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(54) **POLYMERES ANTISTATIQUES**
(54) **ANTISTATICALLY FINISHED POLYMERS**

(57) Cette invention concerne une composition de polymère comprenant : a) un polyéthylène de haute densité (HDPE), un polyamide 11, un polyamide 12 (PA 11, PA 12), un polymère ou un copolymère élastomère naturel ou synthétique ou un vulcanisat synthétique élastique; b) un polyoxyalkylène de formule R_1-O-[CH(R_3)-CH_2-O]$_n$-[CH_2-[CH(OH)]p-CH_2-O]q-[C(O)r-R_2 (I); et c) un sel de formule {M^{Z+}a$A^{(az/b)-}$b}, dans laquelle M est un cation métallique alcalin, un cation métallique alcalino-terreux ou un cation zincique z-valent, a et b sont, de manière indépendante, des nombres allant de 1 à 6, et A est un anion d'un acide inorganique protonique ou d'un acide mono ou polycarboxylique. Dans la formule (I), R_1 représente un atome d'hydrogène, un alkyle en C_1-C_{24}, un alkényle en C_2-C_{24}, CH_2=CH-C(O) ou CH_2=CCH_3-C(O), R_2 représente un alkyle en C_1-C_{24}, un alkényle en C_2-C_{24}, CH_2-COOH ou N(alkyle en C_1-C_{20})$_2$, R_3 représente un atome d'hydrogène ou CH_3, n est un nombre supérieur ou égal à 2, p est un nombre allant de 1 à 6 et q et r sont, de manière indépendante, égaux à 0 ou 1. Cette composition de polymère possède d'excellentes propriétés antistatiques.

(57) This invention relates to a polymer composition comprising (a) high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), a natural or synthetic elastomeric polymer or copolymer or a natural or synthetic elastic vulcanisate, (b) a polyoxyalkylene of formula R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O) or CH_2=CCH_3-C(O), R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH, or N(C_1-C_{20}alkyl)$_2$, R_3 is H or CH_3, n is a number higher than or equal to 2, p is a number from 1 to 6, and q and r are independently of each other 0 or 1; and (c) a salt of formula {M^{Z+}a $A^{(az/b)-}$b}, wherein M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,a and b are independently of each other a number from 1 to 6, and A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid. This polymer composition has excellent antistatic properties.

Abstract of the Disclosure

This invention relates to a polymer composition comprising
(a) high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), a natural or synthetic elastomeric polymer or copolymer or a natural or synthetic elastic vulcanisate,
(b) a polyoxyalkylene of formula
R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein
R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O) or CH_2=CCH_3-C(O),
R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH, or N(C_1-C_{20}alkyl)$_2$,
R_3 is H or CH_3,
n is a number higher than or equal to 2,
p is a number from 1 to 6, and
q and r are independently of each other 0 or 1; and
(c) a salt of formula {$M^{z+}_a A^{(az/b)-}_b$}, wherein
M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,
a and b are independently of each other a number from 1 to 6, and
A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid.
This polymer composition has excellent antistatic properties.

Antistatically finished polymers

The present invention relates to antistatically finished high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers and natural or synthetic elastic vulcanisates, to a process for the preparation of said antistatic co/polymers as well as to the use of an antistatic agent for antistatically finishing HDPE, PA 11, PA12, natural or synthetic elastomeric polymers or copolymers and natural or synthetic elastic vulcanisates.

One drawback of many polymers, and thus of the above-mentioned polymers, is their ready electrostatic chargeability. Once charges are applied, they cannot be discharged quickly enough owing to the low conductivity. However, rapid discharging is required not only for aesthetic and applicational reasons, but also in many cases for reasons of safety. If this is not ensured, there may be soiling of polymer surfaces, electrical shocks to persons touching the polymers, production faults due to film webs sticking together, lump-formation in polymer powders and sparking due to strong charging with subsequent ignition of dust- or solvent/air mixtures.

Static charging is frequently countered by using substances which improve the surface conductivity. However, these substances have the disadvantage of being virtually ineffective at low atmospheric humidity, which is why substances are then used which increase the volume conductivity. However, the known substances for increasing the volume conductivity, for example carbon black or metal powders, reduce the mechanical properties of the polymers and cannot be used for transparent polymers.

Further information on antistatic additives and on the mechanism of static charging may be found, inter alia, in "Plastics Additives Handbook", edited by R. Gächter and H. Müller, Hanser Verlag, 3rd edition, 1990, pages 749-775.

There thus continues to be a demand for an antistatical additive system which, independently of external parametres, makes the polymer enduringly conductive while not adversely affecting its other properties. In particular, there is a desire for additive systems which are effective even at low atmospheric humidity levels and which thus increase, in particular, the volume conductivity of the polymer.

The antistatic agent of this invention is known per se and is described in EP-A-751 179 for halogen-containing polymers.

Surprisingly, it has now been found that the polyoxyalkylenes described there, in combination with a selected inorganic salt, are excellently suitable also for HDPE, polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers and natural or synthetic elastic vulcanisates and that they provide these systems with good conductivity. As the antistatic agents are polar organic compounds and inorganic salts, it is surprising that this system is suitable for unpolar co/polymers and that there are no incompatibilities such exudation of the antistatic agent.

The antistatically finished polymers are exceedingly stable and have high electric conductivity even after a long storage time and/or thermal stress.

The antistatic agent is free of amines and is therefore hardly corrosive for metallic substrates.

In one of its aspects, this invention thus relates to a composition comprising
(a) high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), a natural or synthetic elastomeric polymer or copolymer or a natural or synthetic elastic vulcanisate,
(b) a polyoxyalkylene of formula
R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein
R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O) or CH_2=CCH_3-C(O),
R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH, or N(C_1-C_{20}alkyl)$_2$,
R_3 is H or CH_3,
n is a number higher than or equal to 2,
p is a number from 1 to 6, and
q and r are independently of each other 0 or 1; and
(c) a salt of formula {$M^{z+}_a A^{(az/b)-}_b$}, wherein
M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,
a and b are independently of each other a number from 1 to 6, and
A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid.

Examples of elastomeric polymers or copolymers are copolymers of styrene or α-methylstyrene with dienes or acryl derivatives, such as styrene/butadiene, styrene/butadiene/alkylacrylate and styrene/butadiene/methacrylate, styrene/maleic anhydride, and also block copolymers of styrene, such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.

Other examples are graft copolymers of styrene or α-methylstyrene, such as styrene on polybutadiene, styrene and maleic anhydride on polybutadiene, styrene and maleic acid imide on polybutadiene, or styrene and acrylonitrile on ethylene/propylene/diene terpolymers.

Further examples are EPDM and polyamides condensed during processing ("RIM polyamide systems").

Polyamide 11 and polyamide 12 are also very suitable.

Other suitable compounds are polyurethanes derived on the one hand from polyethers, polyesters and polybutadienes with terminal hydroxyl groups and, on the other hand, from aliphatic or aromatic polyisocyanates.

Of the natural polymers, natural rubber merits special mention.

It is also possible to use mixtures (polyblends) of the above polymers.

Other suitable polymers are aqueous emulsions of natural or synthetic rubbers, for example natural rubber latex or latices of carboxylated styrene/butadiene copolymers.

Component a) is preferably HDPE.

Other preferred components a) are elastomers containing polydiene, for example polybutadiene rubber.

Another preferred group of elastomers are those based on conjugated dienes with monovinyl-substituted aromatic compounds. These are preferably block copolymers in which the one block essentially consists of the vinyl-substituted aromatic compound and the other

block consists of polymerised conjugated diene. The preparation of such polymers and their use is disclosed, inter alia, in EP-A-0 346 823.

Suitable conjugated dienes are in particular 1,3 butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, piperylene or 3-butyl-1,3-octadiene.

Examples of vinyl-substituted aromatic compounds are styrene, 3-methylstyrene, 4-n-propylstyrene, 4-cyclohexylstyrene, 4-decylstyrene, 2-ethyl-4-benzylstyrene, 4-p-toluylstyrene, 4-(4-phenyl-n-butyl)styrene, 1-vinylnaphthalene or 2-vinylnaphthalene.

Star-shaped branched styrene/butadiene block copolymers and their preparation are disclosed, inter alia, in DE-OS-39 14 945.

High impact polystyrenes (HIPS) containing polybutadiene are also suitable.

The polyoxyalkylenes of formula (I) R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein

R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O) or CH_2=CCH_3-C(O),

R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH, or N(C_1-C_{20}alkyl)$_2$,

R_3 is H or CH_3,

n is a number higher than or equal to 2,

p is a number from 1 to 6, and

q and r are independently of each other 0 or 1,

which may be used as component (b) of this invention, are known and can be prepared by analogous methods if not commercially available.

Those substituents in the compounds of formula (I) which are defined as alkyl containing 1 to 24 carbon atoms are suitably radicals such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl, eicosyl, docosyl and tetracosyl and also the corresponding branched isomers.

Those substituents in the compounds of formula (I) which are defined as alkenyl containing 1 to 24 carbon atoms are derived from the cited alkyl radicals, the double bond preferably

being in central position in the hydrocarbon chain. The alkenyl radical is particularly preferably oleyl. If r is 1, then R_2 defined as alkenyl is preferably also CH_2=CH- or CH_2=CCH_3-.

R_1 in the compounds of formula (I) is preferably H or C_1-C_4alkyl and, very particularly preferably, H.

R_2 in the compounds of formula (I) is preferably C_6-C_{20}alkyl or C_6-C_{20}alkenyl.

n in the compounds of formula (I) is preferably a number from 2 to 20 and, very particularly preferably, a number from 2 to 14.

p in the compounds of formula (I) is preferably a number from 2 to 6 and, very particularly preferably, the number 4.

q in the compounds of formula(I) is preferably the number 0 or 1 and r is the number 1 and, very particularly preferably, q is the number 0 and r is the number 1.
Particularly preferred compounds are those of formula (I), wherein R_1 is H, R_2 is C_6-C_{20}alkyl or C_6-C_{20}alkenyl, R_3 is H or CH_3, n is a number from 2 to 14, q is 0, and r is 1.

Particularly preferred are polypropylene glycol lauryl ester, polypropylene glycol oleyl ester, polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, polyethylene glycol lauryl ester, polyethylene glycol oleyl ester, polyethylene glycol oleyl ether, polyethylene glycol sorbitan monolauryl ester, polyethylene glycol stearyl ester, polyethylene glycol polypropylene glycol lauryl ether and polyethylene glycol lauryl ether carboxylic acid.

Polyethylene glycol oleyl ether and, especially, polyethylene glycol lauryl ester are very particularly preferred.

The compound of formula (I) which may be used as component (b) of this invention, may be used in an amount of typically 0.05 to 50 parts by weight, conveniently of 0.05 to 30 parts by weight, particularly preferably of 0.05 to 20 parts by weight, based on 100 parts by weight of polymers.

The salts of formula $\{M^{z+}_a A^{(az/b)-}_b\}$ which may be used as component (c) of this invention, wherein M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation and wherein a and b are independently of each other a number from 1 to 6 and A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid, are commonly known and most of them are commercially available.

M defined as alkali metal cation, alkaline earth metal cation or zinc cation is preferably derived from Li, Na, K, Cs, Ca, Mg, Sr, Ba and Zn. M is particularly preferably derived from Li, Na, K, Ca, Mg and Zn.

A is the anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid, including acids which do not exist in free form but only in the form of their salts. A is preferably derived from acids from the group of the inorganic oxygen acids, inorganic complex acids and organic carboxylic acids. The following anions may be mentioned as examples: perchlorate, hexafluorophosphate, trifluoromethylsulfonate, tetrafluoroborate or perfluorobutylsulfonate, acetate, propionate, maleate or citrate.

Component (c) is particularly preferably an inorganic salt selected from the group: $LiClO_4$, $LiCF_3SO_3$, $NaClO_4$, $NaCF_3SO_3$, $KClO_4$, KPF_6, KCF_3SO_3, $KC_4F_9SO_3$, $Ca(ClO_4)_2$, $Ca(PF_6)_2$, $CaCF_3SO_3$, $Mg(ClO_4)_2$, $Mg(CF_3SO_3)_2$, $Zn(ClO_4)_2$, $Zn(PF_6)_2$ and $Ca(CF_3SO_3)_2$.

Preferred organic salts are sodium acetate, sodium propionate, potassium hydrogen maleate, sodium citrate or potassium sodium citrate.

The salts may also contain different amounts of crystal water.

The inorganic salt (c) in this composition is very particularly preferably $NaClO_4$, $LiCF_3SO_3$, $KClO_4$ or $LiClO_4$.

The inorganic salt which may be used as component (c) in this invention can be used in an amount of, for example, less than 10 parts by weight, conveniently of less than 5 parts by weight, particularly preferably of less than 0.005 to 3 parts by weight, based on 100 parts by weight of polymer.

In a preferred embodiment of this invention, the weight ratio of component (b) to component (c) is from 1:1 to 100:1.

The present invention contains preferably no polyoxyalkylene ammonium salts, particularly no N, polyoxyalkylene N, N, N trialkylammonium salt or N, N, dipolyoxyalkylene N, N dialkylammonium salt. The corresponding amines are also preferably not part of the composition. Further adjuvants which are preferably not present in the composition are alkali salts of alkyl sulfonates, particularly Na-alkylsufonates.

The novel polymeric composition can contain further additives. These additional additives are mainly from the group of heat stabilisers and /or light stabilisers. The thermal stabilisation embraces both processing and use (long-term stability). Said additives are known to the skilled person and most of them are commercially available.

Suitable additional additives are for example:

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-

butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α-tocopherol, β-tocopherol, γ-tocopherol, δ-tocopherol and mixtures thereof (Vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α-methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α-methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α-dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methyl-phenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, didodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris-(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis-(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.15. Esters of β-(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Naugard®XL-1 supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-

N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenlenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- und dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- und dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- und dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis-(2,2,6,6-tetramethyl-piperid-4-yl-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)-sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl- 2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α-dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonylethyl]-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)-phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphenyl)-

benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenylbenzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $\left[R-CH_2CH_2-COO-CH_2CH_2\right]_2$ where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α-dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α-dimethylbenzyl)-phenyl]-benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tertbutyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α-cyano-β,β-diphenylacrylate, isooctyl α-cyano-β,β-diphenylacrylate, methyl α-carbomethoxycinnamate, methyl α-cyano-β-methyl-p-methoxy-cinnamate, butyl α-cyano-β-methyl-p-methoxy-cinnamate, methyl α-carbomethoxy-p-methoxycinnamate and N-(β-carbomethoxy-β-cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimid, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane und epichlorohydrin, 1,1-bis-(1,2,2,6,6-pentamethyl-4-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxy-methylene-malonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, reaction product of maleic acid anhydride-α-olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanlide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-{2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl}-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyladipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

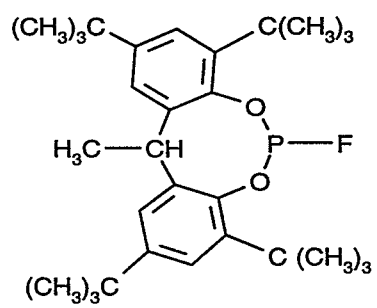
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butyl-

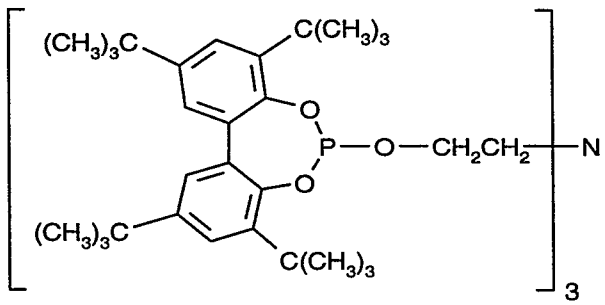
phenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butyl-phenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz-[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 2,2',2"-nitrilo[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite.

Especially preferred are the following phosphites:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos®168, Ciba-Geigy), tris(nonylphenyl) phosphite,

(A)





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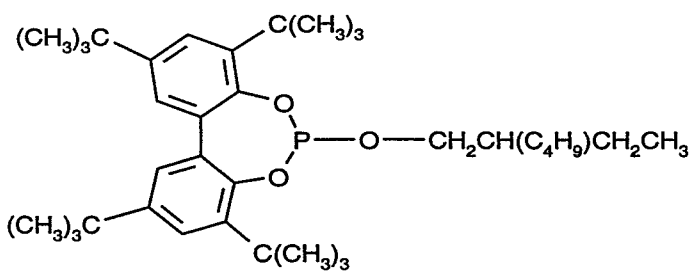

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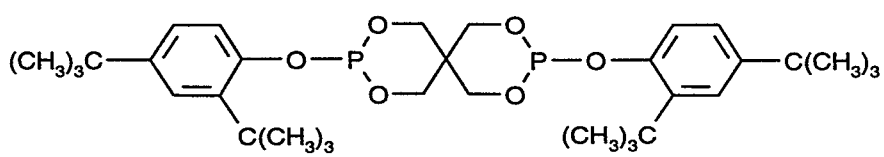

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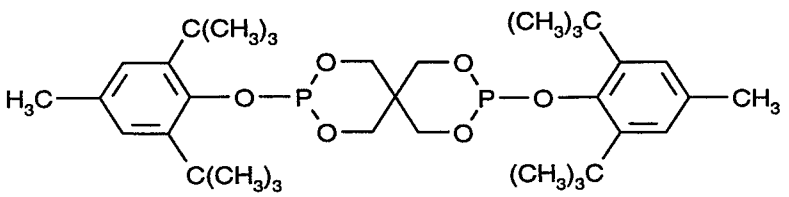

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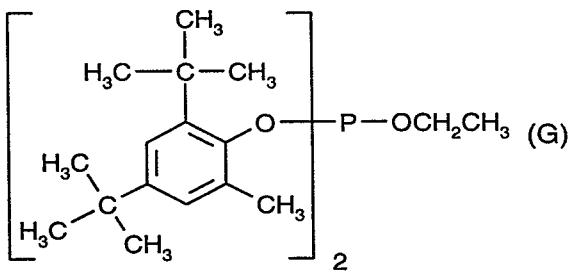

(G)

5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example N-benzyl-alpha-phenyl-nitrone, N-ethyl-alpha-methyl-nitrone, N-octyl-alpha-heptyl-nitrone, N-lauryl-alpha-undecyl-nitrone, N-tetradecyl-alpha-tridcyl-nitrone, N-hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-ocatadecyl-alpha-pentadecyl-nitrone, N-heptadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example dilauryl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β-thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β-dodecylmercapto)propionate.

9. Polyamide stabilisers, for example copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilisers, for example melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids, for example, calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zink pyrocatecholate.

11. Nucleating agents, for example inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers (ionomers).

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

13. Other additives, for example plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

14. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)-phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

Suitable lubricants are for example:

montan wax, fatty acid esters, PE waxes, amide waxes, polyol partial esters, partially saponified PE waxes, so-called complex ester chloroparaffins, glycerol esters, alkaline earth metal soaps or fatty ketones, such as described in DE4204887. Suitable lubricants are also described in "Taschenbuch der Kunststoffadditive", editors R. Gächter and H. Müller, Hanser Verlag, 3rd edition, 1990, pages 443-503. Other lubricant embodiments, in particular combinations of lubricants, are to be found in EP 0062813 and EP 0336289.

A preferred composition is also that which additionally contains a phenolic antioxidant and/or a phosphite, preferably 0.1 to 5.0 parts each per 100 parts of polymer.

In another of its aspects this invention also relates to the use of an additive mixture comprising a polyoxyalkylene of formula

R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein

R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O)- or CH_2=CCH_3-C(O)-,

R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2COOH or N(C_1-C_{20}alkyl)$_2$,

R_3 is H or CH_3,

n is a number higher than or equal to 2,

p is a number from 1 to 6, and

q and r are independently of each other 0 or 1;

and a salt of formula {$M^{z+}_a A^{(az/b)-}_b$}, wherein

M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,

a and b are independently of each other a number from 1 to 6, and

A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid;

for enhancing the antistatic property of high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates.

This invention also relates to a process for the preparation of antistatically finished high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates, which comprises mixing an additive mixture comprising

a polyoxyalkylene of formula

R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein

R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O)- or CH_2=CCH_3-C(O)-,

R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH or $N(C_1$-$C_{20}alkyl)_2$,

R_3 is H or CH_3,

n is a number higher than or equal to 2,

p is a number from 1 to 6, and

q and r are independently of each other 0 or 1;

and a salt of formula $\{M^{z+}{}_aA^{(az/b)-}{}_b\}$, wherein

M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,

a and b are independently of each other a number from 1 to 6, and

A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid;

as such or in the form of its individual components and together with optional further additives with high-density polyethylene (HDPE), PA 11, PA 12, natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates, using appliances such as calenders, mixers, kneaders and extruders.

The individual compounds and the polymer itself have the preferred meanings stated above, it being also possible to use in addition one of the above-described additional components.

The composition of this invention can be prepared in a manner known per se by mixing the cited additives and optional additional additives with the polymer using appliances known per se, such as calender, mixers, kneaders, extruder and the like. The additives can be added singly or in admixture with each other. It is also possible to use so-called masterbatches.

The antistatically finished polymer of this invention can be brought into the desired form by known methods. Such methods are, for example, calendering, extruding, spray coating, spinning, compression melting, rotational casting, thermoforming or extrusion blowing. The antistatically finished polymer can also be processed to foamed articles.

This invention is further illustrated by the following Examples. As in the remainder of the description, and unless otherwise stated, parts and percentages are by weight and numerical intervals given include the limiting values.

Example 1

Production of antistatic HD-PE

58.8 g of HD-PE powder (Hostalen® GF 7660, Hoechst) and 1.2 g of a polyethylene glycol laurate solution (Irgastat® 51, Ciba Spezialitätenchemie), comprising 5 % $NaClO_4 \cdot H_2O$, are mixed using a spatula and this mixture is processed to a rolled sheet in a two-roll calender at 160°C (rolling time 5 min, 26/32 rpm, nip 0.5 mm). In a heated high-pressure press, pressed sheets of 0.5 mm thickness are manufactured from this sheet (heating temperature 180°C, heating time 5 min). These pressed sheets are cooled under pressure in a second, water-cooled press (5 min). One day after production, the sheets have a surface resistance R_{OG} at 20 % rel. humidity of $1.05 \cdot 10^{11}$ ohm (measured using a guard-ring electrode in accordance with DIN 53482, 20 cm^2, nip 5mm, after 5 min at 500 volt), which falls to $1.1 \cdot 10^{10}$ ohm after storing for one week in air at about 50% rel. humidity.

Example 2

Production of antistatic HD-polyethylene injection-moulded sheets

38.5 g of a polyethylene glycol laurate solution (Irgastat® 51, Ciba Spezialitätenchemie), comprising 5 % $NaClO_4 \cdot H_2O$, are added to 1500 g of HD-PE Statoil® H 870 (stabilised, powder) and are mixed for 1 min at 1000 rpm in a Henschel mixer (water cooling). A granulate is prepared from this mixture in a twin-screw extruder (Berstorff 23 D), which granulate is then dried and processed to 1 mm platelets (67x 51 mm) in an Arburg injection moulding machine type 210 (temperature 210-220 degrees Celsius, cycle time 36 sec). One day after production, the surface resistance R_{OG} of these platelets is $8.7 \cdot 10^9$ ohm and after 3 days it is $4.5 \cdot 10^9$ ohm (at 50% rel. humidity). Measurement is carried out according to DIN 53482 using a guard-ring electrode (20 cm^2, nip 5mm, after 5 min at 500 volt). The surface resistances R_{OA}, measured using a spring reed electrode in accordance with DIN 53482, are $1.4 \cdot 10^{10}$ ohm (after 1 day) and $9.1 \cdot 10^9$ ohm (after 3 days).

Example 3

Production of antistatic styrene/butadiene block polymer

59.1 g of SB block copolymer (Styreneux® RE 31, BASF) are charged with 0.90 g of a polyethylene glycol laurate solution (Irgastat® 51, Ciba Spezialitätenchemie), comprising 5 % $NaClO_4 \cdot H_2O$, and are mixed using a spatula. This mixture is processed on a two-roll calender at 180°C (rolling time 5 min, 26/32 rpm, nip 0.50 mm). From the composition collected therefrom, moulded sheets of 0.5 mm thickness are manufactured at 190°C (5 min) in a heated

high-pressure press. The sheets are cooled under pressure in a second, water-cooled press (5 min). One day after production, the sheets have a surface resistance R_{OG} of $1 \bullet 10^{12}$ ohm at 20% rel. humidity, which drops to $2.8 \bullet 10^{9}$ ohm after storing for 1 week in air (50% rel. humidity). Measurement is carried out according to DIN 53482 using a guard-ring electrode. The sheets are white-opaque.

Example 4

Production of an antistatic pale vulcanisate

A mixture consisting of 100 parts of SBR 1502, 10 parts of Kronos CL-220, 70 parts of Tixosil® Einex, 37.5 parts of Naftolen® ZM, 2.5 parts of ZnO, 1 part of stearic acid, 1 part of paraffin, 3 parts of diethylene glycol, 0.65 part of sulfur, 0.8 part of Vulkacit® MOZ and 1 part of Vulkacit D is charged with 5 parts of polyethylene glycol laurate (Irgastat 51®, CIBA Spezialitätenchemie, comprising 5 % $NaClO_4 \cdot H_2O$) and is blended for 20 minutes on a two-roll calender at 60°C (17/21 rpm). The vulcanisation parametres are determined in a rheometer using 5 g of the rolled sheet obtained (Monsanto) at 160°C. Using a press, the remaining mixture is then vulcanised to T 95 in a 2 mm mould at 160°C and 100 bar.
3 days after production, the electric resistance values of the samples are determined according to DIN 53482 using a guard-ring electrode ($20 cm^2$, nip 5 mm, after 5 min at 500 volt). The surface resistance R_{OG} at 50% rel. humidity is $5 \bullet 10^{9}$ ohm and the volume resistance R_V is $4 \bullet 10^{8}$ ohm.

Example 5

Production of an antistatic pale sulfur vulcanisate

A mixture consisting of 100 parts of EPDM BUNA AP 451, 5 parts of ZnO, 1 part of stearic acid, 50 parts of Tixosil® 50, 10 parts of Naftolen® ND, 1 part of sulfur, 0.4 part of Vulkacit® Mercapto and 0.8 part of Vulkacit Thiuram is charged with 5 parts of polyethylene glycol laurate (Irgastat® 51, Ciba Spezialitätenchemie, comprising 5 % $NaClO_4 \cdot H_2O$) and is blended on a two-roll calender for 20 minutes at 60°C (17/21 rpm). The vulcanisation parametres are determined in a rheometer using 5 g of the rolled sheet obtained (Monsanto) at 160°C. Using a heatable press, the remaining mixture is then vulcanised to T 95 in a 2 mm mould at 160°C and 100 bar.
3 days after production, the electric resistance values of the sample are determined according to DIN 53482 using a guard-ring electrode ($20 cm^2$, nip 5mm, after 5 min at 500 volt).

The surface resistance R_{OG} at 50% rel. humidity is $1.4 \bullet 10^9$ ohm and the volume resistance R_V is $4 \bullet 10^7$ ohm.

Example 6

Production of an antistatic pale peroxide-crosslinked vulcanisate

A BR/SBR/IR mixture consisting of 10 parts of Cariflex® IR 305, 20 parts of Cariflex SBR 1210, 70 parts of Tactene® BR 1220, 30 parts of Aerosil® VN 3 and 0.5 part of Dicup® 40 is charged with 5 parts of polyethylene glycol laurate (Irgastat® 51, Ciba Spezialitäten-chemie, comprising 5 % $NaClO_4 \cdot H_2O$) and is blended on a two-roll calender for 20 minutes at 60°C (17/21 rpm). The vulcanisation parametres are determined in a rheometer using 5 g of the rolled sheet obtained (Monsanto) at 160°C. Using a press, the remaining mixture is then vulcanised to T 95 in a 2 mm mould at 160°C and at an atmosphere-gauge pressure of 100. 3 days after production, the electric resistance values of a sample are determined according to DIN 53482 using a guard-ring electrode (20 cm^2, nip 5 mm, after 5 min at 500 volt). The surface resistance R_{OG} at 50% rel. humidity is$1 \bullet 10^9$ ohm and the volume resistance R_V is $6 \bullet 10^7$ ohm.

Example 7

Production of an antistatic highly flexible styrene/butadiene block copolymer

58.8 g of SB block copolymer STYROFLEX® BX 6104 (BASF) and 1.2 g of a polyethylene glycol laurate solution (Irgastat® 51, Ciba Spezialitätenchemie), comprising 5 % $NaClO_4 \cdot H_2O$, are mixed using a spatula and this mixture is blended on a two-roll calender at 185°C (rolling time 5 min, 26/32 rpm, nip 0.5 mm). From the composition obtained pressed sheets of 0.5 mm thickness are then manufactured in a heated high-pressure press (heating temperature 195 °C, heating time 5 min). The pressed sheets are cooled under pressure in a second, water-cooled press (5 min). One week after production, the sheets have a surface resistance R_{OG} (measured using a guard-ring electrode in accordance with DIN 53482, 20 cm^2, nip 5mm, after 5 min at 500 volt) of $1 \bullet 10^{10}$ ohm (at 55 % rel. humidity) and a surface resistance R_{OA} (measured using a spring reed electrode in accordance with DIN 53482) of $2 \bullet 10^{11}$ ohm (at 55 % rel. humdity).

Example 8

Production of antistatic polyamide 12 pressed sheets

57.6 g of polyamide 12 powder (Aldrich) and 2.4 g of a polyethylene glycol laurate solution (Irgastat 51, Ciba Spezialitätenchemie, comprising 4% $NaClO_4 \cdot H_2O$) are mixed using a spatula and this mixture is then blended to homogeneity in a two-roll calender at 188°C (rolling time 5 min, 26/32 rpm, nip 0.5mm). From the polymer composition so obtained pressed sheets of 0.5 mm thickness are then manufactured in a high-pressure press (heating temperature 180°C, press time 5 min). One week after production, the sheets have a surface resistance R_{OG} of $2.5 \cdot 10^{11}$ ohm at 50% rel. humidity (measured using a guard-ring electrode in accordance with DIN 53482, 20 cm^2, nip 5mm, after 5 min at 500 volt).
In contrast, the surface resistance of a comparison sample without antistatic additive is $>2 \cdot 10^{14}$ ohm.

Using a spring reed electrode (also DIN 53482), a surface resistance R_{OA} of $7 \cdot 10^{10}$ ohm and a volume resistance R_v of $4.5 \cdot 10^8$ ohm are measured for pressed sheets containing the inventive antistatic agent.
The corresponding volume resistance of a sample without additive is $2 \cdot 10^{12}$ ohm.

Example 9
Production of antistatic polyamide 12 injection-moulded sheets
3426.5 g of polyamide 12 powder (Vestamid L1901), 3.5 g of Irganox 1098 (Ciba SC) and 70 g of a polyethylene glycol laurate solution (Irgastat 51, Ciba SC), comprising 5% $NaClO_4 \cdot H_2O$, are extruded in a twin-screw extruder at 210 °C. Sheets of 10´10´0.2 cm are manufactured from this compound by injection moulding at 220 °C.
After 3 weeks, the surface resistance R_{OG} is measured in accordance with DIN 53482 using a guard-ring electrode; it is $1 \cdot 10^{10}$ ohm (50% rel. humidity).
A sample without antistatic additive has a surface resistance of $1 \cdot 10^{13}$ ohm.
The volume resistance R_V of the sample containing an antistatic agent is $4.1 \cdot 10^9$ ohm.
The corresponding volume resistance of a sample without additive is $3 \cdot 10^{12}$ ohm (50% rel. humidity).

Comparison Example using a non-inventive polymer
6 g of an Irgastat 51 solution (Ciba Spezialitätenchemie), comprising 5% $NaClO_4 \cdot H_2O$, are added to and incorporated in 54 g of fused ABS Cycolac TCA (GEP) using a two-roll calender (roll temperature 170°C, 22/26 rpm, nip 0.7 mm, rolling time 5min). Pressed sheets of

0.5 mm thickness are manufactured from the rolled sheet obtained. The samples measured according to DIN 53482 have surface and volume resistances of about $1 \bullet 10^{13}$ ohm, whereas those of a comparison sample without additive are $1 \bullet 10^{14}$ ohm.

What is claimed is:

1. A composition, which comprises
(a) high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), a natural or synthetic elastomeric polymer or copolymer or a natural or synthetic elastic vulcanisate,
(b) a polyoxyalkylene of formula
R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein
R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O) or CH_2=CCH_3-C(O),
R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH, or N(C_1-C_{20}alkyl)$_2$,
R_3 is H or CH_3,
n is a number higher than or equal to 2,
p is a number from 1 to 6, and
q and r are independently of each other 0 or 1; and
(c) a salt of formula $\{M^{z+}{}_aA^{(az/b)-}{}_b\}$, wherein
M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,
a and b are independently of each other a number from 1 to 6, and
A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid.

2. A composition according to claim 1, wherein component a) is HDPE.

3. A composition according to claim 1, wherein component a) is a synthetic or natural elastomer which comprises a polydiene.

4. A composition according to claim 1, which comprises a synthetic elastomer based on conjugated dienes with monovinyl-substituted aromatic compounds.

5. A composition according to claim 1, wherein component (b) is polypropylene glycol lauryl ester, polypropylene glycol oleyl ester, polyethylene glycol monomethyl ether, polyethylene glycol dimethyl ether, polyethylene glycol lauryl ester, polyethylene glycol oleyl ester, polyethylene glycol oleyl ether, polyethylene glycol sorbitan monolauryl ester, polyethylene glycol stearyl ester, polyethylene glycol polypropylene glycol lauryl ether or polyethylene glycol lauryl ether carboxylic acid.

6. A composition according to claim 5, wherein component b) is polyethylene glycol oleyl ether or polyethylene glycol lauryl ester.

7. A composition according to claim 1, which comprises 0.05 to 20 parts per weight, based on 100 parts by weight of polymer, of component b).

8. A composition according to claim 1, wherein the inorganic salt (c) is $NaClO_4$, $LiCF_3SO_3$, $KClO_4$ or $LiClO_4$.

9. A composition according to claim 1, which comprises 0.005 to 3 parts by weight, based on 100 parts by weight of polymer, of component c).

10. A composition according to claim 1, wherein the weight ratio of component (b) to component (c) is from 1:1 to 100:1.

11. Use of an additive mixture, which comprises
a polyoxyalkylene of formula

R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein

R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O)- or CH_2=CCH_3-C(O)-,

R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2COOH or N(C_1-C_{20}alkyl)$_2$,

R_3 is H or CH_3,

n is a number higher than or equal to 2,

p is a number from 1 to 6, and

q and r are independently of each other 0 or 1;

and a salt of formula $\{M^{z+}{}_aA^{(az/b)-}{}_b\}$, wherein

M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,

a and b are independently of each other a number from 1 to 6, and

A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid;

for enhancing the antistatic property of high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates.

12. A process for the preparation of antistatically finished high-density polyethylene (HDPE), polyamide 11, polyamide 12 (PA 11, PA 12), natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates, which comprises mixing an additive mixture comprising

a polyoxyalkylene of formula

R_1-O-[CH(R_3)-CH_2-O-]$_n$-[CH_2-[CH(OH)]$_p$-CH_2-O]$_q$-[C(O)]$_r$-R_2 (I), wherein

R_1 is H, C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2=CH-C(O)- or CH_2=CCH_3-C(O)-,

R_2 is C_1-C_{24}alkyl, C_2-C_{24}alkenyl, CH_2-COOH or N(C_1-C_{20}alkyl)$_2$,

R_3 is H or CH_3,

n is a number higher than or equal to 2,

p is a number from 1 to 6, and

q and r are independently of each other 0 or 1;

and a salt of formula $\{M^{z+}{}_aA^{(az/b)-}{}_b\}$, wherein

M is a z-valent alkali metal cation, alkaline earth metal cation or zinc cation,

a and b are independently of each other a number from 1 to 6, and

A is an anion of an inorganic protonic acid or of an organic mono- or polycarboxylic acid;

as such or in the form of its individual components and together with optional further additives with high-density polyethylene (HDPE), PA 11, PA 12, natural or synthetic elastomeric polymers or copolymers or natural or synthetic elastic vulcanisates, using appliances such as calenders, mixers, kneaders and extruders.

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