition according to one of Claims 3 to 5, characterized in that the zinc borate concentration is between 15 and 40 % and the zinc oxide
25 concentration is between 15 and 60 %, said concentrations being expressed as mass of Zn with respect to the weight of red phosphorus.
7. Composition according to one of the



preceding claims, characterized in that the red phosphorus is coated in a resin.

8. Composition according to one of the preceding claims, characterized in that it contains an
5 inorganic filler.

9. Composition according to Claim 8, characterized in that the inorganic filler is glass fibre.

10. Composition according to one of the preceding claims, characterized in that it contains at
10 least one lubricant.

11. Article obtained by moulding a composition according to one of the preceding claims..

