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(54) Title: SCRATCH RESISTANT POLYOLEFINS

(57) Abstract: Polyolefin substrates, for example polypropylene, polyethylene or thermoplastic olefin molded parts, are made scratch resistant by the incorporation therein of an additive combination of a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine and a primary or secondary fatty acid amide. The present polyolefins exhibit good weatherability, scratch resistance, good processability, good mechanical strength, good gloss retention and are non-sticky. The functionalized maleated alpha-olefin is for example the ester or half ester of maleated C_{18}-C_{26} alpha-olefin with tallow fatty alcohol. The fatty acid amide is for example oleyl palmitamide or stearyl erucamide.

WO 2006/003127 A1

Scratch Resistant Polyolefins

The present invention is aimed at scratch resistant polyolefin compositions. The invention is also aimed at a method of imparting scratch resistance to polyolefin compositions by incorporating therein certain anti-scratch additives. The polyolefin compositions are for example thermoplastic olefin (TPO) molded parts. The molded parts are useful for example in automotive applications.

U.S. Pat. No. 6,048,942 discloses thermoplastic olefin compositions comprising mar resistance additives selected from polysiloxanes, metal stearates, saturated fatty acid amides and unsaturated fatty acid amides.

JP-A-2002338778 teaches a graft copolymer compositions comprising fatty acid amides.

U.S. Pat. No. 5,731,376 discloses polypropylene block copolymer with improved scratch resistance by inclusion of a polyorganosiloxane. The compositions may further include a fatty acid amide.

U.S. Pat. No. 5,585,420 teaches scratch resistant polyolefin compositions comprising a plate like inorganic filler. The compositions may further comprise high rubber ethylene-propylene copolymers, fatty acid amides, polyorganosiloxanes or epoxy resins.

JP-A-2002003692 discloses polypropylene resin comprising fatty acid amides.

JP-A-62072739 is aimed at molded articles for automobile parts made by compounding a specific polyolefin with a rubbery substance and a specific amount of mica of a specific particle size. The polyolefin consists of a certain polypropylene and a polyolefin modified with an unsaturated carboxylic acid (anhydride), for example maleic anhydride.

JP-A-63017947 is aimed at scratch resistant propylene polymer compositions.

JP-A-2001261902 is aimed at polypropylene resin compositions useful as molding material for preparation of interior trims.

U.S. published app. No. 2003/0004245 teaches blends of polyolefin and a reaction product of polyolefin and an alpha, beta unsaturated carboxylic ester, acid or anhydride.

Polyanhydride resins are described in a CPChem Specialty Chemicals data sheet of 2004.

Surprisingly, it has been found that polyolefin substrates are made scatch resistance by the incorporation therein of an additive combination of a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine and a primary or secondary fatty acid amide.

The present invention pertains to a composition comprising

a) a polyolefin,
b) a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine, and
c) a primary or secondary fatty acid amide.

Also disclosed is a method for providing scratch resistance to a polyolefin substrate, which method comprises incorporating into said polyolefin an effective amount of (b) a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine and (c) a primary or secondary fatty acid amide.

Examples for polyolefins are:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), (VLDPE) and (ULDPE).

Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, for example polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

i) radical polymerization (normally under high pressure and at elevated temperature).

ii) catalytic polymerization using a catalyst that normally contains one or more than one metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either p- or s-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerization medium. The catalysts can be used by themselves in the polymerization or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1.), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/-alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

4. Blends of polymers mentioned under 1.) with impact modifiers such as ethylene-propylene-diene monomer copolymers (EPDM), copolymers of ethylene with higher alpha-olefins (such as ethylene-octene copolymers), polybutadiene, polyisoprene, styrene-butadiene copolymers, hydrogenated styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers. These blends are commonly referred to in the industry as TPO's (thermoplastic polyolefins).

Polyolefins of the present invention are for example polypropylene or polyethylene including polypropylene homo- and copolymers and polyethylene homo- and copolymers. For instance, polypropylene, high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and polypropylene random and impact (heterophasic) copolymers. Preferred polyolefins of the present invention include polypropylene homopolymers, polypropylene impact (heterophasic) copolymers, blends thereof, and TPO's such as blends of polypropylene homopolymers and impact copolymers with EPDM or ethylene-alpha-olefin copolymers.

The polyolefins of this invention are in particular TPO's. TPO is for example about 10 to about 90 parts propylene homopolymer, copolymer or terpolymer, and about 90 to about 10 parts (parts by weight) of an elastomeric copolymer of ethylene and a C_3-C_8 alpha-olefin. TPO is disclosed for example in U.S. Pat. No. 6,048,942.

The maleated alpha-olefin is for example as disclosed in U.S. app. 2003/0004245. The maleated alpha-olefin is for example a reaction product of an alpha-olefin with maleic anhydride or maleic acid. The reaction is effected by means known in the art. For example, the reaction can be conducted by a melt process in the presence of a free radical initiator. The radical initiators are for example peroxides or organic azo compounds.

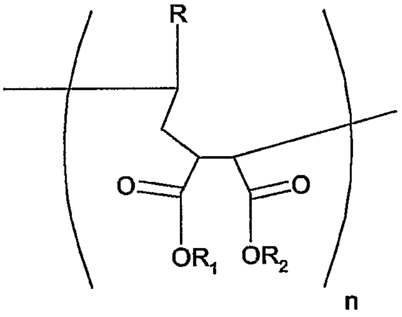
For instance, the alpha-olefin of the present maleated alpha-olefin is from C_3 up to about C_{33}, for example the alpha-olefin is a C_{18}-C_{26} alpha-olefin, for example a C_{22}-C_{26} or a C_{18} alpha-olefin.

The maleated alpha-olefin is functionalized with a long chain alcohol or long chain amine. That is, the maleated alpha-olefin is reacted with a long chain alcohol or long chain amine to form the ester or amide or imide products.

For example, the present functionalized maleated alpha-olefin is an ester or half ester product resulting from reaction with a long chain alcohol, or is an amide or imide product resulting from reaction with a long chain primary or secondary amine. Imides may be prepared by heating the half amide. The present functionalized maleated alpha-olefin may be a mixture of esters and amides.

Half ester derivatives may be formed by dropwise addition of alcohol to a stirred, acid catalyzed solution of the maleated alpha-olefin in an appropriate solvent under conditions such that water is not removed from the reaction mixture. Appropriate solvent is for example methyl isobutyl ketone. Suitable acid catalysts include sulfuric acid, methanesulfonic acid, and p-toluenesulfonic acid. Diesters are prepared using excess alcohol and removing the water to drive the reaction towards full esterification.

For instance, the functionalized maleated alpha-olefin is an ester or half ester of the formula



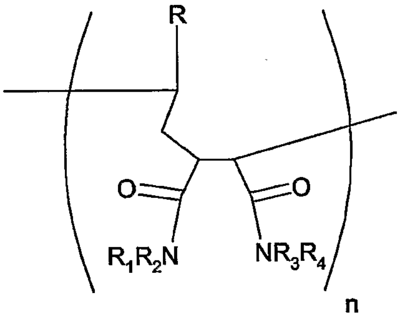
wherein

R is C_{16}-C_{24}alkyl,

R_1 and R_2 are independently hydrogen, C_1-C_{22}alkyl or C_2-C_{22}alkenyl wherein at least one of R_1 and R_2 are C_{12}-C_{22}alkyl or alkenyl, and

n is an integer such that the average molecular weight is between about 20,000 and about 50,000.

For example, the present functionalized maleated alpha-olefins are primary or secondary amides of the formula



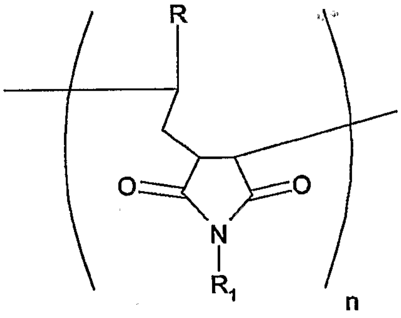
wherein

R is C_{16}-C_{24}alkyl,

R_1, R_2, R_3 and R_4 are independently hydrogen or C_1-C_{22}alkyl or C_2-C_{22}alkenyl, wherein at least one of R_1, R_2, R_3 or R_4 are C_{12}-C_{22}alkyl or alkenyl, and

n is an integer such that the average molecular weight is between about 20,000 and about 50,000.

For instance, the present functionalized maleated alpha-olefins are imides of the formula



wherein

R is C_{16}-C_{24}alkyl,

R_1 is C_{12}-C_{22}alkyl or alkenyl, and

n is an integer such that the average molecular weight is between about 20,000 and about 50,000.

For example R is C_{16}alkyl or is C_{20-24}alkyl.

For instance, the present functionalized maleated alpha-olefin is the half ester or ester of maleated C_{18}-C_{26}alpha-olefin with tallow fatty alcohol, ricinoleyl alcohol [CAS# 540-11-4] or oleyl alcohol. That is, the half ester or ester reaction products of maleated alpha-olefin with the long chain alcohols.

For instance, the present functionalized maleated alpha-olefin is the amide of maleated C_{18}-C_{26}alpha-olefin with oleamide, erucamide, stearamide, behenamide, oleyl palmitamide, stearyl erucamide, ethylene-bis-stearamide or ethylene-bis-oleamide, or is the imide of maleated C_{18}-C_{26}alpha-olefin with oleamide, erucamide, stearamide or behenamide. That is, the amide or imide reaction products of maleated alpha-olefin with long chain amines.

The fatty group of the primary or secondary fatty acid amides are C_{11}-C_{21}alkyl or C_{11}-C_{21}alkenyl. The present secondary fatty acid amides are not bis amides, that is methylene-bis or ethylene-bis amides.

The primary or secondary fatty acid amide is for example at least one compound selected from the group consisting of oleamide, erucamide, stearamide, behenamide, oleyl palmitamide and stearyl erucamide.

In particular, the present fatty acid amides are secondary fatty acid amides, for example stearyl erucamide or oleyl palmitamide.

Suitable fatty acid amides are for example disclosed in U.S. Pat. No. 6,228,915.

Alkyl is straight or branched chain and is for example methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, icosyl or docosyl.

Alkenyl having 2 to 22 carbon atoms is a branched or unbranched radical such as, for example, vinyl, propenyl (allyl), 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl.

The weight:weight ratio of the functionalized maleated alpha-olefin additive [component (b)] to the primary or secondary fatty acid amide additive [component (c)] is for example between about 1:1 and about 20:1, for example between about 1:1 and about 15:1, between about 1:1 and about 10:1, between about 1:1 and about 7:1, or between about 1:1 and about 5:1. For instance, the weight:weight ration of the functionalized maleated alpha-olefin to the primary or secondary fatty acid amide is about 1.5:1, about 2:1, about 3:1, or about 4:1.

The total of functionalized maleated alpha-olefin and primary or secondary fatty acid amide additive combination to be incorporated into the polyolefin substrate is for example between about 1% and about 15% by weight, based on the weight of the polyolefin substrate. For example, the additive combination is present from about 1% to about 10%, from about 3% to about 7%, or from about 3% to about 5% by weight, based on the weight of the polyolefin substrate.

Component (b) is preferably added to the polyolefin in an amount of from 0.05 to 15 %, in particular from 1 to 10 %, for example from 1 to 7%, based on the weight of the polyolefin.

Component (c) is preferably added to the polyolefin in an amount of from 0.05 to 15 %, in particular from 1 to 10 %, for example from 1 to 7%, based on the weight of the polyolefin.

The additives of the invention may be added to the polyolefin substrate individually or mixed with one another. If desired, the individual components can be mixed with one another before incorporation into the polyolefin for example by dry blending, compaction or in the melt.

The incorporation of the additives of the invention is carried out by known methods such as dry blending in the form of a powder, or wet mixing in the form of solutions, dispersions or suspensions for example in an inert solvent, water or oil. The additives of the invention may be incorporated, for example, before or after molding or also by applying the dissolved or dispersed additive or additive mixture to the polyolefin material, with or without subsequent evaporation of the solvent or the suspension/dispersion agent. They may be added directly into the processing apparatus (e.g. extruders, internal mixers, etc), e.g. as a dry mixture or powder or as solution or dispersion or suspension or melt.

The incorporation can be carried out in any heatable container equipped with a stirrer, e.g. in a closed apparatus such as a kneader, mixer or stirred vessel. The incorporation is preferably carried out in an extruder or in a kneader. It is immaterial whether processing takes place in an inert atmosphere or in the presence of oxygen.

The addition of the additives to the polyolefin substrate can be carried out in all customary mixing machines in which the polyolefin is melted and mixed with the additives. Suitable machines are known to those skilled in the art. They are predominantly mixers, kneaders and extruders.

Processing includes extrusion, co-kneading, pultrusion, compression molding, sheet extrusion, thermoforming, injection molding or rotational molding. The process is preferably carried out in an extruder by introducing the additives during processing.

Particularly preferred processing machines are single-screw extruders, contrarotating and corotating twin-screw extruders, rotomolding devices, planetary-gear extruders, ring extruders or cokneaders. It is also possible to use processing machines provided with at least one gas removal compartment to which a vacuum can be applied.

Suitable extruders and kneaders are described, for example, in *Handbuch der Kunststoffextrusion, Vol. 1 Grundlagen, Editors F. Hensen, W. Knappe, H. Potente, 1989, pp. 3-7, ISBN:3-446-14339-4 (Vol. 2 Extrusionsanlagen 1986, ISBN 3-446-14329-7).*

For example, the screw length is 1-60 screw diameters, preferably 35-48 screw diameters. The rotational speed of the screw is preferably 10-600 rotations per minute (rpm), very particularly preferably 25-300 rpm.

The maximum throughput is dependent on the screw diameter, the rotational speed and the driving force. The process of the present invention can also be carried out at a level lower than maximum throughput by varying the parameters mentioned or employing weighing machines delivering dosage amounts.

If a plurality of components are added, these can be premixed or added individually.

The additives of the invention can also be sprayed onto the polyolefin material. They are able to dilute other additives (for example optional conventional additives) or their melts so that they can be sprayed also together with these additives onto the material. Addition by spraying during the deactivation of the polymerization catalysts is particularly advantageous; in this case, the steam evolved may be used for deactivation of the catalyst. In the case of spherically polymerized polyolefins it may, for example, be advantageous to apply the additives of the invention, optionally together with other additives, by spraying.

The additives of the invention and optional further additives can also be added to the polyolefin in the form of a masterbatch ("concentrate") which contains the components in a concentration of, for example, about 1% to about 40% and preferably about 2% to about 20% by weight incorporated in a polymer. The polymer must not necessarily be identical to the polyolefin where the additives are added finally. In such operations, the polymer can be used in the form of powder, granules, solutions, suspensions or in the form of latices.

Incorporation can take place prior to or during the shaping operation, or by applying the dissolved or dispersed compound to the polyolefin, with or without subsequent evaporation of the solvent. A further possibility for incorporating the additives of the invention into polyolefins is to add them before, during or directly after the polymerization of the corresponding monomers or prior to crosslinking. In this context the additives of the invention can be added as it is or else in encapsulated form (for example in waxes, oils or polymers).

The polyolefins containing the additives of the invention described herein can be used for the production of moldings, rotomolded articles, injection molded articles, blow molded articles, profiles, and the like.

The polyolefins of the present invention may optionally also contain from about 0.01 to about 5%, preferably from about 0.025 to about 2%, and especially from about 0.1 to about 1% by weight of various further additives, such as the compouns listed below, or mixtures thereof.

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. 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, 1,3,5-tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, di-(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, 3,5-di-tert-butyl-4-hydroxybenzyl-mercapto-acetic acid isooctyl ester, bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol terephthalate, 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, 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dioctadecyl ester and 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid monoethyl ester, calcium-salt.

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, di-dodecylmercaptoethyl-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-hydroxy-lauric acid anilide, 4-hydroxy-stearic acid anilide, 2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine and 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-phenylenediamine, 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- and dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- and dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene.

2. UV absorbers and light stabilizers

2.1. 2-(2-Hydroxyphenyl)-2H-benzotriazoles, for example known commercial hydroxyphenyl-2H-benzotriazoles and benzotriazoles as disclosed in, United States Patent Nos. 3,004,896; 3,055,896; 3,072,585; 3,074,910; 3,189,615; 3,218,332; 3,230,194; 4,127,586; 4,226,763; 4,275,004; 4,278,589; 4,315,848; 4,347,180; 4,383,863; 4,675,352; 4,681,905, 4,853,471; 5,268,450; 5,278,314; 5,280,124; 5,319,091; 5,410,071; 5,436,349; 5,516,914; 5,554,760; 5,563,242; 5,574,166; 5,607,987, 5,977,219 and 6,166,218 such as 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-chloro-2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 5-chloro-2-(3-t-butyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-sec-butyl-5-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-4-octyloxyphenyl)-2H-benzotriazole, 2-(3,5-di-t-amyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3,5-bis-α-cumyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-(ω-hydroxy-octa-(ethyleneoxy)carbonyl-ethyl)-, phenyl)-2H-benzotriazole, 2-(3-dodecyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-octyloxycarbonyl)ethylphenyl)-2H-benzotriazole, dodecylated 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-octyloxycarbonylethyl)phenyl)-5-chloro-2Hbenzotriazole, 2-(3-tert-butyl-5-(2-(2-ethylhexyloxy)-carbonylethyl)-2-hydroxyphenyl)-5-chloro-2H-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-2H-benzotriazole, 2-(3-t-butyl-5-(2-(2-ethylhexyloxy)carbonylethyl)-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isooctyloxycarbonylethyl)phenyl-2H-benzotriazole, 2,2'-methylene-bis(4-t-octyl-(6-2H-benzotriazol-2-yl)phenol), 2-(2-hydroxy-3-α–cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-t-octyl-5-α–cumylphenyl)-2H-benzotriazole, 5-fluoro-2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole, 5-chloro-2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole, 5-chloro-2-(2-hydroxy-3-α-cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isooctyloxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-octylphenyl)-2H-benzotriazole, methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyhydrocinnamate, 5-butylsulfonyl-2-(2-hydroxy-3-α-cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3-α–cumyl-5-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole, 5-butylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole and 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-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-tert-butylphenyl 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 and malonates, for example, α-cyano-β,β-diphenylacrylic acid ethyl ester or isooctyl ester, α-carbomethoxy-cinnamic acid methyl ester, α-cyano-β-methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, α-carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(β-carbomethoxy-β-cyanovinyl)-2-methyl-indoline, Sanduvor® PR25, dimethyl p-methoxybenzylidenemalonate (CAS# 7443-25-6), and Sanduvor® PR31, di-(1,2,2,6,6-pentamethylpiperidin-4-yl) p-methoxybenzylidenemalonate (CAS #147783-69-5).

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 amine stabilizers, for example 4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-allyl-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-benzyl-4-hydroxy-2,2,6,6-tetramethylpiperidine, 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 and epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyl-oxycarbonyl)-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.

The sterically hindered amine may also be one of the compounds described in U.S. Pat. No. 5,980,783, the relevant parts of which are hereby incorporated by reference, that is compounds of component I-a), I-b), I-c), I-d), I-e), I-f), I-g), I-h), I-i), I-j), I-k) or I-l), in particular the light stabilizer 1-a-1, 1-a-2, 1-b-1, 1-c-1, 1-c-2, 1-d-1, 1-d-2, 1-d-3, 1-e-1, 1-f-1, 1-g-1, 1-g-2 or 1-k-1 listed on columns 64-72 of said U.S. Pat. No. 5,980,783.

The sterically hindered amine may also be one of the compounds described in U.S. Pat. Nos. 6,046,304 and 6,297,299, the disclosures of which are hereby incorporated by reference, for example compounds as described in claims 10 or 38 or in Examples 1-12 or D-1 to D-5 therein.

2.7. Sterically hindered amines substituted on the N-atom by a hydroxy-substituted alkoxy group, for example compounds such as 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-hexadecanoyloxy-2,2,6,6-tetramethylpiperidine, the reaction product of 1-oxyl-4-hydroxy-2,2,6,6-tetramethylpiperidine with a carbon radical from t-amylalcohol, 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) glutarate and 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine.

2.8. 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'-ethyloxanilide, 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.

2.9. Tris-aryl-o-hydroxyphenyl-s-triazines, for example known commercial tris-aryl-o-hydroxyphenyl-s-triazines and triazines as disclosed in, U.S. Patent Nos. 3,843,371; 4,619,956; 4,740,542; 5,096,489; 5,106,891; 5,298,067; 5,300,414; 5,354,794; 5,461,151; 5,476,937; 5,489,503; 5,543,518; 5,556,973; 5,597,854; 5,681,955; 5,726,309; 5,736,597; 5,942,626; 5,959,008; 5,998,116; 6,013,704; 6,060,543; 6,242,598 and 6,255,483, for example 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-octyloxyphenyl)-s-triazine, Cyasorb® 1164, Cytec Corp, 4,6-bis-(2,4-dimethylphenyl)-2-(2,4-dihydroxyphenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-bromophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-acetoxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis(4-biphenylyl)-6-(2-hydroxy-4-octyloxycarbonylethylideneoxyphenyl)-s-triazine, 2-phenyl-4-[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)phenyl]-6-[2-hydroxy-4-(3-sec-amyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-benzyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4-bis(2-hydroxy-4-n-butyloxyphenyl)-6-(2,4-di-n-butyloxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-nonyloxy*-2-hydroxypropyloxy)-5-α-cumylphenyl]-s-triazine (* denotes a mixture of octyloxy, nonyloxy and decyloxy groups), methylenebis-{2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-butyloxy-2-hydroxypropoxy)phenyl]-s-triazine}, methylene bridged dimer mixture bridged in the 3:5', 5:5' and 3:3' positions in a 5:4:1 ratio, 2,4,6-tris(2-hydroxy-4-isooctyloxycarbonylisopropylideneoxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-hexyloxy-5-α-cumylphenyl)-s-triazine, 2-(2,4,6-trimethylphenyl)-4,6-bis[2-hydroxy-4-(3-butyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4,6-tris[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, mixture of 4,6-

bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-dodecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-tridecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine, Tinuvin® 400, Ciba Specialty Chemicals Corp., 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-(2-ethylhexyloxy)-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-diphenyl-2-(4-hexyloxy-2-hydroxyphenyl)-s-triazine.

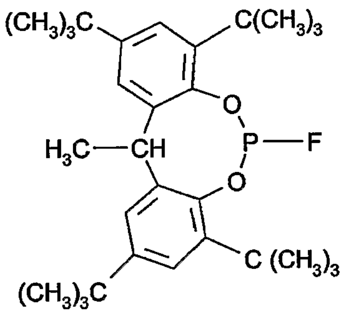
3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl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

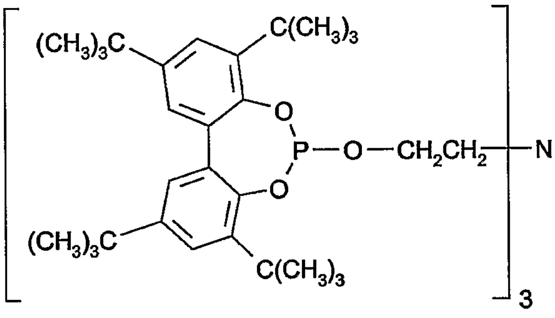
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, 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-butylphenyl)pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-dibenzo[d,f][1,3,2]dioxaphosphepin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[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 Specialty Chemicals Corp.), tris-(nonylphenyl) phosphite,

(A)





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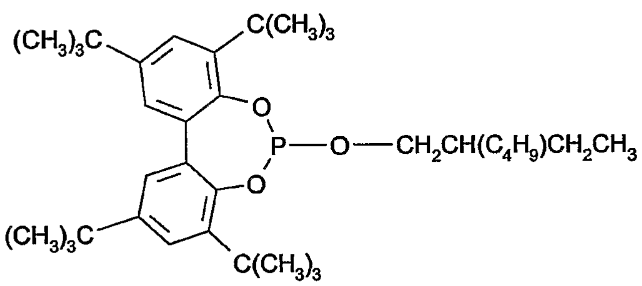

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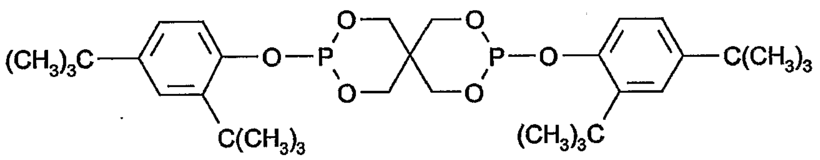

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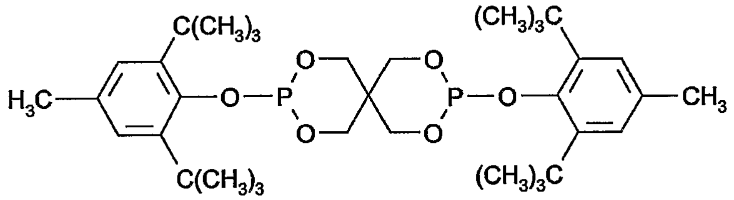

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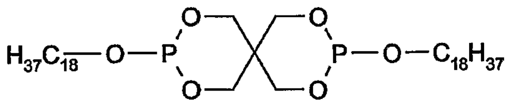
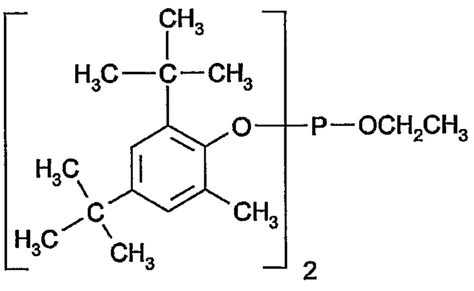




(G)

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-methyl-N-octadecylhydroxylamine and the N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example N-benzyl-α-phenylnitrone, N-ethyl-α-methylnitrone, N-octyl-α-heptylnitrone, N-lauryl-α-undecylnitrone, N-tetradecyl-α-tridcylnitrone, N-hexadecyl-α-pentadecylnitrone, N-octadecyl-α-heptadecylnitrone, N-hexadecyl-α-heptadecylnitrone, N-ocatadecyl-α-pentadecylnitrone, N-heptadecyl-α-heptadecylnitrone, N-octadecyl-α-hexadecylnitrone, N-methyl-α-heptadecylnitrone and the nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Amine oxides, for example amine oxide derivatives as disclosed in United States Patent Nos. 5,844,029 and 5,880,191, didecyl methyl amine oxide, tridecyl amine oxide, tridodecyl amine oxide and trihexadecyl amine oxide.

8. 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, EP-A-0591102; EP-A-1291384 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butylbenzofuran-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-butylbenzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butylbenzofuran-2-one, 3-(2-acetyl-5-isooctylphenyl)-5-isooctylbenzofuran-2-one.

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

10. 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.

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

12. Basic co-stabilizers, 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 zinc pyrocatecholate.

13. 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).

14. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibers, 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.

15. Dispersing Agents, such as polyethylene oxide waxes or mineral oil.

16. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, dyes, optical brighteners, rheology additives, catalysts, flow-control agents, slip agents, crosslinking agents, crosslinking boosters, halogen scavengers, smoke inhibitors, flameproofing agents, antistatic agents, clarifiers such as substituted and unsubstituted bisbenzylidene sorbitols, benzoxazinone UV absorbers such as 2,2'-p-phenylene-bis(3,1-benzoxazin-4-one), Cyasorb® 3638 (CAS# 18600-59-4), and blowing agents.

Preferred further additives are one or more additives selected from the group consisting of the hindered amine light stabilizers, the hydroxylamine stabilizers, the organic phosphorus stabilizers, the benzofuranone stabilizers and the hydroxyphenylbenzotriazole, hydroxyphenyl-s-triazine or benzophenone ultraviolet light absorbers.

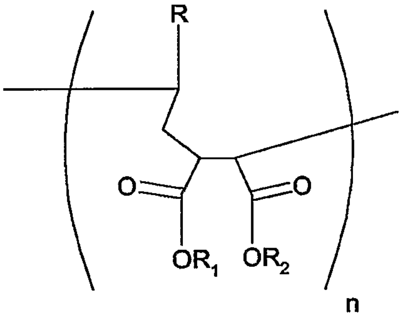
The present polyolefin compositions exhibit good weatherability (stability towards heat, oxygen and light), scratch resistance, good processability, good mechanical strength, good gloss retention, and are non-sticky. The polyolefin molded parts are suitable for example for automotive applications, i.e. bumper fascia and the like.

Another part of this invention is the use of of a mixture of components (b) and (c) as scratch resistant agent for polyolefins.

The following Examples illustrate the invention in more detail. Unless otherwise indicated, all percentages are in parts by weight.

Example 1: Scratch resistance of polyolefins.

A 2:1 weight:weight blend [mixture of components (b) and (c); inventive blend] of the functionalized maleated alpha-olefin to stearyl erucamide is prepared. The present functionalized maleated alpha-olefin is the tallow fatty alcohol ester of the polymer of C_{22}-C_{26} alpha-olefin with maleic anhydride:



wherein

R_1 and R_2 are tallow, R is C_{20}-C_{24}alkyl and n is an average value of about 45.

Other additives evaluated for comparative performance are oleamide, stearyl erucamide and Dow Corning MB 50-321 polysiloxane additive. Weight percents are on polypropylene. The additives are compounded in impact modified copolymer polypropylene (PROFAX 7523 commercially available from Basell) and high impact polypropylene (3-5 melt flow) containing 20-30% talc and 2-3% carbon black. All compounding is done using 25 mm twin-screw extruder using industry standard conditions. All of the formulations also contain stabilizers such as a hydroxyphenylbenzotriazole ultraviolet light absorber, a hindred amine light stabilizer, a hindered phenolic antioxidant and an organic phosphorus processing stabilizer. Injection molded plaques are made from the compounded samples using BOY 50-M injection molding machine using standard conditions.

Several tests are performed to evaluate scratch resistance before and after weathering, in addition to impact properties. Results are given below.

Standard Five Finger Scratch test guidelines (Daimler Chrysler Corporation Test Number LP-463DD-18-1, dated 2002-07-24)

Rating	Scratch Width	Whitening
1 (best)	<0.2 mm wide, almost invisible	none
2	0.2-0.3 mm wide, slight deformation, visible at close range	none
3	0.3-0.4 mm wide, clearly visible	
4	0.4-0.5 mm wide	visible whitening over entire scratch
5 (worst)	>0.5 mm wide	white over entire scratch and possibly accompanied by debris

Results (N = Newtons)

	3 N	6 N	10 N	15 N
Control	1.5	4	4.5	5
1% oleamide	1.5	2	3.5	4.5
3% Dow Corning MB 50-321	1.5	2.5	4	5
3% Inventive Blend	1.0	2	2	3.5

Results after Weathering

In a separate detailed study, results are shown after weathering. Xenon arc WeatherOmeter at 0.55 W/m^2 irradiance (340 nm), SAE J 1885 – NAFTA interior automotive protocol, 89°C black panel temperature, dry conditions. Scratch resistance to 600 kJ/m^2 is desirable. Standard five-finger test ratings are given below.

	Initial Rating			Rating after 600 KJS Weathering		
	3N	6N	10N	3N	6N	10N
3% stearyl erucamide	3.5	3.5	4.0	3.5	3.5	4.5
3% functionalized maleated alpha-olefin	3.5	4.5	4.5	3.5	4.0	4.5
3% Inventive Blend	2.5	3	3.5	3	3	4
BLANK	3.5	4	4.5	3.5	4	4.5

Plaques containing stearyl erucamide become sticky after exposure to 600KJS. The inventive blend gives a surprising synergistic effect without any adverse effect upon weathering.

Modified Taber Abrasion Test

Visual inspection guidelines

Rating	Scratch Width	Relative Performance
1 (best)	<50 mm	excellent
2	200-300 mm	good
3	300-400 mm	fair
4	400-500 mm	poor
5 (worst)	>500 mm	very poor

Modified Taber Abrasion Test Data

Control	4
1% oleamide	2.5
3% Dow Corning MB 50-321	2.5
3% Inventive Blend	1.5

The above results show remarkable scratch resistance improvements with the Inventive Blend in polyolefin.

What is claimed is:

1. A composition comprising

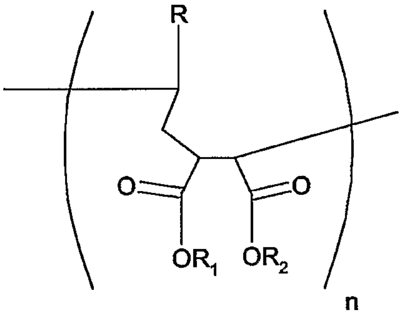
a) a polyolefin,

b) a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine, and

c) a primary or secondary fatty acid amide.

2. A composition according to claim 1 wherein the polyolefin is polypropylene or polyethylene.

3. A composition according to claim 1 wherein the functionalized maleated alpha-olefin is an ester or half ester of the formula



wherein

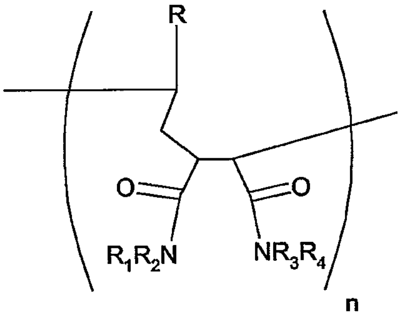
R is C_{16}-C_{24}alkyl,

R_1 and R_2 are independently hydrogen, C_1-C_{22}alkyl or C_2-C_{22}alkenyl, wherein at least one of R_1 and R_2 are C_{12}-C_{22}alkyl or alkenyl, and

n is an integer such that the average molecular weight is between about 20,000 and about 50,000.

4. A composition according to claim 1 where the functionalized maleated alpha-olefin is the half ester or ester of maleated C_{18}-C_{26}alpha-olefin with tallow fatty alcohol, ricinoleyl alcohol or oleyl alcohol.

5. A composition according to claim 1 where the functionalized maleated alpha-olefin is a primary or secondary amide of the formula



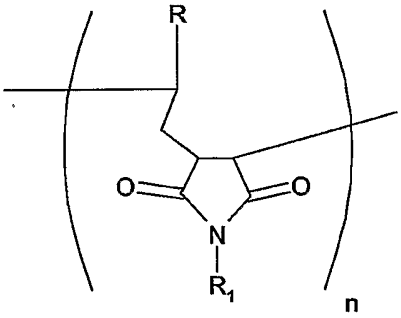
wherein

R is C_{16}-C_{24}alkyl,

R_1, R_2, R_3 and R_4 are independently hydrogen or C_1-C_{22}alkyl or C_2-C_{22}alkenyl, wherein at least one of R_1, R_2, R_3 or R_4 are C_{12}-C_{22}alkyl or alkenyl, and

n is an integer such that the average molecular weight is between about 20,000 and about 50,000; or

wherein the functionalized maleated alpha-olefin is an imide of the formula



wherein

R is C_{16}-C_{24}alkyl,

R_1 is C_{12}-C_{22}alkyl or alkenyl, and n is an integer such that the average molecular weight is between about 20,000 and about 50,000.

6. A composition according to claim 1 where the functionalized maleated alpha-olefin is the amide of maleated C_{18}-C_{26}alpha-olefin with oleamide, erucamide, stearamide, behenamide, oleyl palmitamide, stearyl erucamide, ethylene-bis-stearamide or ethylene-bis-oleamide; or where the functionalized maleated C_{18}-C_{26}alpha-olefin is the imide of maleated C_{18}-C_{26}alpha-olefin with oleamide, erucamide, stearamide or behenamide.

7. A composition according to claim 1 where the fatty group of the primary or secondary fatty acid amide is C_{11}-C_{21}alkyl or C_{11}-C_{21}alkenyl.

8. A composition according to claim 1 where the fatty acid amide is stearyl erucamide or oleyl palmitamide.

9. A composition according to claim 1 wherein component (b) is present in an amount of from 0.05 to 15%, based on the weight of component (a).

10. A composition according to claim 1 wherein component (c) is present in an amount of from 0.05 to 15%, based on the weight of component (a).

11. A composition according to claim 1, comprising in addition to components (a), (b) and (c) further additives.

12. A composition according to claim 11, comprising as further additives one or more additives selected from the group consisting of the hindered amine light stabilizers, the hydroxylamine stabilizers, the organic phosphorus stabilizers, the benzofuranone stabilizers and the hydroxyphenylbenzotriazole, hydroxyphenyl-s-triazine or benzophenone ultraviolet light absorbers.

13. A method for providing scratch resistance to a polyolefin substrate, which method comprises incorporating into said polyolefin an effective amount of (b) a maleated alpha-olefin functionalized with a long chain alcohol or long chain amine and (c) a primary or secondary fatty acid amide.

14. Use of a mixture of components (b) and (c) according to claim 1 as scratch resistant agent for polyolefins.

INTERNATIONAL SEARCH REPORT

Intern[illegible]nal Application No
PCT/EP2005/052981

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/08 C08K5/20 C08K5/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2004/099303 A (HONDA MOTOR CO., LTD; ADVANCED COMPOSITES, INC; MCENHILL, COREY, S; CE) 18 November 2004 (2004-11-18) page 6, line 6 - page 7, line 3; claims -----	1
X	US 5 973 070 A (BAANN ET AL) 26 October 1999 (1999-10-26) column 3, lines 29-59; claims; example 1 -----	1
A	US 6 300 419 B1 (SEHANOBISH KALYAN ET AL) 9 October 2001 (2001-10-09) claims; examples -----	1-14

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search
16 September 2005

Date of mailing of the international search report
23/09/2005

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INTERNATIONAL SEARCH REPORT

Intern[illegible]nal Application No
PCT/EP2005/052981

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