

The present invention relates to new compositions based on polyamide made fire-resistant by means of red phosphorus and intended especially for the manufacture of articles for the electrical and electronics industries. More particularly, it relates to compositions leading to fire-resistant articles offering a good compromise of properties in particular with regard to fire resistance, resilience, arc tracking resistance and surface appearance.

It is known that the addition of red phosphorus into polyamide-based compositions makes it possible to attain a high degree of fire resistance.

In US Patent US-A-3,883,475 there is a description of compositions based on fire-resistant polyamide, in which attempts have been made to inhibit the release of highly toxic phosphine, which is formed following a disproportionation reaction of red phosphorus under the action of the traces of water which are present in the polymer and of the high heat needed for its conversion, by addition to the composition of a metal compound advantageously consisting of cupric oxide.

In French Patent FR-A-2,367,100 an improvement has been proposed, consisting of the use of cadmium oxide instead of CuO ; in addition to its effectiveness (at least equal to that of CuO) for inhibiting the release of phosphine, cadmium oxide also produces articles exhibiting a particularly high arc tracking resistance (within the meaning of the NF standard C 26220), which is equal to or higher than 400 volts in the case of unfilled compositions and 375 volts in the case of compositions filled with approximately 40 % by weight of glass fibres relative to the weight of the polyamide of the compositions.

In French Patent FR-A-2,553,783 a replacement product has been proposed for cadmium oxide (which exhibits a certain toxicity), consisting of a lanthanide-based compound. With this adjuvant, the compositions based on fire-resistant polyamide which are obtained result in articles offering a compromise of properties,

in particular with regard to fire resistance, resilience and arc tracking resistance, which is better than that associated with the use of cadmium oxide.

However, there still remains to be solved a problem concerning the appearance and the development, to a variable degree, of whitish stains (whitish exudations) on the surface of articles made fire-resistant with the aid of red phosphorus, when these articles are subjected to the twin effect of a high temperature and of humidity. Such a deterioration of the articles in question is encountered, for example, in hot and humid tropical countries.

Continuing work in this field of technology and attempting, in particular, to improve further the fire-resistant compositions in accordance with the teaching of the abovementioned French Patent FR-A-2,553,783, the Applicant Company has now found that the phenomenon of the appearance and development of stains just referred to can be counteracted, and moreover without appreciable disadvantage to the values of the properties in respect of fire resistance, resilience and arc tracking resistance, by making use of a judiciously chosen stabilizer consisting of a hydrotalcite.

More precisely, the present invention relates to compositions based on polyamide made fire-resistant by means of red phosphorus and comprising at least one lanthanide-I or yttrium-based compound, which are characterized in that they additionally comprise an effective quantity of between 0.1 and 5 % by weight, relative to the weight of the polyamide present in the composition, of at least one hydrotalcite of general formula:



in which:

A denotes the anion SO_4^{2-} or CO_3^{2-} ,

a is a number which satisfies the relationship:

$$0 < a < 0.5,$$

p is a number representing the number of molecules of water per molecule of hydrotalcite, which satisfies the

relationship:

$$0 < p < 1.$$

Among the hydrotalcites of formula (I), preference will be given to hydrotalcites in which A denotes CO_3^{2-} . Still more preferably, use will be made of the hydrotalcites of formula (I) in which A denotes CO_3^{2-} and a is a number which satisfies the relationship $0.2 < a < 0.4$.

These hydrotalcites include natural hydrotalcites and hydrotalcites obtained by treatment of natural hydrotalcites. These hydrotalcites are particularly described in French Patent FR-A-2,483,934.

The polyamides to be made fire-resistant and aimed at in the present invention comprise: the polyamides obtained by polycondensation of saturated aliphatic dicarboxylic acids containing from 6 to 12 carbon atoms with saturated aliphatic diprimary diamines containing from 6 to 12 carbon atoms, the polyaminoacids obtained either by direct homopolycondensation of ω -aminoalkanoic acid comprising a hydrocarbon chain containing from 4 to 12 carbon atoms, or by hydrolytic opening and polymerization of the lactams derived from these acids, and the copolyamides obtained from the starting monomers of the abovementioned polyamides, it being additionally possible for the acidic component of these copolyamides to consist partly of terephthalic acid and/or of isophthalic acid, and mixtures of such polyamides.

By way of illustration of the polyamides obtained by polycondensation of diacids and of diamines there will be mentioned, for example: nylon 66 (polymer of hexamethylenediamine and of adipic acid), nylon 69 (polymer of hexamethylenediamine and of azelaic acid), nylon 610 (polymer of hexamethylenediamine and of sebacic acid), and nylon 612 (polymer of hexamethylenediamine and of dodecanedioic acid).

By way of illustration of the polyaminoacids which may be suitable there will be mentioned: nylon 4 (polymer of 4-aminobutanoic acid or of γ -butyrolactam),

nylon 5 (polymer of 5-aminopentanoic acid or of δ -amylolactam), nylon 6 (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 12 (polymer of 12-aminododecanoic acid or of lauro lactam).

By way of illustration of the copolyamides there will be mentioned, for example: nylon 66/610 (copolymer of hexamethylenediamine, adipic acid and sebacic acid), nylon 66/6 (copolymer of hexamethylenediamine, adipic acid and caprolactam).

The polyamides to be made fire-resistant which are very particularly aimed at in the present invention are nylon 66, nylon 610, nylon 6, nylon 66/610 and nylon 66/6.

Within the meaning of the present invention, the expression "red phosphorus" refers to the various coloured allotropic varieties of phosphorus (red, violet or black phosphorus) marketed under the name of red phosphorus.

The quantity of red phosphorus is generally between 1 and 30 % by weight relative to the weight of the polyamide to be made fire-resistant. This quantity is preferably between 2 and 15 % by weight. Still more preferably, this quantity is between 6 and 12 %. As a general rule, it is desirable to employ red phosphorus in a finely divided form, for example in the form of particles with a mean diameter exceeding 200 μm and preferably between 1 and 100 μm .

In the present specification the name lanthanide will be applied to the metals of the Periodic Classification of the elements having atomic numbers ranging from 57 to 71, and to yttrium, which has closely related properties, despite having an atomic number of 39.

The expression "lanthanide-I or yttrium-based compound" given above means:

- an organic or inorganic derivative of any one of the lanthanides: cerium, lanthanum, praseodymium, neodymium,

promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thulium and lutetium and of yttrium; the expression "at least one lanthanide- or yttrium-based compound" then means that, apart from a single derivative, it is possible to use a mixture of organic derivatives or a mixture of inorganic derivatives or a mixture of organic and inorganic derivatives of any one of the abovementioned elements;

- a mixture of organic and/or inorganic derivatives of a number of these lanthanides; the expression "at least one lanthanide-based compound" means that, apart from a single mixture, it is possible to use a combination of several mixtures of this type.

In general, because of the relative quantities of the compounds of the various lanthanides in the most common ores, especially in monazite and bastnaesite, when a derivative of a single lanthanide is used, the latter is preferably cerium, lanthanum, praseodymium and neodymium. Cerium and lanthanum are the most abundant of these metals and are very particularly suitable.

Mixtures of derivatives of a number of lanthanides may also be employed. It may be advantageous, in fact, not to carry out the long and costly separation of all the lanthanides present in relatively small quantities in the ores which are generally treated. In such cases, use is generally made of the following mixtures:

- mixture of derivatives of cerium and of one or more of the other lanthanides;
- mixture of derivatives of lanthanum and of one or more other lanthanides chosen from praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thulium, lutetium and yttrium;
- mixture of derivatives of praseodymium and of one or more other lanthanides chosen from neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thulium, lutetium or yttrium;
- mixture of derivatives of neodymium and of one or more other lanthanides chosen from promethium, samarium,

europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thulium, lutetium or yttrium.

When such mixtures of derivatives of a number of lanthanides are used in the compositions according to the invention, cerium and/or lanthanum and/or praseodymium and/or neodymium generally represent at least 40 mol% of the total lanthanides.

An organic lanthanide derivative means more particularly the salts of various carboxylic acids, the metal derivatives of phenolic compounds, mercaptides and chelates of β -dicarbonyl compounds.

More precisely, the organic lanthanide derivatives are chosen from:

- the lanthanide salts of:

monocarboxylic aliphatic acids containing from 2 to 30 carbon atoms or dicarboxylic aliphatic acids containing from 3 to 30 carbon atoms, saturated or containing one or more ethylenic double bonds and capable of containing 1 or more substituents such as halogen atoms, hydroxyl groups, alkoxy groups containing from 1 to 12 carbon atoms, mercapto groups, phenyl, phenoxy, naphthyl or cyclohexyl groups, whose rings are optionally substituted by one or more halogen atoms, hydroxyl groups, alkyl groups containing 1 to 6 carbon atoms or alkoxy groups containing 1 to 6 carbon atoms; benzoic, 1-naphthoic, 2-naphthoic, cyclopentanecarboxylic, cyclohexanecarboxylic, cyclopentenecarboxylic or cyclohexenecarboxylic acids, it being possible for the cyclic parts of these acids to comprise one or more substituents such as halogen atoms, hydroxyl groups, alkyl groups containing 1 to 12 carbon atoms, alkenyl groups containing 2 to 12 carbon atoms, alkoxy groups containing 1 to 12 carbon atoms, phenyl, benzyl, phenoxy or cyclohexyl

groups, alkoxycarbonyl groups containing 2 to 24 carbon atoms or alkenoxycarbonyl groups containing 4 to 24 carbon atoms; alkyl monoesters (the alkyl group containing 1 to 24 carbon atoms) or alkenyl monoesters (the alkenyl group containing 3 to 24 carbon atoms) of the dicarboxylic aliphatic acids indicated above;

heterocyclic carboxylic acids, especially those derived from pyridine, furan, thiophene, pyrrole and pyran, capable of containing one or more substituents such as halogen atoms, hydroxyl groups, alkyl groups containing 1 to 12 carbon atoms, alkoxy groups containing 1 to 12 carbon atoms, alkenyl groups containing 2 to 12 carbon atoms, alkoxycarbonyl groups containing 2 to 24 carbon atoms or alkenoxycarbonyl groups containing 4 to 24 carbon atoms;

- lanthanide phenolates derived from phenol, 1-naphthol or 2-naphthol, whose cyclic parts may contain one or more substituents such as halogen atoms, alkyl or alkoxy groups containing 1 to 24 carbon atoms, alkenyl groups containing 2 to 24 carbon atoms, phenyl, benzyl, phenoxy or cyclohexyl groups;

- lanthanide mercaptides, especially those derived from thioglycolic or thiomalic acids and their alkyl esters (the alkyl radical containing 1 to 12 atoms), alkenyl esters (the alkenyl radical containing 2 to 12 carbon atoms), phenyl, benzyl, cyclohexyl, alkane-diol (containing 2 to 12 carbon atoms), dihydroxybenzene, or dihydroxycyclohexane esters, it being possible for the cyclic parts of the said esters to be substituted by one or more alkyl or alkoxy radicals containing from 1 to 6 carbon atoms;

- the lanthanide chelates of β -dicarbonyl compounds, especially those derived from the compounds of general formula (II):



in which:

- R_1 and R_3 , which are identical or different, denote:

- a linear or branched alkyl group containing 1 to 36 carbon atoms, optionally substituted by one or more halogen atoms,

- a linear or branched alkenyl group containing 3 to 36 carbon atoms, optionally substituted by one or more halogen atoms,

- an aryl radical or an aryl radical carrying on the aromatic ring one or more substituents such as:

- alkyl radicals containing 1 to 6 carbon atoms, optionally substituted by one or more halogen atoms,

- alkenyl radicals containing 2 to 6 carbon atoms, optionally substituted by one or more halogen atoms,

- the nitro group,

- the -CHO group,

- the -COOH group,

- alkoxy groups containing 1 to 6 carbon atoms,

- COOR₄ groups, R₄ being an alkyl radical containing 1 to 12 carbon atoms or alkenyl radical containing 2 to 12 carbon atoms,

- the OH group,

- halogen atoms,

- an aralkyl radical in which the aliphatic part contains from 1 to 12 carbon atoms and in which the cyclic part may contain one or more of the substituents indicated above,

- a cycloaliphatic radical containing from 5 to 12 carbon atoms and whose cyclic part may contain one or more carbon-carbon double bonds and carry one or more of the substituents indicated above,

a chain sequence of a number of the radicals indicated above,

it being possible for the various aliphatic radicals defined above to contain one or more oxygen -O- or sulphur -S- atoms or carbonyl -CO- or carboxylate -COO- groups;

- R₂ denotes a halogen atom.

Among the organic lanthanide derivatives which can be employed in the compositions according to the invention, those frequently chosen, in particular for practical reasons or for economic reasons of availability or of price are:

- the lanthanide salts:

of monocarboxylic aliphatic acids containing from 6 to 24 carbon atoms, saturated or containing an ethylenic double bond, and capable of containing one or more substituents such as chlorine atoms, hydroxyl groups, alkoxy groups containing from 1 to 6 carbon atoms, phenyl, phenoxy or cyclohexyl groups, these cyclic groups being optionally substituted by one or more chlorine atoms, hydroxyl groups, alkyl or alkoxy groups containing 1 to 6 carbon atoms;

mercaptomonocarboxylic acids containing from 2 to 6 carbon atoms or mercaptodicarboxylic acids containing from 3 to 6 carbon atoms;

benzoic or cyclohexanecarboxylic acids whose cyclic part may contain one or more substituents such as chlorine atoms, hydroxyl groups, alkyl or alkoxy groups containing 1 to 6 carbon atoms or alkoxycarbonyl groups containing 2 to 12 carbon atoms;

alkyl monoesters (the alkyl group containing 1 to 12 carbon atoms) of dicarboxylic aliphatic acids containing 4 to 24 carbon atoms, saturated or containing an ethylenic double bond and capable of containing one or more substituents such as chlorine atoms,

hydroxyl groups, mercapto groups or alkoxy groups containing 1 to 6 carbon atoms;

- lanthanide phenolates derived from phenol, whose ring may contain one or more substituents such as chlorine atoms, alkyl or alkoxy groups containing 1 to 12 carbon atoms, or phenyl, benzyl, phenoxy or cyclohexyl groups.

By way of nonlimiting examples of organic lanthanide derivatives there may be mentioned:

- lanthanide, especially cerium, lanthanum, praseodymium and neodymium salts of propionic, hexanoic, n-octanoic, 2-ethylhexanoic, isooctanoic, nonanoic, decanoic, lauric, stearic, oleic, ricinoleic, margaric, tetradecanoic, 12-hydroxystearic, docosanoic, 13-docosenoic (erucic acid), 2-chlorodecanoic, 2-octyldecanoic, 2-hydroxyhexanoic, thioglycolic, mercaptopropionic, thiomalic, 6-cyclohexylhexanoic, benzoic, phenylacetic, 2-phenylpropanoic, 2-methylbenzoic, 4-methylbenzoic, 2-phenoxybenzoic, 4-propylbenzoic, 4-methoxybenzoic, 4-tert-butylbenzoic, salicylic, 5-tert-butylsalicylic, 4-hydroxy-3-methoxybenzoic, 3,4-dimethoxybenzoic, 1-naphthoic, 2-naphthoic, cyclohexanecarboxylic, nicotinic, isonicotinic and 4-methyl-3-furancarboxylic acids, of monoisooctyl maleate, of mono(2-ethoxyethyl) maleate, of monobutyl phthalate, of monobutyl thiomalate and of monohexyl thiomalate;
- lanthanide, especially cerium, lanthanum, praseodymium and neodymium phenolates of the following phenolic compounds: phenol, cresols, ethylphenols, xylenols, butylphenols, isopentylphenols, isooctylphenols, tert-nonylphenols,

decylphenols, dodecylphenols, tert-octylphenols, 4-cyclohexylphenol, 4-phenylphenol, di-tert-nonylphenols and methylisohexylphenols;

- lanthanide, especially cerium, lanthanum, praseodymium and neodymium chelates of the following β -diketones: 2,4-heptanedione, 2,4-decanedione, 2-ethyl-2-decene-6,8-dione, 2-methyl-2-nonene-6,8-dione, stearylacetone, 1-stearyl-2-octanone, ethyl 7,9-dioxodecanoate, benzoylacetone, acetylacetone, 1-benzoyl-2-octanone, 1,4-diphenyl-1,3-butanedione, stearylacetophenone, palmitoylacetophenone, 1-benzoyl-4-methylpentanone, benzoyl-octacosanoylmethane, para-methoxy-benzoylstearyl-methane and dibenzoylmethane;
- lanthanide, especially cerium, lanthanum, praseodymium and neodymium mercaptides of thioglicolic acid, of isooctyl thioglycolate, of octadecyl thioglycolate, of benzyl thioglycolate, of lauryl thioglycolate, of 1,4-cyclohexanediol dithioglycolate, of 4-tert-butylcyclohexyl thioglycolate, of thiomalic acid, of hexyl thiomalate, of 2-ethylhexyl thiomalate, of dodecyl thiomalate, of benzyl thiomalate, of cyclohexyl thiomalate, of 1,3-propanediol thiomalate, of 1,4-butanediol thiomalate and of 1,6-hexanediol thiomalate.

Organic lanthanide derivatives which are not available directly are prepared by classical methods such as the reaction of a carboxylic acid or of its anhydride, of a phenolic compound, of a mercaptocarboxylic acid (or of one of its esters) or of a β -diketone with a lanthanide oxide or hydroxide or, as the case may be, with a mixture of such oxides or hydroxides, in a suitable solvent medium and with heating if necessary.

An inorganic lanthanide derivative means more

particularly the oxides, the hydroxides, the salts of inorganic hydracids and the salts of inorganic oxyacids.

More precisely, there are employed, for example, as lanthanide salts of inorganic hydracids: the chloride, bromide, iodide, sulphide, selenide and telluride; as lanthanide salts of inorganic oxyacids: the sulphite, sulphate, sulphonate, nitrite, nitrate, phosphite, phosphate, pyrophosphate, carbonate, perchlorate, antimonate, arsenate, selenite, selenate, vanadate and tungstate.

Among the inorganic lanthanide derivatives which can be employed in the compositions according to the invention, those frequently chosen, in particular for practical reasons or for economic reasons of availability or price, are lanthanide oxides, chlorides, sulphates or nitrates.

In the lanthanide derivatives employed in compositions according to the invention, the lanthanide may be present in the various oxidation states which it can have; in most cases it is in the oxidation states of III or IV.

In accordance with a highly preferred embodiment of the present invention, use is made of an effective quantity of at least one lanthanum-based compound chosen from lanthanum(III) stearate, lanthanum(III) oxide, lanthanum(III) chloride, cerium(III) stearate, cerium(IV) oxide and cerium(III) chloride.

The quantity of lanthanide-based compound(s) which is used can vary within very wide limits. More precisely, this quantity is determined so as to contribute from 0.1×10^{-3} to 100×10^{-3} gram-atoms of metal belonging to the lanthanide group per 100 g of polyamide. This quantity is preferably determined so as to contribute from 0.2×10^{-3} to 30×10^{-3} gram-atoms of metal of the lanthanide group per 100 g of polyamide. Still more preferably, this quantity is determined so as to contribute from 0.3×10^{-3} to 10×10^{-3} gram-atoms of metal of the lanthanide group per 100 g of polyamide.

The lanthanide-based compound can be in a solid or pasty form. In the case of a solid compound, the

latter is generally employed in the form of particles with a mean diameter not exceeding 200 μm and, preferably, of between 0.5 and 100 μm .

As indicated above, the compositions in accordance with the present invention must additionally contain an effective quantity of at least one hydrotalcite of formula (I). These inorganic compounds are generally employed in the form of particles with a mean diameter not exceeding 200 μm in this case either and, preferably, of between 0.1 and 100 μm .

When the compound employed (lanthanum-based compound, hydrotalcite) is available in anhydrous form or in a crystallized form with molecules of water, it is preferred to employ the anhydrous compound or one containing the least possible water of crystallization, to avoid or to limit a release of water during the conversion.

The quantity of hydrotalcite(s) which is used may vary within quite wide limits as a function of the desired degree of stabilization; more precisely, this quantity is between 0.1 and 5 % by weight relative to the weight of the polyamide present in the composition, and preferably between 0.4 and 2 % by weight.

The compositions in accordance with the present invention can be prepared simply by mixing the various constituents in all the suitable ways permitting a homogeneous composition to be obtained. The mixing of the various constituents in powder or granular form is preferably carried out by first making a cold premix in a conventional mixer, followed by then homogenizing the whole by blending with heating to a temperature which is generally higher than 200°C in a single- or multi-screw extruder, the extrusion operation being preferably carried out under an inert atmosphere, such as that of nitrogen or argon, for example. At the end of this treatment, rods are obtained which are cooled in water and are then chopped into granules, it being possible for the latter to be optionally then subjected to a drying operation. The compositions according to the invention can,

furthermore, be prepared by producing a masterbatch, present in a granular form based on a part of the polyamide to be made fire-resistant, of red phosphorus, of the lanthanide-based compound and of hydrotalcite(s), which will then be mixed, before use, with the granules of the remainder of the polyamide to be made fire-resistant.

These compositions have been defined above by their essential constituents. It goes without saying that it would not constitute a departure from the scope of the invention to modify these compositions in the manner indicated below. Thus, where red phosphorus, for example, is concerned, it is possible to use either red phosphorus as such, or to use, and this is a preferred measure, red phosphorus particles coated with a film of polymer. Among these polymers there may be mentioned in particular: epoxy resins (cf. French Patent FR-A-2,314,221), polymers containing maleic, fumaric or allyl unsaturated bonds (cf. French Patent FR-A-2,314,219), saturated polyesters with a melting point of between 50 and 90°C and with a molecular mass below 10,000 (cf. French Patent FR-A-2,373,575), thermoplastic phenol-formaldehyde polycondensates of the novolac type (cf. French Patent FR-A-2,344,615), thermoplastic phenol-isobutyraldehyde polycondensates (cf. European Patent Application EP-A-0,071,788); the use of thermoplastic phenol-formaldehyde polycondensates constitutes a particularly preferred measure for making use of the present invention. The quantity of polymer used to coat the phosphorus particles, where appropriate, may vary within wide limits. This quantity generally represents 5 to 50 % of the total weight of the red phosphorus/coating polymer mixture. It should be noted that it is possible to employ without any difficulty quantities of coating polymer which are greater, ranging up to representing 90 % of the total weight of the red phosphorus/coating polymer mixture.

Furthermore, when they are intended, for example, for obtaining shaped objects, the compositions according to the invention may include various additives: thus,

they may contain reinforcing or gelling fillers such as glass or asbestos fibres, ballotini, kaolin, silica, micas, bentonites, bentones or mixtures of these species. Among the abovementioned fillers, those most commonly employed are glass fibres; these fibres generally have a mean diameter of between 1 and 15 μm and a length of between 2 and 8 mm. To obtain particles endowed with optimum mechanical properties it is advantageous to employ fibres which are sized, for example with epoxy resins, polyester resins, polyurethane resins or vinyl resins, these resins being generally used in combination with bridging agents of the aminosilane type. The proportions of fillers may vary between, for example, 10 % and 60 % by weight relative to the weight of the polyamide of the composition.

It is also possible to make use of other additives, such as lubricants, impact improvers, pigments or colorants, antistatic agents or nucleating agents; these latter additives and their use are widely described in the literature.

The compositions in accordance with the invention can be converted into finished or semifinished articles by application of the usual injection moulding or extrusion techniques. One of the advantages of these compositions lies in the fact that this conversion, which is generally carried out at a temperature of the order of 200 to 320°C is accompanied by only a very low emission of phosphine into the atmosphere; the latter is generally below 0.3 ppm and even below 0.1 ppm; the limit of 0.3 ppm represents the maximum permissible concentration (cf. the work by Sax, Dangerous properties of industrial materials, 3rd edition, pages 1019 and 1020). With suitable phosphorus concentrations, the articles obtained are fire-resistant and do not lead to the formation of droplets of molten, possibly flaming, material when acted upon by a flame. The flammability according to the Underwriters Laboratories UL 94 vertical test (for test specimens with a thickness of 1.6 mm) lies in the classification range from V0 to V1. The particles obtained

exhibit an excellent arc tracking resistance, which may be well above 400 volts in the case of compositions filled with, for example, approximately 40 % by weight of glass fibres relative to the weight of the polyamide of the compositions. It is found, furthermore, that the fire-resistant articles obtained also have an excellent resilience which, when starting with compositions filled with, for example, approximately 40 % by weight of glass fibres relative to the weight of the polyamide of the compositions, can go up to and exceed an unnotched Charpy impact strength of 24 kJ/m². The performance recorded in respect of fire-resistance and resilience is substantially of the same order as that obtained in the absence of hydrotalcite. On the other hand, where arc tracking resistance and aging behaviour in a hot and humid atmosphere are concerned, it is found that the performance recorded is superior. In particular, with regard to the whitish exudations which appear when fire-resistant articles are aged in a hot and humid atmosphere, it is observed that, with the compositions according to the present invention, this phenomenon is very markedly counteracted, compared with what happens in the absence of hydrotalcite or with other stabilizing systems of a different kind.

The fire-resistant compositions according to the present invention are particularly suitable for the manufacture of shaped articles which can be employed in the electricity industries (for example electrical and electronics industries, household appliances, radio and vehicle industries). The characteristics of these compositions also make it possible to manufacture articles by spinning and film extrusion.

The following nonlimiting examples show how the present invention can be put to use in practice.

Before these examples are described, test A, described below, will be used to show the behaviour of a control composition comprising:

- nylon 66,
- red phosphorus coated with a phenol-

- formaldehyde polycondensate,
- glass fibres,
- cerium(III) stearate, and
- a lubricant,

in respect of fire-resistance, resilience, arc tracking resistance and aging behaviour in a hot and humid atmosphere.

TEST A

1. Description of the raw materials:

- nylon 66 (polymer of hexamethylenediamine and of adipic acid): this is a product with a viscosity index of 133 ml/g (determined according to ISO standard R 307, 1977 edition, on the fraction soluble in 90% formic acid);

- coated red phosphorus: this is a composition which will be referred to in what follows by the expression "phosphorus masterbatch", containing 60 % by weight of red phosphorus with a mean particle size of 20 to 30 μm , coated with 40 % by weight of a phenol-formaldehyde polycondensate with a melting point of 80°C and a molecular weight of 800 (resin marketed by Bakelite under reference 85 36 29). This coating is performed as follows: the resin is melted in a reactor heated by steam to 120°C and the red phosphorus is added slowly under an inert atmosphere, the temperature of the mixture being raised to 148°C. The mixture is then cast in the form of slabs, which are broken up under an inert atmosphere;

- glass fibres: these are staple fibres with a mean diameter of 10 μm and a length of between 3 and 6 mm, coated with a size for polyamide and marketed by Owens Corning Fiberglas under reference R 17 BX 1;

- cerium(III) stearate $[\text{Ce}(\text{C}_{17}\text{H}_{35}\text{COO})_3]$: this is employed mixed with polyethylene sebacate and a binder based on the nylon 66 referred to above; this mixture, referred to in what follows by the expression "lanthanide masterbatch", contains: 38.06 % by weight of cerium(III) stearate, 13.27 % by weight of polyethylene sebacate and 48.67 % by weight of nylon 66.

2. Contents of this test:

A composition is prepared from:

- 100 parts by weight of nylon 66,
- 39.75 parts by weight of glass fibres,
- 17.49 parts by weight of phosphorus masterbatch (red phosphorus: 10.49 parts by weight), and
- 1.79 parts by weight of lanthanide masterbatch (cerium(III) stearate: 0.681 part by weight and 0.683×10^{-3} gram-atoms of cerium/100 g of nylon).

3. General operating procedure and controls performed:

The composition is prepared in the following manner:

A dry premix of the various constituents is first produced at 25°C by passing through a Moritz trademark mixer.

This premix is then blended in the molten state in a Prodex trademark vented extruder comprises a screw of diameter D equal to 63 mm and 26 D in length; the screw employed is a frustoconical screw which has a suitable profile for processing polyamides; argon is introduced continuously into the feed hopper of the vented extruder; the extruder is also fitted with a die with two 5-mm diameter holes; the extrusion conditions are as follows:

- temperature : 320°C
- vacuum : 93.1×10^2 Pa
- screw speed : 50 revolutions/min.

The material pressure at the end of the screw and the material throughput are noted. The product collected in rod form is cooled by passing through a cold water bath and it is then granulated and dried.

The water content and the viscosity index of the nylon 66 are determined on the moulding powder thus obtained.

To determine the viscosity index, the time for dissolving in formic acid, to obtain a complete

dissolution, is usually 2 hours at 25°C.

The viscosity index of the nylon 66 is determined again, but this time on a moulded test specimen. These test specimens are prepared with the aid of a DK trade-mark type 60 screw press. In this press, the granules of the moulding powder are melted at a temperature of 280°C to 300°C (depending on the type of test specimen) while the mould is kept at a temperature of 80°C; the injection pressure is from 80 MPa to 100 MPa (depending on the type of test specimen); the injection cycle time is from 17 s to 25 s (depending on the type of test specimen).

The following other characteristics are determined on test specimens moulded under the conditions indicated above:

- the resilience, consisting of the Charpy impact strength: this is measured at 23°C on unnotched and notched 60x10x4 mm bar type test specimens aged in a manner known per se at RH 0 (= 0% relative humidity) or RH 50, according to NF standard T 51 035; the results are expressed in kJ/m²;

- the flammability according to the Underwriters Laboratories UL94 vertical test, as described in document 9750-1 of the Bureau for the Standardization of Plastics, to measure the degree of fire resistance; test specimen dimensions: 127x12.7x1.6 mm;

- the arc tracking resistance index (abbreviated to TRI) according to NF standard C 26 220; the measurements are performed on test specimens 50x50x3 mm in size; and

- the aging behaviour in a hot and humid atmosphere, called a tropicalization test in what follows.

The tropicalization test is performed by following the concept of the conditions of NF standard T 51181 (test cycle C 3 A). Test specimen dimensions: 100x100x3 mm. Operating procedure: the test specimens are arranged vertically in a 20-litre desiccator containing 1,500 cm³ of an aqueous solution of sulphuric acid containing 15 % by weight of pure acid so as to obtain a relative humidity of 93 %; two test specimens, used as a

guard, are placed on the periphery of the desiccator; between the test specimens used as a guard are arranged, on the one hand, two test specimens moulded from a composition to be tested (in this case, that in accordance with the example given below) and, on the other hand, two test specimens moulded from a reference composition (in this case, that in accordance with the present test A); the desiccator is then placed in an oven heated to 70°C for 8 hours; the oven heating is then switched off, the oven door is opened and the desiccator and its contents are allowed to cool in these conditions for 16 hours; the combination: heating 8 hours at 70°C + cooling 16 hours to ambient temperature forms 1 aging cycle; the results of the surface appearance of the test specimens are noted after 17 cycles. Scoring of the results: this scoring goes from 0 to 10: the number 0 indicates that there is no exudation; the number 10 indicates that the test specimen is completely covered with whitish stains; the scoring takes into account the extent and the intensity of the whitish exudations.

In addition, during the extrusion, air samples are taken at the outlet of the vacuum pump by means of a CH 31 101 Draeger tube to look for the possible presence of phosphine.

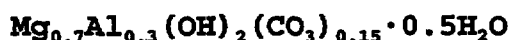
4. Results of test A:

The results obtained are collated in Table 1, given below.

EXAMPLE

1. Contents of this example:

This experimental part will make it possible to assess the behaviour of a composition based on polyamide and on glass fibres, made fire-resistant by means of coated red phosphorus and containing cerium(III) stearate and a lubricant, into which there has additionally been incorporated a hydrotalcite of formula:



distributed commercially by Mitsui under the name Alcamizer.

More precisely, a quantity of hydrotalcite

representing 0.79 % by weight relative to the nylon 66 present in the composition (bearing in mind the polyamide present in the lanthanide masterbatch) is introduced into the composition in accordance with that of test A.

The composition obtained from the following constituents has therefore been prepared:

- 100 parts by weight of nylon 66,
- 40.06 parts by weight of glass fibres,
- 17.63 parts by weight of phosphorus masterbatch (red phosphorus: 10.58 parts by weight),
- 1.81 parts by weight of lanthanide masterbatch (cerium(III) stearate: 0.688 part by weight and 0.689×10^{-3} gram-atoms of cerium/100 g of nylon),
- 0.80 part by weight of hydrotalcite.

In this example, the nylon 66, the glass fibres, the phosphorus masterbatch and the lanthanide masterbatch are identical with the constituents used in test A. With regard to the hydrotalcite newly introduced, its particle size distribution is the following: 100 % of particles of less than 5 μm .

2. General operating procedure and controls performed:

The preparation of the composition is carried out in the manner indicated above in section 3 of the description of test A. It should be noted that the extrusion running conditions are here as follows:

- temperature : 320°C
- vacuum : 93.1×10^2 Pa
- screw speed : 50 revolutions/min.

With regard to the controls performed, the various physicommechanical characteristics referred to above in section 3 of the description of test A are determined. It should be noted that the conditions shown in section 3 of the description of test A are reproduced to make the moulded test specimens.

3. Results of the example:

The results obtained are collated in Table 1, given below.

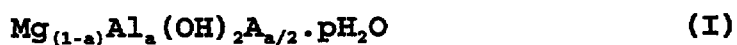
TEST EXAM PLE	EXTRUSION			MOULDING POWDER			CHARPY IMPACT		UL94 classi- fica- tion thick- ness 1.6 mm	TRI		Vis- cosity index on moulded test speci- mens ml/g	Tropi- caliza- tion 17 cycles
	Material pressure at screw end MPa	Material through- put kg/h	PH ₃ release ppm	Calcu- lated phos- phorus content %	Water con- tent %	Vis- cosity index ml/g	UN- NOTCHED 0 RH kJ/m ²	NOTCHED 0 RH kJ/m ²		Volt- age V	Ero- sion mm		
A	~20	35	<0.2	10.39	0.15	142	26	8	V-0	375	0.1	130	7
Exam- ple	~20	35	<0.1	10.48	0.19	136	24	7.6	V-1	450	0.1	120	2



AT BE CH DE FR GB GR IT LI LU NL SE

CLAIMS

1. Compositions based on polyamide made fire-resistant by means of red phosphorus and comprising at least one lanthanide- or yttrium-based compound, characterized in that they additionally comprise from 0.1 to 5 % by weight, relative to the weight of the polyamide present in the composition, of at least one hydrotalcite of general formula:



in which:

A denotes the anion SO_4^{2-} or CO_3^{2-} ,

a is a number which satisfies the relationship:

$$0 < a < 0.5,$$

p is a number representing the number of molecules of water per molecule of hydrotalcite, which satisfies the relationship:

$$0 < p < 1.$$

2. Compositions according to Claim 1, characterized in that the polyamide is chosen from the group consisting of: the polyamides obtained by polycondensation of saturated aliphatic dicarboxylic acids containing from 6 to 12 carbon atoms with saturated aliphatic diprimary diamines containing from 6 to 12 carbon atoms, the polyaminoacids obtained either by direct homopolycondensation of ω -aminoalkanoic acid comprising a hydrocarbon chain containing from 4 to 12 carbon atoms, or by hydrolytic opening and polymerisation of the lactams derived from these acids, the copolyamides obtained from the starting monomers of the abovementioned polyamides, it being additionally possible for the acidic component of these copolyamides to consist partly of terephthalic acid and/or of isophthalic acid, and mixtures of such polyamides.

3. Compositions according to either of Claims 1 to 2, characterized in that the lanthanide- and yttrium-based compound consists of:

- an organic or inorganic derivative of any one of the lanthanides: cerium, lanthanum, praseodymium, neodymium,



promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, ytterbium, thulium, lutetium or yttrium;

- or a mixture of organic and/or inorganic derivatives of a number of these elements.

4. Compositions according to any one of Claims 1 to 3, characterized in that the quantity of lanthanide- and yttrium-based compound(s) which is used is determined so as to contribute from 0.1×10^{-3} to 100×10^{-3} gram-atoms of metal belonging to the lanthanide group per 100 g of polyamide.

5. Compositions according to any one of Claims 1 to 4, characterized in that they contain red phosphorus in proportions of between 1 and 30 % by weight relative to the weight of the polyamide to be made fire-resistant.

6. Compositions according to any one of Claims 1 to 5, characterized in that the red phosphorus is in the form of particles coated with a film of polymer.

7. Compositions according to Claim 6, characterized in that the coating polymer is chosen from the group consisting of: epoxy resins, polymers containing maleic, fumaric or allyl unsaturated bonds, saturated polyesters, thermoplastic phenol-formaldehyde polycondensates and phenol-isobutyraldehyde polycondensates.

8. Compositions according to any one of Claims 1 to 7, characterized in that they additionally contain glass fibres in a quantity varying from 10 to 60 % relative to the weight of the polyamide of the composition.

9. Shaped objects prepared from compositions according to any one of Claims 1 to 8.