

ANTISTATIC STYRENIC POLYMER COMPOSITIONS

[Field of the invention]

The present invention relates to antistatic styrenic polymer compositions and more specifically to a composition comprising a styrenic polymer (A), a copolymer (B) containing polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$, a compatibilizer (C) and an antistatic mixture (D) based on fibres.

The aim of the invention is to give the styrenic polymer (A) antistatic properties. The formation and retention of static-electricity charges on the surface of most plastics are known. The presence of static electricity on thermoplastic films results, for example, in these films sticking to one another, making them difficult to separate. The presence of static electricity on packaging films may cause the accumulation of dust on the articles to be packaged and thus impede their use. Styrenic resins, such as polystyrene or ABS, are used for making compartmentalized boxes and for making trays on which loose electronic components are placed prior to their assembly on cards, and it is necessary for these boxes and these trays to be antistatic, so that they do not irretrievably damage the components. These resins are useful in making casings for computers, for telephones, for televisions, for photocopiers and also for many other articles. Static electricity causes dust to accumulate, but above all it can damage the microprocessors or the components of the electronic circuits present in these articles.

Antistatic styrenic resins are also used to make reels and pieces for photocopy machines.

Plastic Reels uses a 3-piece concept. A special locking mechanism enables 2 pieces of 13" flange and a hub to be assembled easily. Flanges and hubs are packed in a compact format and assembled when needed, this reducing storage space at user's end. Hubs are available in different widths of 8.5 to 56.5mm. Reels and hubs are manufactured by injection

moulding. These plastic reels are used for IC packaging. IC's are packed in a flexible strap and then this strap can wound on these reels.

Today normal HIPS / ABS are used in Mail / Paper sorters for Photo copy machines, printer trays and paper feeding systems for OA products. Paper is
5 one of the main sources for the static source generation. High -speed photocopy generates static charge in the paper causing malfunctioning of automated paper handling devices and the possibility may exist to get electric shock. By replacing with this antistatic Polystyrene, the static charge can decay through the plastic parts in the equipments and can achieve 100% functioning
10 of automated paper feeding. The paper feeders and the trays are made by Injection moulding.

The prior art has described antistatic agents, such as ionic surfactants of the ethoxylated amine or sulphonate type, which are added to polymers. However, the antistatic properties of the polymers depend on the ambient
15 moisture level and are not permanent since these agents migrate to the surface of the polymers and disappear. It has therefore been proposed to use, as antistatic agents, copolymers containing polyamide blocks and hydrophilic polyether blocks, these agents having the advantage of not migrating and therefore of giving permanent antistatic properties which are also independent
20 of the ambient moisture level.

[Prior art]

Japanese Patent Application JP 60 170 646 A published on 4 September
25 1985 describes compositions consisting of from 0.01 to 50 parts of a polyether-block-amide and 100 parts of polystyrene; these are useful for making sliding parts and wear-resistant parts. No mention is made of antistatic properties.

Patent Application EP 167 824 published on 15 January 1986 describes compositions similar to those mentioned previously, and in one embodiment of
30 the invention polystyrene may be blended with a polystyrene functionalized by an unsaturated carboxylic anhydride. These compositions are useful for making injection mouldings. No mention is made of antistatic properties.

Japanese Patent Application JP 60 023 435 A published on 6 February 1985 describes antistatic compositions comprising from 5 to 80% of polyetheresteramide and from 95 to 20% of a thermoplastic resin chosen, inter alia, from polystyrene, ABS and PMMA, this resin being functionalized by acrylic acid or maleic anhydride. The quantity of polyetheresteramide in the examples is 30% by weight of the compositions.

Patent EP 242 158 describes antistatic compositions comprising from 1 to 40% of polyetheresteramide and from 99 to 60% of a thermoplastic resin chosen from styrenic resins, PPO and polycarbonate. According to a preferred embodiment the compositions also comprise a vinyl polymer functionalized by a carboxylic acid. This may, for example, be a methacrylic-acid-modified polystyrene.

The above prior art presents either blends (i) of styrenic resin and polyetheresteramide without compatibilizer or blends (ii) of polyetheresteramide and of functionalized styrenic resin, or else blends (iii) of polyetheresteramide, non-functionalized styrenic resin and functionalized styrenic resin.

Patent EP 829 520 describes substrates such as PVC, HDPE, LLDPE, polypropylene, ABS and polystyrene, rendered antistatic by adding an antistatic mixture consisting of a copolymer having polyamide blocks and polyether blocks, a salt such as sodium perchlorate and a fibrous material or a material which forms fibres in the course of introducing the mixture into the substrate. The proportion by weight of the antistatic mixture is from 0.1 to 15%, preferably from 1 to 15%, of the substrate. The proportion by weight of the salt is from 0.05 to 10%, preferably from 0.5 to 5%, of the quantity of copolymer containing polyamide blocks and polyether blocks. The ratio by weight of the quantity of fibres to copolymer containing polyamide blocks and polyether blocks is from 20/1 to 1/10, preferably from 10/1 to 1/3. In Example 19, 3.84 g of copolymer containing polyamide blocks and polyether blocks, 0.16 g of sodium perchlorate and 4 g of Nylon-6 fibres are added to 191.8 g of polystyrene. This corresponds to about 4% of antistatic mixture in 96% of polystyrene, the fibres representing half of the mixture. In Example 20, 4.8 g of copolymer containing polyamide blocks and polyether blocks, 0.2 g of sodium perchlorate and 5 g of Nylon-6

fibres are added to 189 g of polystyrene. This corresponds to about 5% of antistatic mixture in 95% of polystyrene, the fibres representing half of the mixture. In these two examples the surface resistivities are of the order of 10^{11} ohms.

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[The technical problem]

The blends of styrenic resin and polyetheresteramide without compatibilizer are antistatic if the polyetheresteramide is carefully chosen, but
10 they have poor mechanical properties, in particular the elongation at break is far inferior to that of styrenic resin by itself. As regards the blends of polyetheresteramide and functionalized styrenic resin and the blends of polyetheresteramide, non-functionalized styrenic resin and functionalized
15 styrenic resin, it is necessary to use a functionalized styrenic resin, and this is complicated and expensive. One aim of the invention is to render antistatic the ordinary styrenic resins used for making the abovementioned articles, these resins not being functionalized.

The applicant wished to repeat Examples 19 and 20 of patent EP 829 520 but on quantities of a number of kilograms, and obtained resistivities of at
20 least 10^{13} ohms. This value is excessively high, in particular for compartmentalized boxes and for trays made from polystyrene used for loose electronic components, for which it is desirable to have resistivities of at most 10^{12} ohms. The conditions for carrying out the examples of the prior art are actually suitable for small quantities but inapplicable on a larger scale. To obtain
25 surface resistivities of the order of 10^{11} ohms it was necessary to add from 8 to 10% of antistatic mixture to, respectively, from 92 to 90% of polystyrene, but with these proportions poor mechanical properties are sometimes found, such as delamination phenomena or defects in thermoformed parts.

It has now been found that by using a copolymer (B) containing polyether
30 blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$, a compatibilizer (C) and an antistatic mixture (D) based on fibres it is possible to obtain antistatic

styrenic resin compositions retaining the properties of the styrenic resin on which they are based.

[Brief description of the invention]

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The present invention relates to a composition comprising, per 100 parts by weight :

- from 95 to 80%, advantageously from 92 to 84% of a styrenic polymer (A),
- from 3 to 11%, advantageously from 5 to 8% of a copolymer (B) containing
10 polyether blocks comprising essentially ethylene oxide units $-(C_2H_4-O)-$,
- from 1 to 3% of a compatibilizer (C) chosen from low-mass copolymers (C1) of styrene and of an unsaturated carboxylic anhydride, copolymers (C2) of ethylene and of an unsaturated carboxylic anhydride, copolymers (C3) of ethylene and of an unsaturated epoxide, blocks copolymers (C4) of
15 butadiene and styrene and mixtures of these,
- from 1 to 6%, advantageously from 2 to 5% of a mixture (D) consisting of:
 - a polymer (D1) in the form of fibres or forming fibres in the course of the mixing of the constituents of the composition, and insoluble in (A),
 - a copolymer (D2) containing polyether blocks comprising essentially
20 ethylene oxide units $-(C_2H_4-O)-$,
 - a low-molar-mass inorganic or organic salt (D3).

[Detailed description of the invention]

- 25 **By way of example of styrenic polymer (A)** mention may be made of polystyrene, elastomer-modified polystyrene, copolymers of styrene and acrylonitrile (SAN), elastomer-modified SAN, in particular ABS, which is obtained, for example, by grafting (graft polymerization) of styrene and acrylonitrile on a backbone of polybutadiene or of butadiene-acrylonitrile
30 copolymer, and mixtures of SAN and ABS. Possible examples of the abovementioned elastomers are EPR (the abbreviation for ethylene-propylene rubber or ethylene-propylene elastomer), EPDM (the abbreviation for ethylene-

propylene-diene rubber or ethylene-propylene-diene elastomer), polybutadiene, acrylonitrile-butadiene copolymer, polyisoprene and isoprene-acrylonitrile copolymer.

In the polymers (A) just mentioned, part of the styrene may be replaced
5 by unsaturated monomers copolymerizable with styrene, for example
alpha-methylstyrene or (meth)acrylates. Other examples of styrene copolymers
which may be mentioned are chloropolystyrene, poly-alpha-methylstyrene,
styrene-chlorostyrene copolymers, styrene-propylene copolymers, styrene-
butadiene copolymers, styrene-isoprene copolymers, styrene-vinyl chloride
10 copolymers, styrene-vinyl acetate copolymers, styrene-alkyl acrylate
copolymers (methyl, ethyl, butyl, octyl, phenyl acrylate), styrene-alkyl
methacrylate copolymers (methyl, ethyl, butyl, phenyl methacrylate), styrene-
methyl chloroacrylate copolymers and styrene-acrylonitrile-alkyl acrylate
copolymers. The comonomer content in these copolymers will generally be up
15 to 20% by weight. The present invention also relates to metallocene
polystyrenes of high melting point.

It would not be outside the scope of the invention if (A) were a blend of
two or more of the above polymers.

By way of example of copolymer (B) mention may be made of
20 copolymers (B1) containing polyamide blocks and polyether blocks, copolymers
(B2) containing polyester blocks and polyether blocks and copolymers (B3)
containing polyurethane blocks and polyether blocks (polyetherurethane).

The polyether blocks may represent from 5 to 85% by weight of (B).
The polyether blocks may contain units other than ethylene oxide units, for
25 example propylene oxide units or polytetrahydrofuran units (leading to
polytetramethylene glycol chain linkages). It is also possible to use at the same
time PEG blocks, i.e. blocks consisting of ethylene oxide units, PPG blocks, i.e.
blocks consisting of propylene oxide units, and PTMG blocks, i.e. blocks
consisting of tetramethylene glycol units, also called polytetrahydrofuran. It is
30 advantageous to use PEG blocks or blocks obtained by oxyethylation of
bisphenols, such as bisphenol A. The latter products are described in patent EP

613 919. The number-average molar mass $\overline{M}_n$ of the polyether sequences is between 100 and 6000, preferably between 200 and 3000.

The quantity of polyether blocks in (B) is preferably from 10 to 50% by weight of (B).

5 **The copolymers (B2) containing polyester blocks and polyether blocks** are copolymers having polyether units derived from polyetherdiols, such as polyethylene glycol (PEG), dicarboxylic acid units, such as terephthalic acid, and glycol (ethanediol) units or 1,4-butanediol units. The chain linkage of the polyethers and diacids forms the flexible segments, while the chain linkage of
10 the glycol or of the butanediol with the diacids forms the rigid segments of the copolyetherester.

Some copolyetheresters of this type are described in the patents EP 402 883 and EP 405 227, the content of which is incorporated into the present application.

15 **By way of example of copolymers (B3) containing polyurethane blocks and polyether blocks** mention may be made of polyetherurethanes, such as those containing diisocyanate units, units derived from polyetherdiols and units derived from ethanediol or from 1,4-butanediol.

20 **The polymers (B1) containing polyamide blocks and polyether blocks** result from copolycondensation of polyamide blocks having reactive end groups with polyether blocks having reactive end groups, such as for example:

- 1) polyamide blocks having diamine chain ends with polyoxyalkylene blocks having dicarboxylic chain ends;
- 2) polyamide blocks having dicarboxylic chain ends with
25 polyoxyalkylene blocks having diamine chain ends obtained by cyanoethylation and hydrogenation of aliphatic dihydroxylated alpha,omega-polyoxyalkylene blocks called polyetherdiols;
- 3) polyamide blocks having dicarboxylic chain ends with
30 polyetherdiols, the products obtained being in this particular case polyetheresteramides. The copolymers (B1) are advantageously of this type.

The polyamide blocks having dicarboxylic chain ends stem, for example, from the condensation of alpha-omega aminoacboxylic acids, of lactams or of dicarboxylic acids and diamines in the presence of a chain-limiting dicarboxylic acid.

5 The number-average molar mass $\overline{M}_n$ of the polyamide blocks is between 300 and 15,000, preferably between 600 and 5000. The mass $\overline{M}_n$ of the polyether blocks is between 100 and 6000, preferably between 200 and 3000.

10 The polymers containing polyamide blocks and polyether blocks may also contain randomly distributed units. These polymers may be prepared by simultaneous reaction of the polyether and of the precursors of the polyamide blocks

15 For example, it is possible to react a polyetherdiol, a lactam (or an alpha,omega-amino acid) and a chain-limiting diacid in the presence of a little water. This gives a polymer having essentially polyether blocks and polyamide blocks of variable length, but also the various reactants which, having reacted randomly, are distributed randomly along the polymer chain.

20 These polymers containing polyamide blocks and polyether blocks, which stem from copolycondensation of polyamide and polyether blocks prepared previously or from a one-step reaction have a Shore D hardness which may, for example, be between 20 and 75, advantageously between 30 and 70, and an intrinsic viscosity between 0.8 and 2.5, measured in metacresol at 250°C for an initial concentration of 0.8 g/100 ml. The MFI values may be between 5 and 50 (235°C under a load of 1 kg).

25 The polyetherdiol blocks are used either as they are and copolycondensed with polyamide blocks having carboxylic end groups or are aminated in order to be converted into polyether diamines and condensed with polyamide blocks having carboxylic end groups. They may also be mixed with precursors of polyamide and a chain-limiting compound to make the polymers
30 containing polyamide blocks and polyether blocks and having randomly distributed units.

Polymers containing polyamide blocks and polyether blocks are described in patents US 4 331 786, US 4 115 475, US 4 195 015, US 4 839 441, US 4 864 014, US 4 230 838 and US 4 332 920.

According to a first embodiment of the invention, the polyamide blocks
 5 having dicarboxylic chain ends stem, for example, from condensation of alpha-omega aminoacboxylic acids, of lactams or of dicarboxylic acids and diamines in the presence of a chain-limiting dicarboxylic acid. By way of example of alpha-omega aminocarboxylic acids mention may be made of aminoundecanoic acid, by way of example of lactams mention may be made of caprolactam and
 10 laurolactam, by way of example of dicarboxylic acids mention may be made of adipic acid, decanedioic acid and dodecanedioic acid and by way of example of a diamine mention may be made of hexamethylenediamine. The polyamide blocks are advantageously of Nylon-12 or Nylon-6. The melting point of these polyamide blocks, which is also that of the copolymer (B1), is generally from 10
 15 to 15°C below that of Nylon-12 or Nylon-6.

Depending on the nature of (A) it may be useful to use a copolymer (B1) having a lower melting point so as not to degrade (A) during the incorporation of (B1), this being the subject of the second and third embodiments below.

20 According to a second embodiment of the invention, the polyamide blocks result from condensation of one or more alpha-omega aminocarboxylic acids and/or of one or more lactams having from 6 to 12 carbon atoms in the presence of a dicarboxylic acid having from 4 to 12 carbon atoms and have low mass, i.e. an $\overline{M}_n$ of from 400 to 1000. By way of example of alpha-omega
 25 aminocarboxylic acids mention may be made of aminoundecanoic acid and aminododecanoic acid. By way of example of dicarboxylic acids mention may be made of adipic acid, sebacic acid, isophthalic acid, butanedioic acid, 1,4-cyclohexyldicarboxylic acid, terephthalic acid, the sodium or lithium salt of sulphoisophthalic acid, dimerized fatty acids (these dimerized fatty acids have a
 30 content of at least 98% of dimer and are preferably hydrogenated) and dodecanedioic acid $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$.

By way of example of lactams mention may be made of caprolactam and laurolactam.

Caprolactam should be avoided unless the polyamide is purified to remove residual dissolved caprolactam monomer.

5 Polyamide blocks obtained by condensation of laurolactam in the presence of adipic acid or dodecanedioic acid and having a mass $\overline{M}_n$ of 750 have a melting point of 127-130°C.

According to a third embodiment of the invention, polyamide blocks result from condensation of at least one alpha-omega aminocarboxylic acid (or
10 a lactam), at least one diamine and at least one dicarboxylic acid. The alpha-omega aminocarboxylic acid, the lactam and the dicarboxylic acid may be chosen from those mentioned above.

The diamine may be an aliphatic diamine having from 6 to 12 atoms, and may be an aryl diamine and/or a saturated cyclic diamine.

15 By way of examples, mention may be made of hexamethylenediamine, piperazine, 1-aminoethylpiperazine, bisaminopropylpiperazine, tetramethylenediamine, octamethylenediamine, decamethylenediamine, dodecamethylenediamine, 1,5 diaminohexane, 2,2,4-trimethyl-1,6-diaminohexane, diamine polyols, isophoronediamine (IPD),
20 methylpentamethylenediamine (MPDM), bis(aminocyclohexyl)methane (BACM) and bis(3-methyl-4-aminocyclohexyl)methane (BMACM).

In a second and third embodiment of the invention, the various constituents of the polyamide block and their proportion are chosen so as to obtain a melting point below 150°C, advantageously between 90 and 135°C.
25 Low-melting-point copolyamides are described in patents US 4 483 975, DE 3 730 504 and US 5 459 230, and the same proportions of the constituents are used for the polyamide blocks of (B). (B) may also be the copolymers described in US 5 489 667.

The copolymers of the invention may be prepared by any means which
30 allows the polyamide blocks and the polyether blocks to be linked together. In practice, use is essentially made of two processes, known as the 2-stage process and 1-stage process.

The 2-stage process consists in firstly preparing the polyamide blocks having carboxylic end groups by condensation of the precursors of polyamide in the presence of a chain-limiting dicarboxylic acid, and then in a second step adding the polyether and a catalyst. If the precursors of polyamide are not-
5 lactams or alpha-omega aminocarboxylic acids, a dicarboxylic acid is added. If the precursors already comprise a dicarboxylic acid, this is used in excess with respect to the stoichiometry of the diamines. The reaction usually takes place at between 180 and 300°C, preferably from 200 to 260°C, and the pressure in the reactor is set between 5 and 30 bar and maintained for approximately 2 hours.
10 The pressure is reduced slowly to atmospheric pressure and then the excess water is distilled off for, for example, one or two hours.

Once the polyamide having carboxylic acid end groups has been prepared, the polyether and a catalyst are added. The polyether may be added in one or more portions, and the same applies to the catalyst. According to one
15 advantageous embodiment, the polyether is added first, and the reaction of the OH end groups of the polyether with the COOH end groups of the polyamide begins, with the formation of ester linkages and elimination of water. The water is removed as far as possible by distillation from the reaction mixture, and then the catalyst is introduced in order to complete the linking of the polyamide
20 blocks to the polyether blocks. This second step takes place with stirring, preferably under a vacuum of at least 5 mm Hg (650 Pa) at a temperature such that the reactants and the copolymers obtained are in the molten state. By way of example, this temperature may be between 100 and 400°C, usually between 200 and 300°C. The reaction is monitored by measuring the torque exerted by
25 the polymer melt on the stirrer or by measuring the electrical power consumed by the stirrer. The end of the reaction is determined by the value of the torque or of the target power. The catalyst is defined as being any product promoting the linking of the polyamide blocks to the polyether blocks by esterification. The catalyst is advantageously a derivative of a metal (M) chosen from the group
30 consisting of titanium, zirconium and hafnium.

By way of example of derivatives mention may be made of the tetraalkoxides which satisfy the general formula $M(OR)_4$, in which M represents

titanium, zirconium or hafnium and the radicals R are identical or different and denote alkyl radicals, linear or branched, having from 1 to 24 carbon atoms.

Examples of the C₁-C₂₄-alkyl radicals from which the radicals R are chosen in the tetraalkoxides used as catalysts in the process according to the invention include methyl, ethyl, propyl, isopropyl, butyl, ethylhexyl, decyl, dodecyl and hexadodecyl. Preferred catalysts are the tetraalkoxides in which the radicals R are identical or different and are C₁-C₈-alkyl radicals. Particular examples of catalysts of this type are Zr(OC₂H₅)₄, Zr(O-isoC₃H₇)₄, Zr(OC₄H₉)₄, Zr(OC₅H₁₁)₄, Zr(OC₆H₁₃)₄, Hf(OC₂H₅)₄, Hf(OC₄H₉)₄ and Hf(O-isoC₃H₇)₄.

The catalyst used in this process according to the invention may consist of only one, or of a number, of the tetraalkoxides of formula M(OR)₄ defined above. It may also be formed by a combination of one or more of these tetraalkoxides with one or more alkali metal alcoholates or alkaline earth metal alcoholates of the formula (R₁O)_pY in which R₁ denotes a hydrocarbon residue, advantageously a C₁-C₂₄ alkyl residue, preferably a C₁-C₈ alkyl residue, Y represents an alkali metal or alkaline earth metal and p is the valency of Y. The quantities of alkali metal alcoholate or alkaline earth metal alcoholate and of tetraalkoxides of zirconium or of hafnium which are combined to constitute the mixed catalyst may vary within wide limits. However, it is preferable for the quantities of alcoholate and of tetraalkoxides used to be such that the molar proportion of alcoholate is approximately equal to the molar proportion of tetraalkoxide.

The proportion by weight of catalyst, that is to say of the tetraalkoxide(s) if the catalyst does not contain an alkali metal alcoholate or alkaline earth metal alcoholate or else all of the tetraalkoxide(s) and of the alkali metal alcoholate(s) or alkaline earth metal alcoholate(s) if the catalyst is formed by a combination of these two types of compounds, advantageously varies from 0.01 to 5% by weight of the mixture of the dicarboxylic polyamide with the polyoxyalkylene glycol and is preferably between 0.05 and 2% of this weight.

By way of example of other derivatives mention may also be made of the salts of the metal (M), in particular the salts of (M) and an organic acid and the complex salts between the oxide of (M) and/or the hydroxide of (M) and an organic acid. The organic acid may advantageously be formic, acetic, propionic, 5 butyric, valeric, caproic, caprylic, lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic, cyclohexanecarboxylic, phenylacetic, benzoic, salicylic, oxalic, malonic, succinic, glutaric, adipic, maleic, fumaric, phthalic and crotonic acid. Acetic and propionic acids are particularly preferred. M is advantageously zirconium. These salts may be called zirconyl salts. The applicant believes, 10 without being bound by this explanation, that these salts of zirconium and an organic acid or the complex salts mentioned above release ZrO^{++} during the course of the process. The product used is the one sold as zirconyl acetate. The quantity to be used is the same as for the $M(OR)_4$ derivatives.

Both this process and these catalysts are described in the patents US 15 4,332,920, US 4,230,838, US 4,331,786, US 4,252,920, JP 07145368A, JP 06287547A, WO 99 33 659 and EP 613919.

With regard to the one-step process, all the reactants used in the two-step process are mixed together, that is to say the precursors of polyamide, the chain-limiting dicarboxylic acid, the polyether and the catalyst. They are the 20 same reactants and the same catalyst as in the two-step process described above. If the precursors of polyamide are not lactams it is advantageous to add a little water.

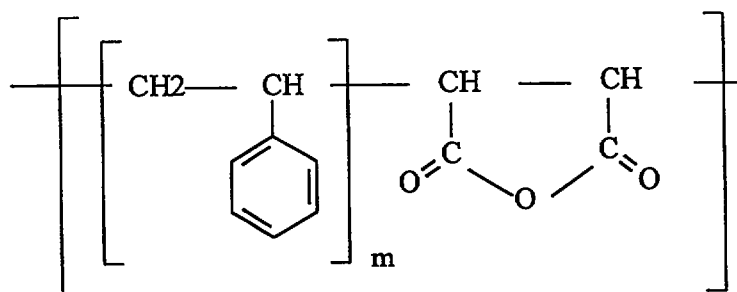
The copolymer has essentially the same polyether blocks and the same polyamide blocks, but also a small portion of the various reactants that have 25 reacted randomly and are distributed randomly along the polymer chain.

The reactor is closed and heated with stirring, as in the first step of the two-step process described above. The pressure established is between 5 and 30 bar. When there is no further pressure change a reduced pressure is applied to the reactor while maintaining vigorous stirring of the molten reactants. The 30 reaction is monitored as previously for the two-step process.

The catalyst used in the one-step process is preferably a salt of the metal (M) and an organic acid or a complex salt between the oxide of (M) and/or the hydroxide of (M) and an organic acid.

By way of example of copolymer (B) use is made of utilise Pebax®
 5 MV1074 or Pebax® MH1657 marketed by ELF ATOCHEM, Pelestat® 7530 or
 Pelestat® 7490 or Pelestat® 6321 marketed by Sanyo Chemicals Japan or C-
 2300 marketed by BF Goodrich.

With regard to the compatibilizers (C1), the unsaturated carboxylic
 acid anhydride may be chosen, for example from maleic, itaconic, citraconic,
 10 allylsuccinic, cyclohex-4-ene-1,2-dicarboxylic, 4-methylenecyclohex-4-ene-1,2-
 dicarboxylic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic and x—
 methylbicyclo[2.2.1]hept-5-ene-2,2-dicarboxylic anhydride. It is advantageous to
 use maleic anhydride. The number-average molar mass is between 800 and
 10,000, preferably between 1000 and 3500. (C1) may be represented by the
 15 following formula:



in which MAH denotes maleic anhydride, m varies from 1 to 3 and n
 varies from 6 to 8. These copolymers may be partially esterified, between 35
 and 75%, by alcohols. These products are marketed as SMA® Resins by ELF
 ATOCHEM.

20 With regard to the compatibilizers (C2), these may be polyethylenes
 grafted by an unsaturated carboxylic anhydride or copolymers of ethylene and

of an unsaturated carboxylic anhydride, obtained, for example, by free-radical polymerization.

With regard to polyethylenes on which the unsaturated carboxylic anhydride is grafted, these should be understood to mean homo- or
5 copolymers.

By way of comonomers, mention may be made of:

- alpha-olefins, advantageously those having from 3 to 30 carbon atoms; by way of examples of alpha-olefins, mention may be made of propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 4-methyl-1-
10 pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1—eicosene, 1-docosene, 1-tetracosene, 1-hexacosene, 1—octacosene and 1-triacontene; these alpha-olefins may be used alone or as a mixture of two or more of the same,

- unsaturated carboxylic esters, such as for example alkyl
15 (meth)acrylates, where the alkyl radicals may have up to 24 carbon atoms and examples of alkyl acrylates and methacrylates are in particular methyl methacrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate,

- vinylic esters of saturated carboxylic acids, such as vinyl acetate and
20 vinyl propionate,

- dienes, such as 1,4-hexadiene,

- and the polyethylene may contain a number of comonomers.

The polyethylene, which may be a mixture of a number of polymers, advantageously contains at least 50%, preferably 75% (in moles) of ethylene
25 and its density may be between 0.86 and 0.98 g/cm³. The MFI (index of the viscosity at 190°C and 2.16 kg) is advantageously between 1 and 1000 g/10 min.

By way of examples of polyethylenes, mention may be made of:

- low-density polyethylene (LDPE)
- 30 - high-density polyethylene (HDPE)
- linear low-density polyethylene (LLDPE)
- very-low-density polyethylene (VLDPE)

- polyethylene obtained by metallocene catalysis, that is to say polymers obtained by copolymerizing ethylene and alpha-olefin, such as propylene, butene, hexene or octene, in the presence of a single-site catalyst generally consisting of a zirconium or titanium atom and of two cyclic alkyl
5 molecules linked to the metal. More specifically, metallocene catalysts are usually composed of two cyclopentadiene rings linked to the metal. These catalysts are frequently used with aluminoxanes as cocatalysts or activators, preferably methylaluminoxane (MAO). Hafnium may also be used as the metal to which the cyclopentadiene is bonded. Other metallocenes may include
10 transition metals from groups IV A, V A, or VI A. Metals from the lanthanide series may also be used.

- EPR (ethylene-propylene rubber) elastomers
- EPDM (ethylene-propylene-diene) elastomers
- mixtures of polyethylene with an EPR or an EPDM
- 15 - ethylene-alkyl (meth)acrylate copolymers, which may contain up to 60% by weight of (meth)acrylate, preferably from 2 to 40%.

Grafting is an operation known per se.

With regard to the copolymers of ethylene and unsaturated carboxylic anhydride, that is to say those in which the unsaturated carboxylic anhydride is
20 not grafted, these are copolymers of ethylene, unsaturated carboxylic anhydride and possibly another monomer which may be chosen from the comonomers mentioned above as ethylene copolymers for grafting.

It is advantageous to use ethylene-maleic anhydride copolymers or ethylene-alkyl (meth)acrylate-maleic anhydride copolymers. These copolymers
25 contain from 0.2 to 10% by weight of maleic anhydride and from 0 to 40% by weight of alkyl (meth)acrylate. Their MFI is between 1 and 50 (190°C – 2.16 kg). The alkyl (meth)acrylates have been described above.

It would not be outside the scope of the invention to replace the unsaturated carboxylic anhydride in (C2) with an unsaturated carboxylic acid,
30 such as (meth)acrylic acid, and this function may be partially neutralized by an alkali metal (Li) or another metal (Zn), giving ionomers. Ionomers of this type are marketed by the company DUPONT with the trade mark Surlyn®.

With regard to the compatibilizers (C3), the copolymer of ethylene and an unsaturated epoxide can be obtained by copolymerizing ethylene and an unsaturated epoxide, or by grafting the unsaturated epoxide onto the polyethylene. The grafting may be carried out in a solvent phase or on the polyethylene melt in the presence of a peroxide. These grafting techniques are known per se. As regards the copolymerization of ethylene with an unsaturated epoxide, use may be made of what are known as free-radical polymerization processes, which usually operate at pressures between 200 and 2500 bar.

By way of example of unsaturated epoxides, mention may be made of:

- aliphatic glycidyl ethers and esters, such as allyl glycidyl ether, vinyl glycidyl ether, glycidyl maleate, glycidyl itaconate and glycidyl (meth)acrylate, and
- alicyclic glycidyl ethers and esters, such as 2-cyclohexen-1-yl glycidyl ether, diglycidyl cyclohexene-4,5-dicarboxylate, glycidyl cyclohexene-4-carboxylate, glycidyl 2-methyl-5-norbornene-2-carboxylate and diglycidyl endo-cis-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate.

With regard to grafting, the compatibilizer (C3) is obtained by grafting a polyethylene homo- or copolymer as described for (C2) except that an epoxide is grafted instead of an anhydride. With regard to copolymerization, this is also similar to the case of (C2) except that an epoxide is used, and there may also be other comonomers present, as in the case of (C2).

The compatibilizer (C3) is advantageously an ethylene/alkyl (meth)acrylate/unsaturated epoxide copolymer. It may advantageously contain up to 40% by weight of alkyl (meth)acrylate and up to 10% by weight of unsaturated epoxide, preferably from 0.1 to 8%.

The epoxide is advantageously glycidyl (meth)acrylate.

The alkyl (meth)acrylate is advantageously chosen from methyl (meth)acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate and 2-ethylhexyl acrylate. The quantity of alkyl (meth)acrylate is advantageously from 20 to 35%. The MFI is advantageously between 1 and 50 (g/10 min at

190°C under a load of 2.16 kg). This copolymer may be obtained by free-radical polymerization of the monomers.

With regard to the compatibilizers (C4), they are copolymers with styrene blocks and blocks made of butadiene or isoprene or of a mixture
 5 butadiene /isoprene. They can be linear blocks copolymers or star blocks copolymers. These copolymers are described in ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY , fifth edition (1995) Vol A26, pages 655-659. They can be hydrogenated. They can be fonctionnalized, advantageously by grafted functions as explained for (C2) an (C3).

10 It would not be outside the scope of the invention to use one or more compatibilizers (C1), one or more compatibilizers (C2), one or more compatibilizers (C3), one or more compatibilizers (C4), or a mixture of at least two of these compatibilizers.

15 The antistatic behaviour increases with the proportion of (B) and, for equal amounts of (B), with the proportion of ethylene oxide units present in (B).

With regard to the polymer (D1), this polymer is described in EP 829 520, in which it is called b1. With regard to (D1) in the abovementioned form of
 fibres, these fibres may also be in the form of nonwoven or felt. These fibres
 20 advantageously have a length of from 0.01 to 200 mm, preferably from 0.1 to 20 mm. The size of these fibres is advantageously from 0.5 to 500 dtex, preferably from 1 to 100 dtex (where dtex corresponds to g/10,000 m). The material of these fibres is advantageously polyamide or polyester, with the proviso that it is insoluble in (A). With regard to (D1) which is not in the form of
 25 fibres prior to entering the composition of the invention, but in the form of pellets use is made of pellets of polyamide or of polyester, with the proviso that they are insoluble in (A). During the course of mixing with the other constituents of the composition, (D1) turns into fibres.

The copolymer (D2) is described in EP 829 520, in which it is called b2.
 30 It is advantageously from the same family as (B1), and may be identical to or different from (B1).

With regard to (D3), this compound is described in EP 829 520, in which it is called b3. These are advantageously salts of alkali metals or alkaline earth metals, of zinc or of ammonium. The organic salts advantageously have from 1 to 4 carbon atoms, and examples of these are salts of acetic, trifluoroacetic, 5 methanesulphonic or trifluoromethanesulphonic acid. Examples of the inorganic salts are, for example, LiClO_4 , NaClO_4 , LiBF_4 , NaBF_4 , KBF_4 , KClO_4 .

The proportion by weight of the salt (D3) is from 0.05 to 10%, preferably from 0.5 to 5%, of the quantity of copolymer (D2). The ratio by weight of the quantity of fibres (D1) to the quantity of copolymer (D2) is from 20/1 to 1/10, 10 preferably from 10/1 to 1/3. In one particular embodiment this ratio (D1)/(D2) is between 2/1 and 1/2. In another embodiment the ratio (D1)/(D2+D3) by weight is between 0.8 and 1.2.

The mixture (D) may also comprise polyamides, advantageously Nylon-6 if the polyamide blocks of (D2) are of Nylon-6, and advantageously Nylon-12 if 15 the polyamide blocks of (D2) are of Nylon-12.

By way of example of mixtures (D), use is made of IRGASTAT®P22 and IRGASTAT®P18 marketed by Ciba Specialty Chemicals.

It would not be outside the scope of the invention to add mineral fillers (talc, CaCO_3 , kaolin, etc.), reinforcing materials (glass fibre, mineral fibre, 20 carbon fibre, etc.), stabilizers (heat, UV), flame-retardants or colorants.

The compositions of the invention are prepared by the techniques usual for thermoplastics, such as extrusion, or with the aid of twin-screw mixers. The compositions could be directedly injected or moulded but generally they are cooled and recovered as pellets. These pellets are then further melted in an 25 extruder and processed as any thermoplastic. The compositions of the invention remain antistatic whichever they are further extruded, or injected or thermoformed.

The present invention also relates to the articles manufactured with the above compositions, for example films, tubes or pipes, sheets, packaging, 30 casings for computers or telephones and uses described in the previous chapter [field of the invention].

[Examples]

The ingredients used in the examples below are as follows:

- **HIPS** : this is an impact-modified polystyrene. This copolymer is characterized by a melt flow index between 3 and 5 g/10 min (ISO 1133:91) at 200°C under a load of 5 kg. It is also characterized by a Vicat temperature of 97°C (ISO 306A50) and an Izod impact resistance (ISO 180/1A) of 10 kJ/m². It is marketed by ELF ATOCHEM as LACQRENE®4241.
- **Pebax®1074** : this is a copolyether-block-amide having Nylon-12 blocks of number-average molar mass 1500 and PEG blocks of number-average molar mass 1500; the MFI is 14 at 235°C/1kg and the melting point is 158°C.
- **Pebax®1657** : this is a copolyether-block-amide having Nylon-6 blocks of number-average molar mass 1500 and PEG blocks of number-average molar mass 1500; the MFI is 14 at 235°C/1kg and the melting point is 204°C.
- **Lotader® AX** : terpolymer of ethylene, methyl acrylate and glycidyl methacrylate. This copolymer has an MFI of 6 (190°C/325 g) and a melting point of 63°C.
- **SMA ®2625** : Partially esterified styrene-maleic anhydride copolymer (such that m = 2 in the abovementioned formula) of number-average molar mass 1900, having a melting range of 135-150°C and an acid number of between 200 and 240 mg KOH/g.
- **Zinc stearate**
- **K-resin KK 38**: SBS block copolymer.
- **Irgastat®P22** : mixture (D) in which (D2) is a block copolymer with PA 6 blocks and PEG blocks.
- **Irgastat®P18** : mixture (D) in which (D2) is a block copolymer with PA 12 blocks and PEG blocks.

The following characterization methods were used in the examples below:

- Antistatic properties :

Plaques of dimensions 100 mm x 100 mm x 2 mm are injection-moulded and can be used to carry out surface resistivity measurements with the aid of two electrodes. This very simple apparatus allows surface resistivities of up to

$2 \cdot 10^{12}$ ohms to be measured and classifies higher values as "insulative". This apparatus is sufficient and very simple to use for rapid classification of antistatic polystyrenes for trays or compartmentalized boxes in which loose electronic components are placed prior to their assembly on cards.

- 5 The surface resistivity is measured in ohm per unit area.

Examples

- 10 An extruder of length equal to eleven times the diameter with a total throughput of 25 kg/h is used. This throughput represents the total of the throughputs of the ingredients used. The temperature settings for the barrels are those normally used for a polystyrene, that is to say from 200 to 220°C. The strands discharged from the machine are cooled in a water tank and converted into pellets. These pellets are injection-moulded to give plaques or dumbbells at a temperature between 220 and 240°C. The results are reported in Tables 1-3 below, in which
- 15 the quantities are weights. Tables 1 and 2 are comparative, and Table 3 is in accordance with the invention.

TABLE 1

	Q	P	R	M	S	A1	B1	C1
HIPS	87.70	89.70	89.70	90.00	91.70	92.70	93.70	94.70
Irgastat	12 (P22)	10 (P22)	10 (P18)	10 (P22)	8 (P22)	7 (P22)	6 (P22)	5 (P22)
Zinc Stearate	0.30	0.30	0.30	-	0.30	0.30	0.30	0.30
Surface Resistivity	10^{10}	10^{11}	10^{11}	10^{11}	10^{11}	Insulative	Insulative	Insulative

TABLE 3

	T	W	E1	V	D1	Z	F1	Y	X
HIPS	87.70	87.70	88.70	87.70	88.70	89.70	88.20	87.70	87.70
Irgastat	5 (P22)	4 (P22)	3 (P22)	2 (P22)	2 (P22)	2 (P22)	1.50 (P22)	1 (P22)	0.5 (P22)
Pebax	5 (1074)	6 (1657)	6 (1657)	8 (1657)	7 (1657)	6 (1657)	8 (1657)	9 (1657)	9.5 (1657)
Lotader AX	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Zinc Stearate	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Surface Resistivity	10^{12}	10^{11}	Insulative	10^{11}	Insulative	Insulative	Insulative	Insulative	Insulative

TABLE 2

	F	D	E	H	I	G	J
HIPS	82.00	88.00	88.00	88.00	88.00	85.00	84.00
Pebax	15 (1074)	10 (1074)	10 (1074)	10 (1074)	10 (1074)	10 (1074)	10 (1074)
Lotader AX	3.00	2.00	2.00	2.00	-	5.00	2.00
SMA 2625	-	-	-	-	2.00	-	-
K-resin, KK38	-	-	-	-	-	-	4.00
Zinc Stearate	-	-	-	-	-	-	-
Surface Resistivity	Insulative	Insulative	Insulative	Insulative	Insulative	Insulative	Insulative

TABLE 2 (CONTINUATION)

	K	L	L1	N	O	U
HIPS	87.70	83.70	83.70	87.70	85.70	87.70
Pebax	10 (1074)	10 (1074)	10 (1074)	10 (1074)	10 (1074)	10 (1657)
Lotader AX	2.00	2.00	2.00	2.00	4.00	2.00
SMA 2625	-	-	-	-	-	-
K-resin, KK38	-	4.00	4.00	-	-	-
Zinc Stearate	0.30	0.30	0.30	0.30	0.30	0.30
Surface Resistivity	Insulative	Insulative	Insulative	Insulative	Insulative	Insulative



CLAIMS

- 1 Composition comprising, per 100 parts by weight :
- from 95 to 80%, advantageously from 92 to 84% of a styrenic polymer
5 (A),
- from 3 to 11%, advantageously from 5 to 8% of a copolymer (B)
containing polyether blocks comprising essentially ethylene oxide units —
(C₂H₄—O)— ,
- from 1 to 3% of a compatibilizer (C) chosen from low-mass copolymers
10 (C1) of styrene and of an unsaturated carboxylic anhydride, copolymers
(C2) of ethylene and of an unsaturated carboxylic anhydride, copolymers
(C3) of ethylene and of an unsaturated epoxide and mixtures of these,
blocks copolymers (C4) of butadiene and styrene,
- from 1 to 6%, advantageously from 2 to 5% of a mixture (D)
15 consisting of:
- a polymer (D1) in the form of fibres or forming fibres in the course of
the mixing of the constituents of the composition, and insoluble in (A),
- a copolymer (D2) containing polyether blocks comprising essentially
ethylene oxide units —(C₂H₄—O)— ,
20 - a low-molar-mass inorganic or organic salt (D3).
- 2 Composition according to Claim 1, in which (A) is polystyrene.
- 3 Composition according to any one of the preceding claims, in
25 which (C1) is a copolymer of styrene and of maleic anhydride and has an
average molar mass of between 800 and 10,000.
- 4 Composition according to either of Claims 1 and 2, in which (C2) is
chosen from ethylene-alkyl (meth)acrylate-maleic anhydride copolymers, these
30 copolymers containing from 0.2 to 10% by weight of maleic anhydride and from
0 to 40% by weight of alkyl (meth)acrylate.



- 5 5 Composition according to either of Claims 1 and 2, in which (C3) is advantageously an ethylene/alkyl (meth)acrylate/unsaturated epoxide copolymer which may contain up to 40% by weight of alkyl (meth)acrylate and up to 10% by weight of unsaturated epoxide.
- 6 6 Compositions according to any one of the preceding claims, in which (B) is a copolymer (B1) containing Nylon-6 blocks or Nylon-12 blocks and PEG blocks.
- 10 7 Compositions according to any one of the preceding claims, in which (D1) is made of polyamide or polyester.
- 8 8 Compositions according to any one of the preceding claims, in which (D2) is a copolymer containing polyamide blocks and polyether blocks.
- 15 9 Compositions according to any one of the preceding claims, in which the proportion by weight of the salt (D3) is from 0.05 to 10%, preferably from 0.5 to 5%, of the quantity of copolymer (D2).
- 20 10 Compositions according to any one of the preceding claims, in which the ratio by weight of the quantity of fibres (D1) to the quantity of copolymer (D2) is from 20/1 to 1/10, preferably from 10/1 to 1/3.
- 25 11 Compositions according to any one of the preceding claims, in which the ratio (D1)/(D2) is between 2/1 and 1/2.
- 12 12 Compositions according to any one of the preceding claims, in which the ratio by weight (D1)/(D2+D3) is between 0.8 and 1.2.
- 30 13 Articles manufactured from a composition according to any one of the preceding claims.



- 14 Articles according to Claim 13 which are compartmentalized boxes or are trays on which loose electronic components are placed prior to their assembly on cards.
- 5 15 Articles according to claim 13 which are reels.
- 16 Articles according to claim 13 which are printer trays and paper feeding systems in photocopy machines.