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THERMOPLASTIC COMPOSITIONS WITH IMPROVED FIRE RESISTANCE

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(56) Prior Art Documents
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(57) Claim

1. A thermoplastic composition with improved fire resistance, which composition comprises thermoplastic material, Sb_2O_3, melamine cyanurate and at least one polyol.

12. A process for preparing a composition according to any one of the preceding claims which comprises mixing the constituents at a temperature above the softening point of the thermoplastic material.

15. A masterbatch for use in preparation of a thermoplastic composition as claimed in any one of claims 1 to 11 which masterbatch comprises a resin, Sb_2O_3, melamine cyanurate and at least one polyol.

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ORIGINAL

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Invention Title: Thermoplastic Compositions with Improved Fire Resistance

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

[redacted]

The present invention relates to thermoplastic compositions with improved fire resistance and in particular compositions based on polyamide resins and/or on alkenylaromatic (co)polymers. Fire resistance is assessed, on the one hand, by resistance to combustion or to self-ignition and, on the other hand, by susceptibility to dripping.

Due to their excellent physical properties, thermoplastic polyamide resins are widely used in many applications in the automobile industry, aeronautics, the electrical field, and the like, but their development is sometimes held back because of their combustibility.

Many proposals have been made in the literature for improving the resistance to combustion of polyamide-based thermoplastic compositions.

Halogenated derivatives such as decabromodiphenyl ether or decabromodiphenyl, optionally in combination with Sb_2O_3, have been added but the halogenated compounds generate acid halides which are given off during the manufacture and/or during the use of the compositions in which they are incorporated, thus resulting in risks of corrosion of the equipment and pollution of the environment.

Antimony oxide Sb_2O_3 is also used in combination with magnesium hydroxide and optionally melamine cyanurate in European Patent Specification EP 571,241 for imparting flame-retardancy to thermoplastic polyamide compositions.

It is also known to incorporate phosphorus or its derivatives, such as red phosphorus (US 3,778,407), phosphites or phosphates, but these products are difficult to use and confer a reddish tinge on polyamide compositions.

Melamine cyanurate improves the resistance to combustion of polyamides but it is not as effective, weight for weight, as compounds containing a high chlorine or bromine content.

While the above compounds significantly reduce the combustibility of resins in which they are incorporated, their influence on the susceptibility to dripping is low.

According to European Patent Specification EP 169,085 a polyol and melamine cyanurate are simultaneously added to polyamide-based compositions, and this reduces susceptibility to dripping but to a still insufficient extent.

Alkenylaromatic hydrocarbon polymers and copolymers exhibit poor fire resistance and burn easily.

It is known to add flame-retardant agents to these polymers or copolymers and to compositions containing them. The most commonly used are compounds containing at least one halogen atom, generally bromine.

It is also known, from Japanese Patent Specification JP-A-54/85242, to impart flame-retardancy to polystyrene by means of 3 to 50 parts by weight of melamine cyanurate per 100 parts by weight of polystyrene.

Non-flammable, injection-mouldable thermoplastic compositions comprising at least 60% by weight of melamine and at most 40% by weight of polystyrene are known from French Patent Specification FR-A-2,096,230.

Compositions comprising from 30 to 80 parts by weight of polystyrene, from 20 to 70 parts by weight of melamine and from 0.05 to 5 parts by weight (expressed as phosphorus) of a phosphorus-containing compound are known from Japanese Patent Specification JP-A-54/46250.

European Patent Specification EP 438,939 describes thermoplastic compositions containing at least one alkenylaromatic hydrocarbon (co)polymer, at least one nitrogen-containing compound chosen from melamine and melamine isocyanurate, at least one polyol containing at least 4 hydroxyl functional groups per molecule and, optionally, at least one organic ester of phosphoric acid.

The thermoplastic compositions according to the invention comprise

* antimony oxide Sb_2O_3,
* melamine cyanurate,
* one or more polyols.

According to the invention there is, in particular, provided a thermoplastic composition with improved fire resistance, which composition comprises thermoplastic material, Sb_2O_3, melamine cyanurate and at least one polyol.

Mention is in particular to be made, among the thermoplastic compositions according to the invention, of those based on polyamide resin(s) which contain aliphatic and/or cycloaliphatic and/or aromatic units. These can be obtained by anionic polymerisation of one or more lactams, such as caprolactam, oenantholactam, dodecalactam, or laurolactam, or by hydrolytic lactam polycondensation, either of one or more amino acids, such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic and 12-aminododecanoic acids, or of one or more salts or mixtures of diamines, such as hexamethylenediamine, dodecamethylenediamine, meta-xylenediamine, bis(para-aminocyclohexyl)methane or trimethylhexamethylenediamine, with diacids, such as iso- and terephthalic, adipic, azelaic, suberic, sebacic and dodecanedicarboxylic acids, or from mixtures of these monomers resulting in copolyamides.

The term "polyamide" (PA) used according to the invention is also understood to mean polyamide-based thermoplastic elastomers (TPE) which are block copolymers, also known as polyetheramides or polyesteramides, the rigid blocks of which are composed of polyamide and the crystallizable flexible blocks of polyether or of polyester.

Polyamide according to the invention is also understood to mean mixtures of different polyamides such as those listed above with each other and also their mixtures with other polymers, such as polyolefins, provided with polyamide or polyamides represent at least 50% of the total weight of the mixture. Mention is very particularly to be

made of mixtures of polyamide and of polyolefin elastomers which improve the impact strength of polyamides. Mention may be made, as examples of these impact reinforcers, of ethylene and propylene rubbers (EPR), ethylene, propylene and diene rubbers (EPDM), ethylene and vinyl acetate (EVA) copolymers, ethylene-acrylic ester-maleic anhydride terpolymers or terpolymers based on ethylene-acrylic derivative (EAD).

Preferred polyamides includes PA-11, PA-12, PA-12,12, coPA-6/12 and/or PEBA (polyether block amide).

The polyamides can be plasticized using additives commonly used for this type of modification. They can contain fillers and/or contain various additives, for example additives intended to protect the polyamide against thermal oxidation or thermal/UV degradation, processing aids, such as lubricants, dyes or pigments, and the like.

Mention will also very particularly be made, among the thermoplastic compositions according to the invention, of those based on alkenylaromatic hydrocarbon (co)polymer(s).

The term "alkenylaromatic hydrocarbon polymer" is understood to mean according to the present invention, the products from the homopolymerization of an ethylenically unsaturated aromatic hydrocarbon, such as styrene, alpha-methylstyrene, vinyltoluenes, vinylxylenes or methylethylstyrenes.

Alkenylaromatic hydrocarbon copolymer is understood to mean according to the pesent invention the products from the copolymerization of a plurality of the alkenylaromatic hydrocarbon monomers or of at least one of these hydrocarbon monomers with at least one other copolymerizable monomer, such as acrylic acid, methacrylic acid, maleic anhydride, alkyl (meth)acrylates in which the alkyl radical comprises from 1 to 8 carbon atoms, acrylonitrile or 1,3-butadiene.

Preferred alkenylaromatic polymers include polystyrene and high-impact polystyrene.

Other thermoplastic resins which may, if appropriate, be combined with the alkenylaromatic hydrocarbon polymer or copolymer according to the present invention include in particular:

- poly(phenylene ether)
- polyethylene and copolymers of ethylene and of at least one alpha-olefin having from 3 to 8 carbon atoms, it being possible for these last two resins to be made more compatible by means of a grafted or branched ethylene/styrene copolymer, in accordance, for example, with British Patent Specification GB 870,650,
- homopolymers and copolymers based on esters of acrylic or methacrylic acid, such as poly(methyl methacrylate),
- copolymers of ethylene and of at least one unsaturated polar comonomer, such as vinyl acetate, alkyl (meth)acrylates, acrylic acid, methacrylic acid or maleic anhydride,
- polycarbonate.

The thermoplastic material can comprise the alkenylaromatic hydrocarbon polymer or copolymer and other thermoplastic resin in any proportion. It will advantageously comprise from 10 to 90 % by weight of one and from 90 to 10 % by weight of the other. Preferably, when the thermoplastic material comprises an ethylene-based polymer or copolymer, the alkenyl-aromatic hydrocarbon polymer or copolymer makes up more than 50 % by weight in the thermoplastic material.

Other elastomeric resins which may, if appropriate, be combined with the alkenylaromatic hydrocarbon polymer or copolymer include in particular according to the present invention at least one of the following polymers, which may or may not carry polymerized alkenylaromatic hydrocarbon grafts: a polyolefin elastomer, such as a terpolymer of ethylene with at least one alpha-olefin having from 3 to 6 carbon atoms and at least one diene, particularly ethylene-

propylene-diene terpolymers, the diene being chosen from conjugated or non-conjugated, linear or cyclic dienes, such as, for example, butadiene, isoprene, 1,3-pentadiene, 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, 1,9-decadiene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 2-alkyl-2,5-norbornadienes, 5-ethylidene-2-norbornene, 5-(2-propenyl)-2-norbornene, 5-(5-hexenyl)-2-norbornene, 1,5-cyclooctadiene, bicyclo[2.2.2]octa-2,5-diene, cyclopentadiene, 4,7,8,9-tetrahydroindene and isopropylidenetetrahydroindene. Such elastomeric terpolymers which can be used in accordance with the present invention generally comprise between 15 mol % and 60 mol% of units derived from propylene and between 0.1 mol % and 20 mol % of units derived from the diene. Other such elastomeric resins include a styrene/butadiene rubber, a polydiene rubber, such as polybutadiene and polyisoprene, nitrile rubber or ethylene/propylene rubber. These other elastomeric resins are generally used in an amount of at most 20 weight %, and preferably between 5 weight % and 15 weight %, with respect to the weight of the thermoplastic material.

In addition to the preceding resins, the compositions according to the invention can also contain other thermoplastic resins, such as polyolefins, polyurethanes, and the like.

The antimony oxide is generally provided in the form of a fine powder, the particle size of which is of the order of one μm.

Melamine cyanurate is understood to mean compounds obtainable from the reaction of melamine with cyanuric acid and particularly the compound resulting from the equimolar reaction of melamine with cyanuric acid, it being possible for the latter to be in the enol or ketone form.

Polyol is understood to mean compounds containing at least four alcohol functional groups such as tetrols, such as erythrol or monopentaerythritol (PER) and its polysubstituted derivatives, pentols such as xylitol or arabitol and hexols such as mannitol or sorbitol and its

higher homologues.

Compositions according to the invention may be prepared by mixing the different constituents (in the molten state) at a temperature greater than the softening point of the thermoplastic resin. The compositions according to the invention may also be obtained by dry mixing of the constituents.

The incorporation of Sb_2O_3, melamine cyanurate and polyol or polyols, called the three fire-retardant additives according to the invention, and optional further additives, which are finely divided, in the compositions according to the invention, in particular polyamide-based compositions, is generally carried out by mixing in polyamide resin in the molten state; the mixing temperature is generally between 150 and 300°C and preferably between 180 and 230°C.

Compositions according to the invention based on an alkenylaromatic hydrocarbon (co)polymer, e.g. a polystyrene (PS) resins, are generally prepared by dry mixing the constituents, if they are all solid at ambient temperature, in a powder mixer into which the different constituents of the composition are introduced in the powder state, or at most in the form of pearls in the case of the alkenylaromatic hydrocarbon (co)polymers. After mixing for 20 minutes, the mixture is generally ready to use. It is also possible to prepare these compositions by mixing the different constituents at a temperature greater than the softening point of the alkenylaromatic hydrocarbon (co)polymer, and of any additional resin as described above if present, for example in the region of 150 to 200 C, in an internal mixer or in an extruder, generally for 1 to 5 minutes. The compositions are then extruded and then converted to homogeneous ready-to-use granules.

A masterbatch or a final product can be prepared.

The masterbatch has the advantage of ensuring good predispersion of the constituents which will be mixed once again during the dilution of the masterbatch in the final

resin.

The resin of the masterbatch may be identical to or different from the final resin.

It has been noted that a masterbatch based on a thermoplastic elastomer based on PA was particularly advantageous for subsequent dilutions in many PA resins, among which may be mentioned PA-11, PA-12, PA-12,12, PA-6, PA-6,12 or thermoplastic elastomers based on PA-11, PA-12 or PA-6.

It is possible to produce a masterbatch based on an additional resin or resins and then to dilute it in the final resin. This system is particularly advantageous in the case of PA resins impact strengthened with polyolefinic elastomers: the three fire-retardant additives mixed with the polyolefinic elastomer constitute the masterbatch which may subsequently be diluted in the PA or PS resin.

The three fire-retardant additives according to the invention generally represent from 40 to 60 % of the total weight of the masterbatch. In the final, e.g. PA-based, compositions, they generally represent from 5 to 20 % of the total weight of the composition and preferably from 10 to 15 % by weight. Each of the three additives according to the invention typically represents at least 15 % of the total weight of the three additives. The preferred compositions are those in which each of the three fire-retardant additives represents approximately one third of the total weight of these three additives.

The compositions according to the invention find applications in different fields by conversion into industrial items intended in particular for the automobile, aeronautics, domestic electrical appliance, audio-visual equipment and electrical equipment industries; they are well suited to the production of cable-related components, for example of electrical equipment. They are particularly suited to conversion into moulded, extruded or injected articles, into films, into sheets, into fibres, into

composite materials such as coextruded articles or multilayer films, and into powders for coating substrates.

The invention is further illustrated in the following Examples.

Throughout the Examples, the intrinsic viscosity of the PAs is measured at 25°C in meta-cresol for 0.5 g of polymer in 100 ml of meta-cresol.

The melting point of the PA resins is measured according to ASTM Standard D 3418 and their Shore D hardness is measured according to ASTM Standard D 2240.

Except where otherwise indicated, the proportions are expressed by weight.

Preparation of masterbatches MB1 to MB8

Various additives, the respective nature and proportions (% by weight) of which are listed in Table 1, and coPA-6/12 granules are charged to a Melli internal mixer, the vessel of which has been preheated to 100 C. The additives represent 50 % of the total weight of the masterbatch.

coPA-6/12 (melting point: 130 C; Shore D hardness: 60) is marketed by Elf Atochem S.A.

The melamine cyanurate (MC) used is marketed by the Company Chemie-Linz AG.

The monopentaerythritol (PER) used is marketed by the Company Celanese.

Sb_2O_3 is marketed by the Company Cookson under the name Timonox®.

The ammonium polyphosphate (APP) is marketed by the Company Hoechst under the name Exolit 622.

The zeolite (ZEO) is marketed by the Company Ceca S.A. under the name of zeolite A4.

The titanium oxide of fine particle size (approximately 1 μm) is marketed by the Company Thann & Mulhouse under the name RL 90.

Table 1

Master-batch No.	MC	PER	Sb_2O_3	APP	ZEO	TiO_2
MB1	27.75	5.55		16.7		
MB2	35.75	7.15		7.1		
MB3	35.75	7.15			7.1	
MB4	35.75	7.15				7.1
MB5	35.75	7.15	7.1			
MB6	35.75	7.15		3.55	3.55	
MB7	31.25	12.5		3.125	3.125	
MB8	41.7	8.3				

Examples 1 to 14

The above masterbatches are then diluted with PA-11 (intrinsic viscosity: 1; melting point: 185°C) or PA-12 (intrinsic viscosity: 1; melting point: 175°C), marketed by the Applicant Company, in a Brabender ZSK counterrotating twin-screw extruder (screw speed 60 rev/min; throughput 2 kg/h; temperature profile 180-210-230°C).

The fire resistance is evaluated by measuring the oxygen limit index (OLI) on ISO Standard R178 rods (80 x 10 x 4 mm^3) obtained on a Mining press under the following conditions from *the above samples,

and, by way of comparison, from

*PA-12 without fire-resistance additives

*PA-11 without fire-resistance additives

*a composition based on PA-11 according to the teaching of European Patent Specification EP 169,085 containing PER and MC but neither Sb_2O_3 nor halogenated compound (melting point: 185°C).

Injection temperature: 235°C for PA-12 without fire-resistance additives
225°C for composition based on PA-12
215°C for PA-12 without fire-resistance additives
215°C for composition based on PA-11

temperature of the mould: ambient temperature

injection cycle: 15 s of injection proper then maintenance under a press for 15 s.

The results of OLI measurement and the concentration of masterbatch (% by weight) are combined in Table 2.

Table 2

Example No.	PA Nature	Master-batch	Dilution (%)	OLI (%)
1	PA-12	MB8	24	30
2	PA-12	MB1	36	27
3	PA-12	MB7	36	29
4	PA-12	MB2	28	30
5	PA-12	MB3	28	30
6	PA-12	MB6	28	27
7	PA-12	MB7	28	29
8	PA-12	MB7	32	31
9	PA-11	MB8	24	36
10	PA-12	MB4	28	30
11	PA-12	MB5	28	35
12	PA-12			23
13	PA-11			26
14	PA-12			36

Examples 15 to 23

Compositions containing 86 % by weight of PA-12, 10 % of MC, 2 % of PER which are as described above and 2 % of various additives are produced under operating conditions identical to those of the samples of Examples 1 to 14.

The characteristics of the additives are as follows:

Sb_2O_3 is identical to that used previously.

The magnesium hydroxide $Mg(OH)_2$ with a particle size of 1 μm is marketed by the Company Martinswerke under the name Martinfin®H10.

The aluminium hydroxide $Al(OH)_3$ with a particle size of 1 μm is marketed by the Company Martinswerke under the name Martinal®OL111LE.

The boehmite AlO.OH with a particle size of 1 μm is marketed by the Company Vaw Aluminium.

The silica SiO_2 has a particle size of 1 μm.

The dibutyltin dilaurate (DBTDL) is marketed by the Company Merck.

The ortho-boric acid H_3BO_3 is marketed by the Company Prolabo.

The samples are then shaped in the form of rods in accordance with ISO Standard R178 in a way identical to that of Examples 1 to 14 and their OLI is measured. The results are combined in Table 3.

Table 3

Example No.	Additive nature	OLI (%)
15	-	29.7
16	Sb_2O_3	34
17	$Mg(OH)_2$	26.5
18	$Al(OH)_3$	28
19	AlO.OH	28.5
20	DBTDL	29
21	Fe_2O_3	29.8
22	SiO_2	29.2
23	H_3BO_3	27.2

Examples 24 to 33

Compositions based on different PA-based resins containing 10 % of MC, 2 % of PER which are as described above and 2 % of Sb_2O_3 and, by way of comparison, Sb_2O_3-free

compositions are prepared.

The PA-12 is identical to that used in Examples 1 to 8 and 10 to 12.

The coPA-6/12 is identical to that used in masterbatches MB1 to MB8.

The PEBA (polyether-block amide), marketed by Elf Atochem SA, is a polyamide-based thermoplastic elastomer in which the polyether blocks are of polytetramethylene glycol (PTMG) and represent 33 % of the total weight of the PEBA and the PA blocks are of PA-12 (66 % of the total weight of the PEBA) (melting point: 159°C; Shore D hardness: 55).

The PP/PA-6 mixture (melting point: 220°C) is a compatabilized alloy marketed by Elf Atochem S.A.

The PA-6 used is a moulding grade and its melting temperature is equal to 218°C.

The samples are then shaped in the form of rods in accordance with ISO Standard R178 in a way identical to that of the samples of Examples 1 to 23 and their OLI and the difference between the OLI of the compositions with and without Sb_2O_3 are measured. The results are combined in Table 4.

Table 4

Example No.	PA resin nature	Presence or absence of Sb_2O_3	OLI (%)	ΔOLI
24	PA-12	-	29.7	
25	PA-12	Sb_2O_3	33.6	+3.3
26	PA-6/12	-	28.3	
27	PA-6/12	Sb_2O_3	30.2	+1.9
28	PEBA	-	22.7	
29	PEBA	Sb_2O_3	26.5	+3.8
30	PA-6/PP mixture	-	20.3	
31	PA-6/PP mixture	Sb_2O_3	21.6	+1.3
32	PA-6	-	24	
33	PA-6	Sb_2O_3	38	+14

Examples 34 to 43

Different mixtures according to the invention in which the melamine cyanurate, the monopentaerythritol and/or the Sb_2O_3 represent 12 % of the total weight of each of the mixtures are prepared from the PA-12 described above by direct extrusion of the PA-12 and additives in a Buss Ko-Kneader extruder (screw speed 45 rev/min; throughput 25 kg/h; temperature profile 220-270-220-220-240°C).

The samples are then shaped in the form of rods in accordance with ISO Standard R178 in a way identical to that of the samples of Examples 1 to 33 and their OLI is measured.

Table 5

Example No.	MC (%)	PER (%)	Sb_2O_3 (%)	OLI (%)
34	10.2	1.8	0	29
35	7.56	0.84	3.6	32
36	4.2	4.2	3.6	35
37	3.6	3.6	4.8	36
38	3.6	7.2	1.2	32
39	2.4	2.4	7.2	34
40	0	6	6	28
41	12	0	0	32
42	0	12	0	28
43	0	0	12	27

Preparation of the masterbatch MB9

A masterbatch based on 40 % by weight of coPA-6/12 described above, 43 % of melamine cyanurate, 8.5 % of monopentaerythritol and 8.5 % of Sb_2O_3 is prepared in a Werner® 40 extruder equipped with a corotating twin screw (screw speed 150 rev/min; throughput 24 kg/h; temperature profile 230-180-195-180-180-180-185-190-195-170-190-230°C).

Examples 44 to 52

Different amounts of the above masterbatch are then mixed mechanically with PA-11 or PA-12 with an intrinsic viscosity equal to 1. The degrees of dilution and the PA which is being diluted are shown in Table 6.

Table 6

Example No.	0 % dilution	10 % dilution	20 % dilution	30 % dilution
PA-12	44	45	46	47
PA-11	48	49	50	51+52*

*Example 52 is prepared by direct extrusion of all the constituents without an intermediate masterbatch.

The fire resistance (OLI & UL 94) and the mechanical properties of the compositions obtained are evaluated on rods, dumbbells or sheets according to the operating conditions of the measuring standards used. The results are combined in Table 7.

Table 7

	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49	Ex. 50	Ex. 51	Ex. 52
EB (%)	383	79	42	17	379	16	22	13	96
TS	64	32	33	39	63	33	32	35	35
FM	1184	1202	1243	1349	1124	1257	1124	1152	1348
Impact at 23°C	100 nb	14.1	14.7	10.2	100 nb	17.7	11.3	14.1	100 nb
Impact at -40°C	100 nb	15.8	11.4	8.3	100 nb	12.6	9	9	100 nb
Vicat point	173	170	168	164	183	181	179	176	182
OLI 1.6 mm	25	33.7	35.7	34	24.5	32.9	37.4	37.2	39.5
OLI 3.2 mm	23.4	31.1	34.9	34.7	25.8	30.2	35.9	35	35.5
UL 94 1.6 mm	94V2	94V0	94V0	94V0	94V2	94V2	94V0	94V0	94V0
UL 94 3.2 mm	94V2	94V2	94V0	94V0	94V2	94V2	94V2	94V0	94V0

The dynamometric properties EB (elongation at break) and TS (tensile strength) are measured according to ISO Standard R 527 1B.

The flexural modulus (FM) is measured according to ISO Standard 178.

The Charpy impact strength is measured at 23 and -40°C according to ISO Standard 179.

The Vicat point is measured according to ISO Standard 306.

The OLI is measured as above.

The resistance to dripping is evaluated according to NF Standard T 51 0272.

Preparation of masterbatch MB10

Under the same operative conditions as for MB9 and with the same proportions of additives, a masterbatch MB10 is prepared in which the PA resin is a PEBA based on PTMG (50 % of the total weight of the PEBA) and on PA-12 (50 % of the total weight of the PEBA) marketed by Elf Atochem S.A. under the name Pebax MX1205 (melting point : 147°C; Shore D hardness : 40).

Examples 53 to 65

Different amounts of the above masterbatch are then diluted with PA-based resins using an extruder. The fire resistance (UL 94 and OLI) of the samples of Examples 53 to 58 is measured according to the standards thus defined above. Table 8 gives the UL 94/OLI ratio.

Table 8

Example No.	MB10 dilution (%)	Rigid PA-12	Rigid PA-11	Plasticized PA-12	Rigid PA-12 + 30 % FG	PEBA 1	PEBA 2	PEBA 3
53	0	V2/24	V2/25					
54	10	V2/30	V2/31	V2/24				
55	12.5					V2/26	V2/26	V2/26
56	15			V2/26				
57	20	V0/35	V0/36	V2/27	V2/23	V2/27	V2/26	V2/27
58	30	V0/35	V0/37					

The rigid PA-12 has an intrinsic viscosity equal to 1 and its melting point is equal to 175°C.

The rigid PA-11 has an intrinsic viscosity equal to 1 and its melting point is equal to 185°C.

The PEBA 1 marketed by Elf Atochem S.A. is a thermoplastic elastomer of PEBA (polyether-block amide) type based on PA-12 (80 %) and on PTMG (20 %) (melting point : 169°C; Shore D hardness: 63).

The PEBA 2 marketed by Elf Atochem S.A. is a thermoplastic elastomer of PEBA type based on PA-12 (80 %) and on polyethylene glycol (PEG) (20 %) (melting point: 158°C; Shore D hardness: 40).

The PEBA 3 marketed by Elf Atochem S.A. is a thermoplastic elastomer of PEBA type based on PA-12 (75 %) and on PEG (25 %) (melting point: 169°C; Shore D hardness: 60).

The fire resistance of the samples of Examples 59 to 62 (diluted in the plasticized PA-12 used previously) is measured according to the incandescent wire technique at 850°C according to CEI Standard 695-2-1; the results are combined in Table 9.

Table 9

Example No.	MB10 dilution	Extinction time (s)	Flame height (cm)
59	0	28	15
60	10	15	14
61	20	14	12
62	30	10	10

Some mechanical properties (EB, TS, FM and Charpy impact) of the samples of Examples 59 to 65 are evaluated. The results are combined in Table 10.

The samples of Examples 63 to 65 are MB10-based

compositions which are or are not diluted in PEBA 1 in the proportion of 0 % (Example 63)
12.5 % (Example 64)
20 % (Example 65)

Table 10

Example No.	EB (%)	TS (MPa)	FM (MPa)	Impact at 23°C (kJ/m²)	Impact at -40°C (kJ/m²)
59	382	49	438	nb	4.4
60	352	41	474	45.1	6.1
61	338	37	492	39.2	6.2
62	310	34	507	36.8	6
63			290	nb	15
64			370	nb	16
65			380	nb	16.5

nb = not broken

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A thermoplastic composition with improved fire resistance, which composition comprises thermoplastic material, Sb_2O_3, melamine cyanurate and at least one polyol.

2. A composition according to claim 1, wherein the thermoplastic material is based on polyamide resin.

3. A composition according to claim 1, wherein the thermoplastic material is based on PA-11, PA-12, PA-12,12, coPA-6/12, and/or PEBA.

4. A composition according to claim 1, wherein the thermoplastic material is based on alkenylaromatic hydrocarbon (co)polymer(s).

5. A composition according to claim 1, wherein the thermoplastic material is based on polystyrene or high-impact polystyrene.

6. A composition according to any one of the preceding claims, wherein the Sb_2O_3, melamine cyanurate and the polyol or polyols each represent at least 15% of the total weight of these three additives.

7. A composition according to any one of claims 1 to 5 wherein the Sb_2O_3, melamine cyanurate and the polyol or polyols each represent approximately one third of the total weight of these three additives.

8. A composition according to any one of the preceding claims, wherein the Sb_2O_3, melamine cyanurate and the polyol or polyols represent from 5 to 20% of the total weight of the composition.

9. A composition according to any one of claims 1 to 7 wherein the Sb_2O_3, melamine cyanurate and the polyol or polyols represent from 10 to 15% of the total weight of the composition.

10. A thermoplastic composition according to claim 1 substantially as hereinbefore described.

11. A thermoplastic composition according to claim 1 substantially as described in any one of the Examples.

12. A process for preparing a composition according to any one of the preceding claims which comprises mixing the constituents at a temperature above the softening point of the thermoplastic material.

13. A process for preparing a composition according to any one of claims 1 to 11 which comprises dry mixing the constituents.

14. A composition as defined in any one of claims 1 to 11 prepared by the process claimed in claim 13 or 14.

15. A masterbatch for use in preparation of a thermoplastic composition as claimed in any one of claims 1 to 11 which masterbatch comprises a resin, Sb_2O_3, melamine cyanurate and at least one polyol.

16. A masterbatch according to claim 15 substantially as hereinbefore described.

17. A masterbatch according to claim 15 substantially as described in any one of the Examples.

18. An industrial item obtained by conversion of a composition as claimed in any one of claims 1 to 11.

19. An article formed from a composition as claimed in any one of claims 1 to 11.

DATED this TWENTY-SECOND day of JULY 1996
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Thermoplastic Compositions with Improved Fire Resistance

ABSTRACT

The present invention relates to thermoplastic compositions with improved fire resistance. According to the invention, thermoplastic resins in particular based on polyamide resin(s) or on alkenylaromatic resin(s), with improved fire resistance, comprises Sb_2O_3, melamine cyanurate, and one or more polyols. These compositions can be used for the preparation of moulded, extruded or injected articles, in the form of sheets or films, of composite materials and of powders for coating substrates.