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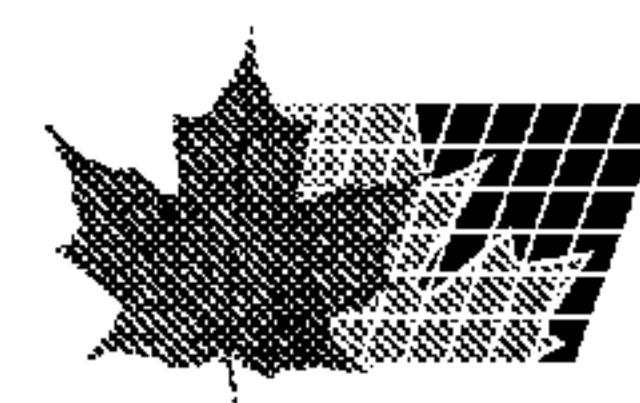
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N-SUBSTITUEES ET STERIQUEMENT ENCOMBREES
(54) Title: TRANSITION-METAL-CATALYZED PROCESS FOR THE PREPARATION OF STERICALLY HINDERED N-
SUBSTITUTED ALKOXYAMINES

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Sterically hindered N-substituted alkoxyamines are prepared by the transition-metal-catalyzed decomposition of diazonium salts in the presence of a sterically hindered nitroxyl radical. These compounds are useful as thermal and light stabilizers for a variety of organic substrates.



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(54) Title: TRANSITION-METAL-CATALYZED PROCESS FOR THE PREPARATION OF STERICALLY HINDERED N-SUBSTITUTED ALKOXYAMINES

(57) Abstract: Sterically hindered N-substituted alkoxyamines are prepared by the transition-metal-catalyzed decomposition of diazonium salts in the presence of a sterically hindered nitroxyl radical. These compounds are useful as thermal and light stabilizers for a variety of organic substrates.

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TRANSITION-METAL-CATALYZED PROCESS FOR THE
PREPARATION OF STERICALLY HINDERED
N-SUBSTITUTED ALKOXYAMINES

This invention pertains to the novel process for preparing sterically hindered N-substituted alkoxyamines by the transition-metal-catalyzed decomposition of a diazonium salt in the present of a sterically hindered nitroxyl radical.

Background of the Invention

N-Aryloxyamines have been prepared in the prior art by the reaction of a phenylhydrazine with a stable nitroxide. In certain instances, N-aryloxyamines have been prepared in low yield by the decomposition of aryl diazonium salts in the presence of a nitroxyl radical, but without a transition metal catalyst being present. These papers are often about mechanistic studies with poor yields and state that the reaction described is limited in scope. A. C. Scott et al., J. Chem. Soc., Perkin Trans. 2, 1980, 260-266.

In another study, an aryl radical formed from a diazonium salt added intramolecularly to a double bond and the result alkyl radical was trapped by a stable nitroxyl radical. A. L. J. Beckwith and G. F. Meijis, J. Chem. Soc., Chem. Commun. 1981, 595-597.

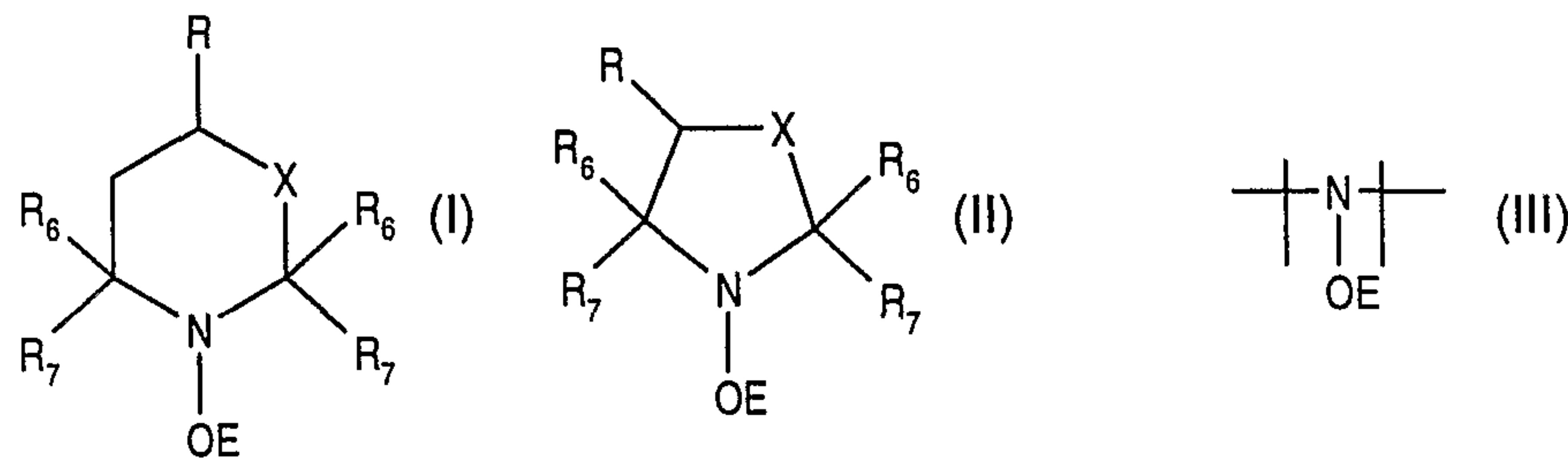
It is clear that the instant process is a facile and direct way to prepare these interesting and useful instant stabilizer compounds in yields far exceeding anything found in the related prior art. Additionally, the prior art processes often use the nitroxide component as a solvent, i.e. in large excess, in contrast to the instant process.

In respect to wax stabilization, the use of selected hindered amines and/or benzotriazole UV absorbers is known in the prior art. This is seen in Japanese Hei 3-278554; WO 00/22037; and United States Patent Nos. 3,530,084; 4,379,721; 4,616,051 and 5,964,905.

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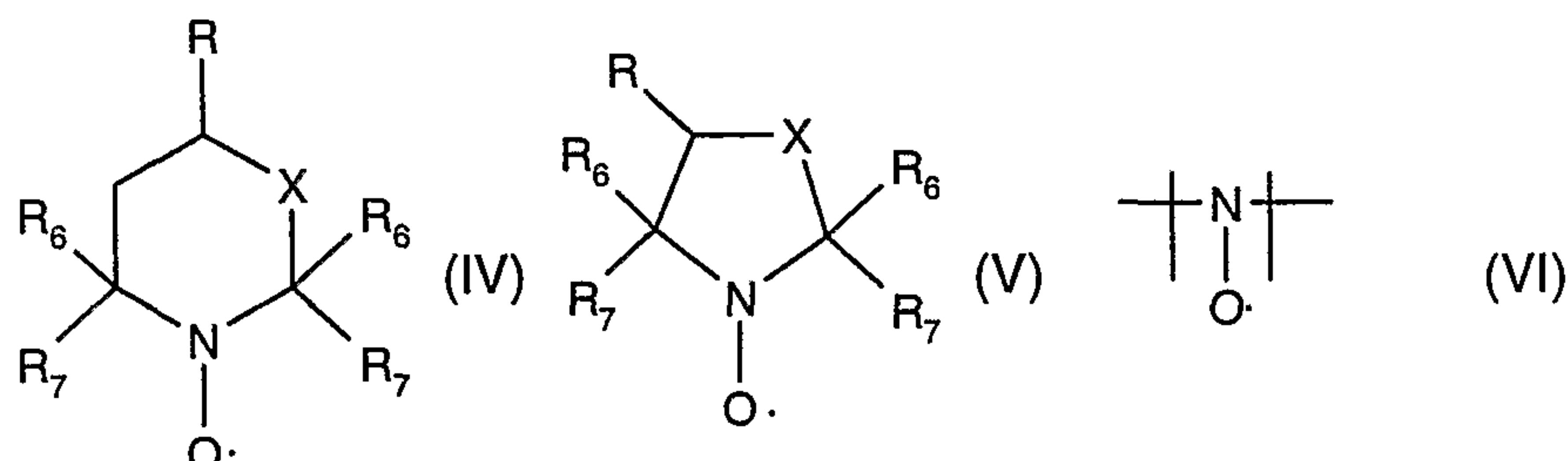
Detailed Disclosure

The instant invention pertains to a process for preparing a sterically hindered N-alkoxyamine of formula I,
II or III



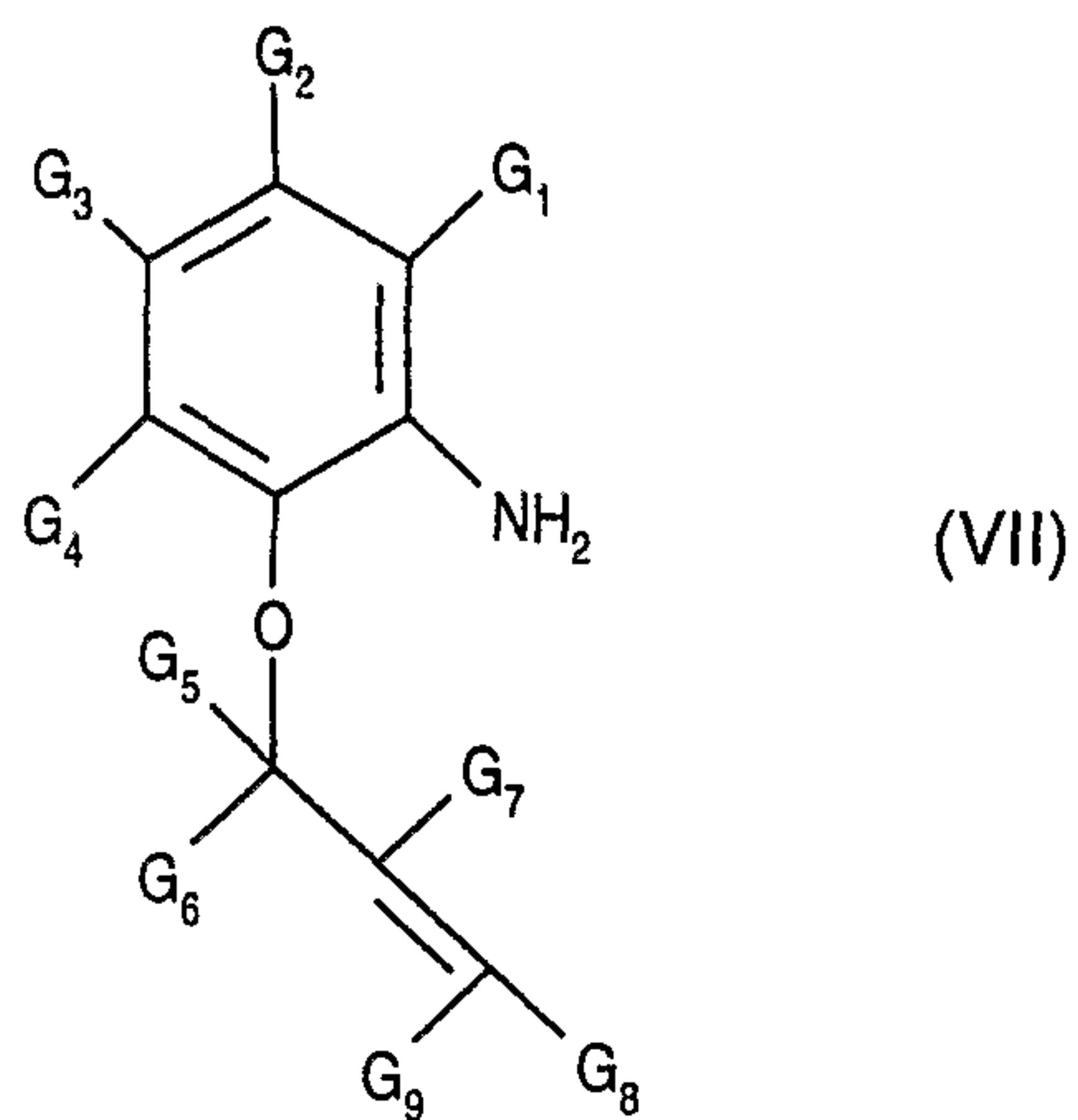
which comprises

reacting a sterically hindered nitroxyl compound of formula IV, V or VI



with a diazonium salt of an aromatic amine of formula VII

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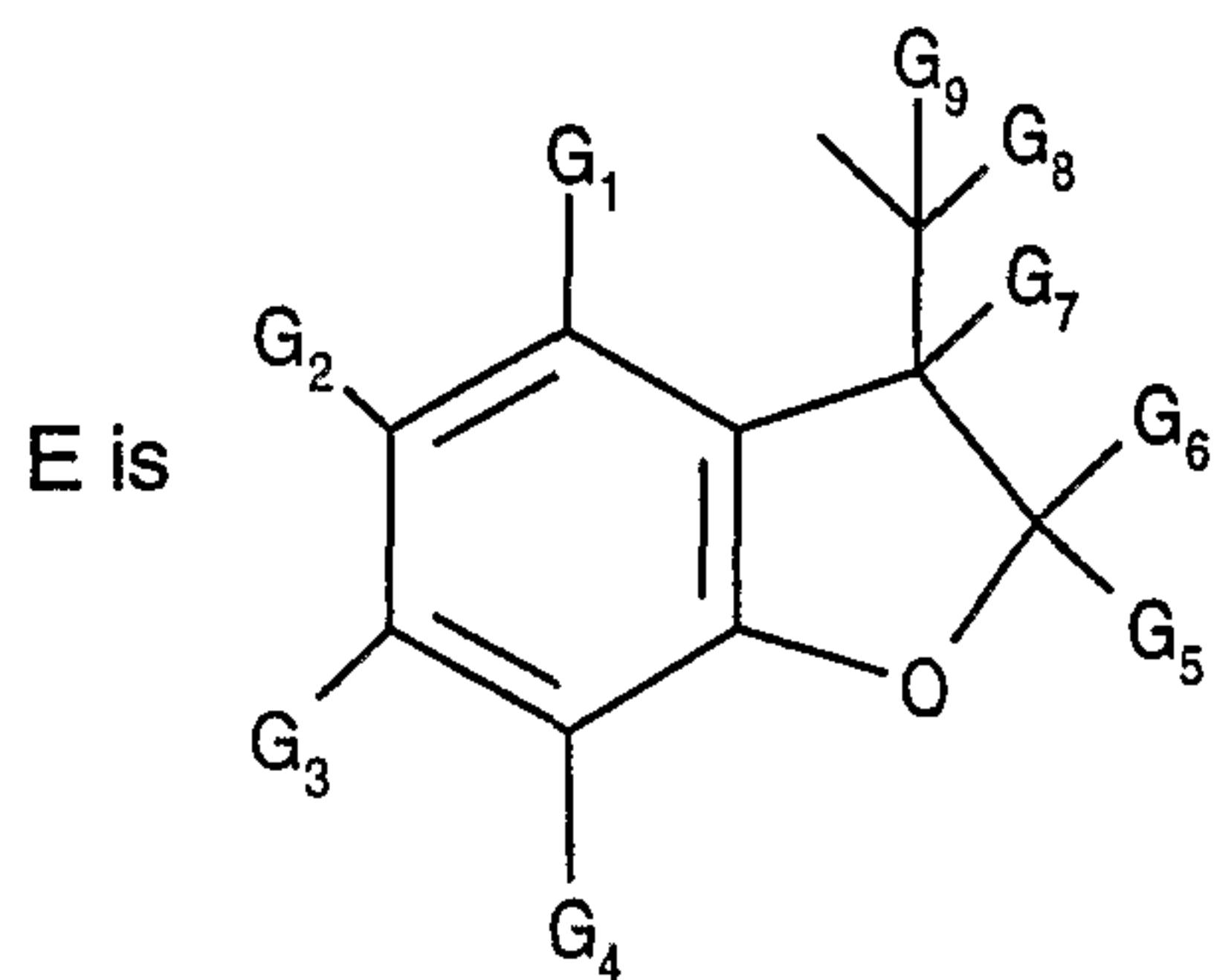


in the presence of a transition-metal catalyst

wherein

X is -CH₂-, -O-, -S- or -NR₈- where R₈ is hydrogen or alkyl of 1 to 12 carbon atoms,

R₆ and R₇ are independently alkyl of 1 to 8 carbon atoms, or R₆ and R₇ together are tetramethylene or pentamethylene,



R is hydrogen, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, hydroxyl, carboxyl, amino, alkylamino of 1 to 18 carbon atoms, dialkylamino of 2 to 36 carbon atoms, oxo, alkylthio of 1 to 18 carbon atoms, alkoxy of 1 to 18 carbon atoms, aryloxy of 7 to 15 carbon atoms, alkylcarbonyloxy of 2 to 18 carbon atoms or alkylcarbonylamino of 2 to 18 carbon atoms,

G_1 to G_4 are independently hydrogen, halogen, nitro, cyano, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, hydroxyl, carboxyl, alkylthio of 1 to 18 carbon atoms, alkoxy of 1 to 18 carbon atoms, aryloxy of 7 to 15 carbon atoms, alkylcarbonyloxy of 1 to 18 carbon atoms, alkylsulfonyl of 1 to 18 carbon atoms, arylsulfonyl of 6 to 15 carbon atoms, sulfo or phosphono, or any two vicinal substituents connected together to form a mono or polycyclic ring, so that formula VII can represent inter alia 1-naphthylamine or 2-naphthylamine.

G_5 to G_9 are independently hydrogen, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms or aryl of 6 to 10 carbon atoms.

In a preferred embodiment of the instant invention, any one of G_1 to G_9 is phenyl.

Alkyl residues contained in one of the present definitions include, within the limits defined, for example methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl.

The diazonium salt of the aromatic amine of formula VII can be prepared by reaction with an alkyl nitrite ester, such as tert-butyl nitrite. The diazonium salt can also be prepared using a nitrite salt and an acid, such as sodium nitrite and hydrochloric acid.

Indeed, the instant compounds can be made directly from nitroxides which are commercially available such as TEMPO (1-oxyl-2,2,6,6-tetramethylpiperidine), 4-OXOTEMPO (1-oxyl-2,2,6,6-tetramethyl-4-oxopiperidine) and di-tert-butyl nitroxide.

The reaction is conveniently carried out at a temperature of 0 to 100°C, or between 20 and 70°C.

The transition metal is a metal of Group 4, 5, 6, 7, 8, 9 ("copper group") or 10 ("zinc group") of the periodic table; such as copper(I), copper(II), cobalt(II), manganese(II) or gold(I).

The process is preferably carried out in the presence of 0.05 mole % to stoichiometric quantities of the transition metal catalyst.

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The transition metal catalyst is, for example, ligated by a salcoamine ligand such as (S,S)-(+)-N,N-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) or N,N-bis(salicylidene)ethylenediaminocobalt(II).

In one embodiment, X is methylene.

In another embodiment, R is hydrogen, hydroxyl, oxo or acetamido.

In still another embodiment, R₆ and R₇ are each methyl.

A further aspect of this invention is the addition of pyridine to the reaction mixture either as a component of the reaction mixture or as the solvent in the presence of the transition metal catalyst. Pyridine has been found to increase further the yield of the reaction as well as having superior solvent properties in certain cases. For example, when the diazonium salt is made using sodium nitrite and hydrochloric acid, pyridine also serves as a basic medium for neutralizing excess acid. A further preferred solvent is chlorobenzene.

The stabilization of diazonium salts by pyridine has been reported by Heinrich Zollinger et al. (*Helv. Chimica Acta*, **59**, 1438 (1976). Furthermore it is stated that pyridine promotes a homolytic radical pathway. Without a transition metal catalyst, however, the homolytic cleavage at 70°C is slow and is not useful.

Most preferred compound of formula I, II or III is

- (i) 1-(2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine;
- (ii) the cis and trans isomers of 1-(2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetra-methylpiperidine;
- (iii) N,N-di-*tert*-butyl-N-(2,3-dihydrobenzofuran-3-ylmethoxy)amine; or
- (iv) 1-(3-phenyl-2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine.

The instant invention also pertains to a composition stabilized which comprises

(a) an organic material subject to degradation by heat, light or oxygen, and

(b) an effective stabilizing amount of a compound of formula I, II or III as described above.

Preferably, the organic material is a natural, semi-synthetic or synthetic polymer, especially a thermoplastic polymer.

Most preferably, the polymer is a polyolefin or polycarbonate, especially polyethylene or polypropylene; most especially polypropylene; or the polymer is a styrenic, ABS, a nylon, a polyester such as poly(ethylene terephthalate) or poly(butylene terephthalate), a polyurethane, an acrylate, a rubber modified styrenic, poly(vinyl chloride), poly(vinyl butyral), polyacetal (polyoxymethylene), poly(ethylene naphthalenedicarboxylate), or other blends or copolymers such as poly(ethylene/1,4-cyclohexylenedimethylene terephthalate) PETG or an ionomer as described on page 29.

In another preferred embodiment of the instant invention, the organic material is a resin selected from the group consisting of a thermoset acrylic melamine resin, an acrylic urethane resin, an epoxy carboxy resin, a silane modified acrylic melamine, an acrylic resin with carbamate pendant groups crosslinked with melamine or an acrylic polyol resin crosslinked with melamine containing carbamate groups.

Most preferably, the resin is a thermoset acrylic melamine resin or an acrylic urethane resin.

In yet another preferred embodiment of the instant invention, the organic material is a recording material.

The recording materials according to the invention are suitable for pressure-sensitive copying systems, photocopying systems using microcapsules, heat-sensitive copying systems, photographic materials and ink jet printing.

The recording materials according to the invention are distinguished by an unexpected improvement in quality, especially with regard to the fastness to light.

The recording materials according to the invention have the construction known for the particular use. They consist of a customary carrier, for example, paper or plastic film, which has been coated with one or more layers. Depending on the type of material, these layers contain the appropriate necessary components, in the case of photographic materials, for example, silver halide emulsions, dye couplers, dyes and the like. Material particularly suitable for ink jet printing has a layer particularly absorptive for ink on a customary carrier. Uncoated paper can also be employed for ink jet printing. In this case the paper acts at the same time as the carrier

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material and as the ink-absorbent layer. Suitable material for ink jet printing is, for example, described in United States Patent No. 5,073,448.

The recording material can also be transparent as, for example, in the case of projection films.

The compounds of formula I, II, and/or III can be incorporated into the carder material as early as the production of the latter, in the production of paper, for example, being added to the paper pulp. A second method of application is to spray the carder material with an aqueous solution of compounds of formula I, II, III, or to add the compounds to the coating composition.

Coating compositions intended for transparent recording materials suitable for projection cannot contain any particles which scatter light, such as pigments and fillers.

The dye-binding coating composition can contain a number of other additives, for example, antioxidants, light stabilizers (including also UV absorbers which do not fall under the scope of the UV absorbers of this invention), viscosity improvers, fluorescent brighteners, biocides and/or antistatic agents.

The coating composition is usually prepared as follows: the water-soluble components, for example, the binder, are dissolved in water and stirred together; the solid components, for example, fillers and other additives already described, are dispersed in this aqueous medium; and dispersion is advantageously carried out by means of devices, for example, ultrasonic systems, turbine stirrers, homogenizers, colloid mills, bead mills, sand mills, high-speed stirrers and the like. The compounds of formula I, II, III can be easily incorporated into the coating composition.

The recording material according to this invention preferably contains 1 to 5000 mg/m², in particular 50-1200 mg/m², of a compound of formula I, II and/or III.

As already mentioned, the recording materials according to the invention embrace a wide field. The compounds of formula I, II, III can, for example, be employed in pressure-sensitive copying systems. They can be introduced either into the paper in order to protect the micro-

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encapsulated dye precursors there from light, or into the binder of the developer layer in order to protect the dyes formed there.

Photocopying systems using light-sensitive microcapsules which are developed by means of pressure are described in United States Patent Nos. 4,416,966; 4,483,912; 4,352,200; 4,535,050; 4,535,463; 4,551,407; 4,562,137 and 4,608,330; and also in EP-A 139,479; EP-A 162,664; EP-A 164,931; EP-A 237,024; EP-A 237,025 and EP-A 260,129. In all these systems, the compounds can be put into the dye-receiving layer. The compounds can, however, also be put into the donor layer in order to protect the color formers from light.

Photographic materials which can be stabilized are photographic dyes and layers containing such dyes or precursors thereof, for example, photographic paper and films. Suitable materials are, for example, described in United States Patent No. 5,364,749. The compounds of formula I, II, III act here as a UV filter against electrostatic flashes. In color photographic materials, couplers and dyes are also protected against photochemical decomposition.

The instant compounds can be used for all types of color photographic materials. For example, they can be employed for color paper, color reversal paper, direct-positive color material, color negative film, color positive film, color reversal film and the like. They are preferably used inter alia for photographic color material which contains a reversal substrate or form positives.

Color-photographic recording materials usually contain, on a support, a blue-sensitive and/or a green-sensitive and/or a red-sensitive silver halide emulsion layer and, if desired, a protection layer, with the instant compounds being, preferably, either in the green-sensitive or the red-sensitive layer or in a layer between the green-sensitive and the red-sensitive layer or in a layer on top of the silver halide emulsion layers.

The compounds of formula I, II, III can also be employed in recording materials based on the principles of photopolymerization, photoplasticization or the rupture of microcapsules, or in cases where heat-sensitive and light-sensitive diazonium salts, leuko dyes having an oxidizing agent or dye lactones having Lewis acids are used.

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Furthermore, the instant compounds can be employed in recording materials for dye diffusion transfer printing, thermal wax transfer printing and non-matrix printing and for use with electrostatic, electrographic, electrophoretic, magnetographic and laser-electrophotographic printers and pen-plotters. Of the above, recording materials for dye diffusion transfer printing are preferred, for example, as described in EP-A 507,734.

The instant compounds can also be employed in inks, preferably for ink jet printing, for example, as described in United States Patent No. 5,098,477.

The compounds of this invention exhibit superior hydrolytic stability, handling and storage stability as well as good resistance to extractability when present in a stabilized composition.

The methodology to make the instant compounds is described in the prior art. The intermediates needed to make the instant compounds are largely items of commerce.

Preferred compounds are those in which one of X and Y is -O-; and particularly those in which both X and Y are -O-.

In general polymers which can be stabilized include

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), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), branched low density polyethylene (BLDPE).

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

- a) radical polymerisation (normally under high pressure and at elevated temperature).

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b) catalytic polymerisation 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 π - or σ -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 polymerisation medium. The catalysts can be used by themselves in the polymerisation 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/iso-butylene 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. Hydrocarbon resins (for example C₅-C₉) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.

5. Polystyrene, poly(p-methylstyrene), poly(α -methylstyrene).
6. Copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, for example styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/-acrylonitrile/methyl acrylate; mixtures of high impact strength of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene such as styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.
7. Graft copolymers of styrene or α -methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene; styrene, acrylonitrile and methyl methacrylate on polybutadiene; styrene and maleic anhydride on polybutadiene; styrene, acrylonitrile and maleic anhydride or maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpolymers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.
8. Halogen-containing polymers such as polychloroprene, chlorinated rubbers, chlorinated or sulfochlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homo- and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.
9. Polymers derived from α,β -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates; polymethyl methacrylates, polyacrylamides and polyacrylonitriles, impact-modified with butyl acrylate.

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10. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/ butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/ alkyl methacrylate/butadiene terpolymers.
11. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine; as well as their copolymers with olefins mentioned in 1) above.
12. Homopolymers and copolymers of cyclic ethers such as polyalkylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.
13. Polyacetals such as polyoxymethylene and those polyoxymethylenes which contain ethylene oxide as a comonomer; polyacetals modified with thermoplastic polyurethanes, acrylates or MBS.
14. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.
15. Polyurethanes derived from hydroxyl-terminated polyethers, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.
16. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylene diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4,-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers; or with polyethers, e.g. with polyethylene glycol, polypropylene glycol or polytetramethylene glycol; as well as

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polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems).

17. Polyureas, polyimides, polyamide-imides and polybenzimidazoles.
18. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate and polyhydroxybenzoates, as well as block copolyether esters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.
19. Polycarbonates and polyester carbonates.
20. Polysulfones, polyether sulfones and polyether ketones.
21. Crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins.
22. Drying and non-drying alkyd resins.
23. Unsaturated polyester resins derived from copolymers of saturated and unsaturated dicarboxylic acids with polyhydric alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability.
24. Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates.
25. Alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, polyisocyanates or epoxy resins.
26. Crosslinked epoxy resins derived from polyepoxides, for example from bisglycidyl ethers or from cycloaliphatic diepoxides.

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27. Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionates and cellulose butyrates, or the cellulose ethers such as methyl cellulose; as well as rosins and their derivatives.
28. Blends of the aforementioned polymers (polyblends), for example PP/EPDM, Polyamide/-EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PBTP/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6.6 and copolymers, PA/HDPE, PA/PP, PA/PPO.
29. Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based on synthetic esters (e.g. phthalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials.
30. Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latices of carboxylated styrene/butadiene copolymers.
31. Polysiloxanes such as the soft, hydrophilic polysiloxanes described, for example, in U.S. Patent No. 4,259,467; and the hard polyorganosiloxanes described, for example, in U.S. Patent No. 4,355,147.
32. Polyketimines in combination with unsaturated acrylic polyacetoacetate resins or with unsaturated acrylic resins. The unsaturated acrylic resins include the urethane acrylates, polyether acrylates, vinyl or acryl copolymers with pendant unsaturated groups and the acrylated melamines. The polyketimines are prepared from polyamines and ketones in the presence of an acid catalyst.
33. Radiation curable compositions containing ethylenically unsaturated monomers or oligomers and a polyunsaturated aliphatic oligomer.
34. Epoxymelamine resins such as light-stable epoxy resins crosslinked by an epoxy functional coetherified high solids melamine resin such as LSE-4103 (Monsanto).

In general, the compounds of the present invention are employed in from about 0.01 to about 5% by weight of the stabilized composition, although this will vary with the particular substrate and application. An advantageous range is from about 0.05 to about 3%, and especially 0.05 to about 1%. However, some high performance films or in UV absorbing layers of laminates such as those produced by coextrusion may contain from 5-15% by weight of the instant compounds. Concentrations of 5-10% by weight are typical in certain coextrusion applications.

The stabilizers of the instant invention may readily be incorporated into the organic polymers by conventional techniques, at any convenient stage prior to the manufacture of shaped articles therefrom. For example, the stabilizer may be mixed with the polymer in dry powder form, or a suspension or emulsion of the stabilizer may be mixed with a solution, suspension, or emulsion of the polymer. The resulting stabilized polymer compositions of the 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 conventional additives, such as the materials 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-di-methylphenol, 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-methoxy-phenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octade-

cyloxyphenol, 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-methylphenyl)-3-n-dodecylmercaptopbutane, 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-hydroxy-2-methylphenyl)-4-n-dodecylmercaptopbutane, 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, isoctyl-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, 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, dioctadecyl-3,5-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-nonenediol, 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-phospho-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-nanonediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene 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; 3,9-bis[2-{3-(3-tert-butyl-4-hydroxy-5-methylphenyl)propionyloxy}-1,1-dimethylethyl]-2,4,8,10-tetraoxaspiro[5.5]-undecane.

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-nanonediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene 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-nanonediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiidiethylene 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 (Nau-gard[®]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-nanoylaminophenol, 4-dodecanoylaminophenol, 4-octa-decanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethyl-phenol, 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/isoxyldiphenylamines, 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-octylphenothiazines, N-allylphenothiazine, 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-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 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-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyl-oxy)carbonylethyl]-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-

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methoxycarbonylethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxy-carbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonylethyl)-phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonylethyl]-2'-hydroxyphe-nyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenylbenzotriazole, 2,2'-methylenebis[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;

$\left[R-\text{CH}_2\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_2 \right]_2$, 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, 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, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphe-nylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl α -cyano- β -methyl-p-methoxycinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thiobis[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-methylphenylundecylketoxime, 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-butanetetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyl-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]decane-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)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, 5-(2-ethylhexanoyl)-oxymethyl-3,3,5-trimethyl-2-morpholinone, 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 1,3,5-tris(N-cyclohexyl-N-(2,2,6,6-tetramethylpiperazin-3-on-4-yl)amino)-s-triazine, 1,3,5-tris(N-cyclohexyl-N-(1,2,2,6,6-pentamethylpiperazin-3-on-4-yl)amino)-s-triazine, the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine), a mixture of 4-hexadecyloxy- and 4-stearyl-2,2,6,6-tetramethylpiperidine, a condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate 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]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 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-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, a diester of 4-methoxymethylenemalonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a 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'-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.

2.8. 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-propoxyphenyl)-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-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)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-hydroxypropoxy]phenyl}-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

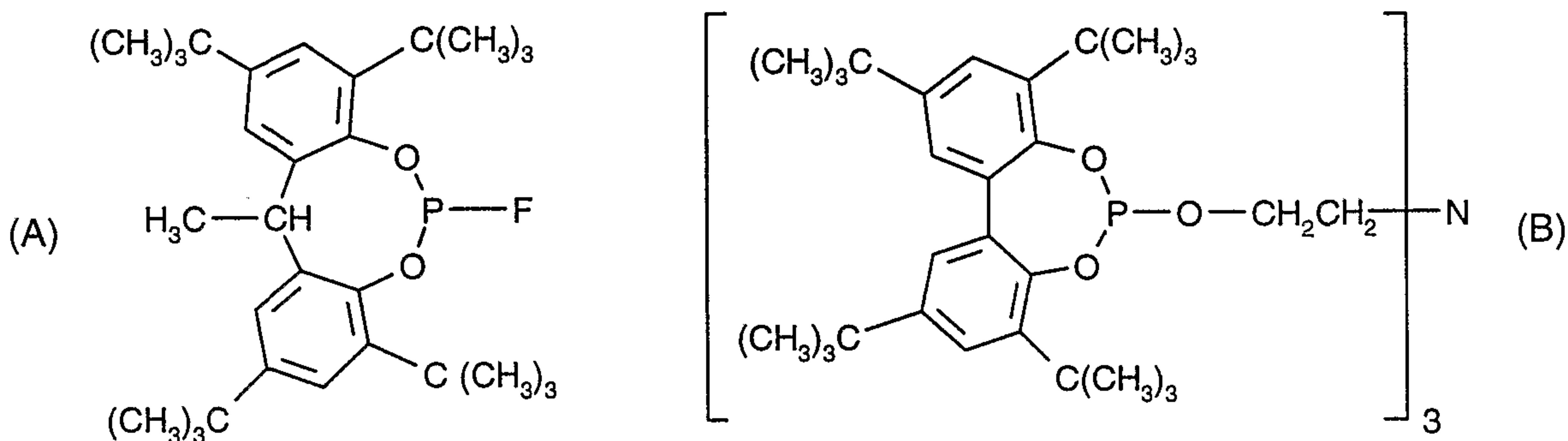
3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl)hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxaryl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacyl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

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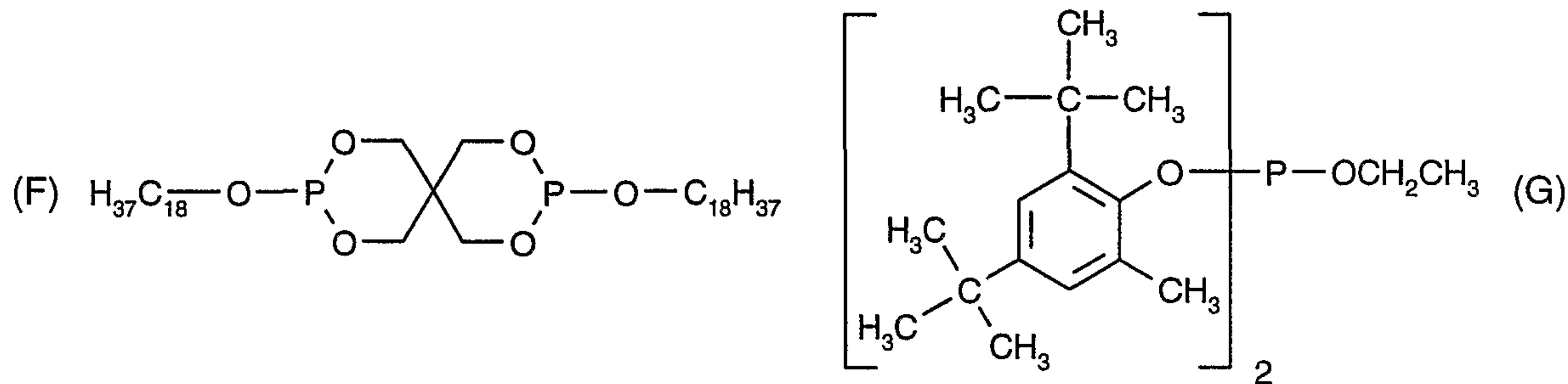
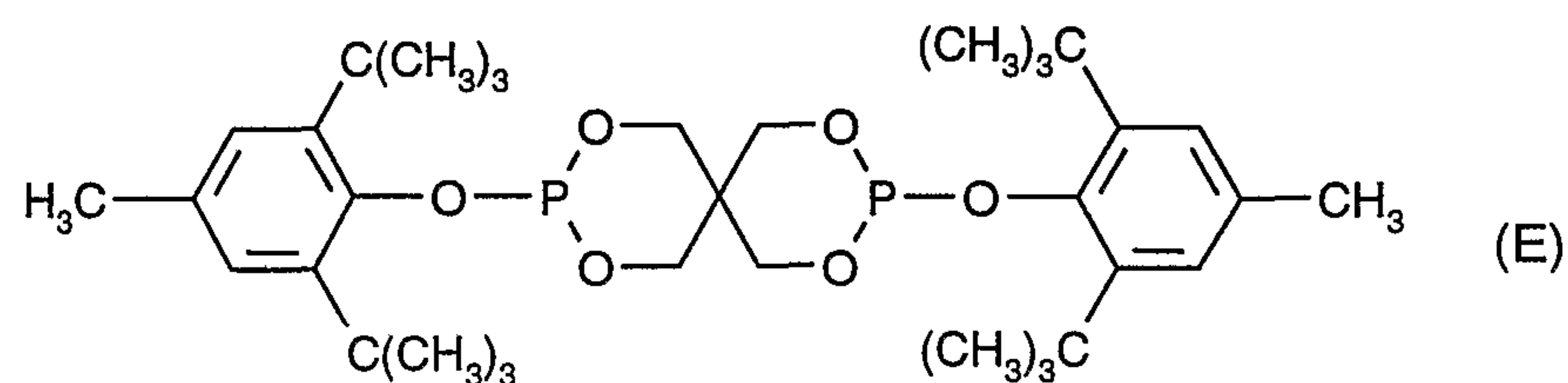
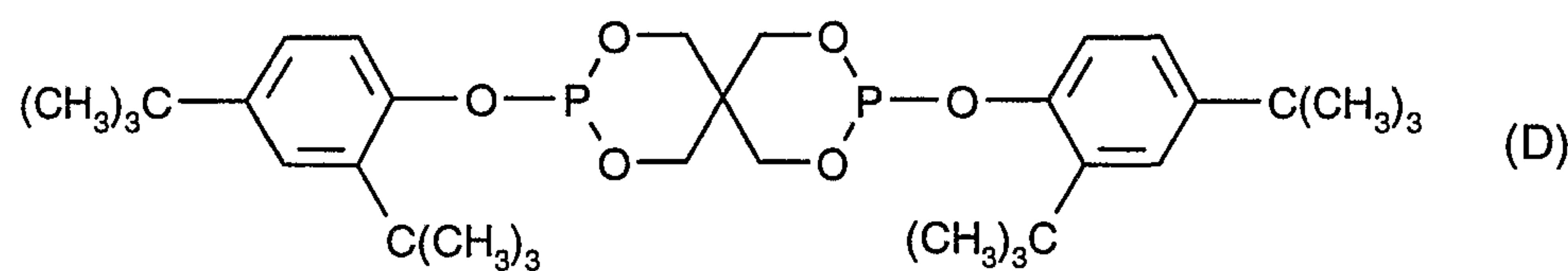
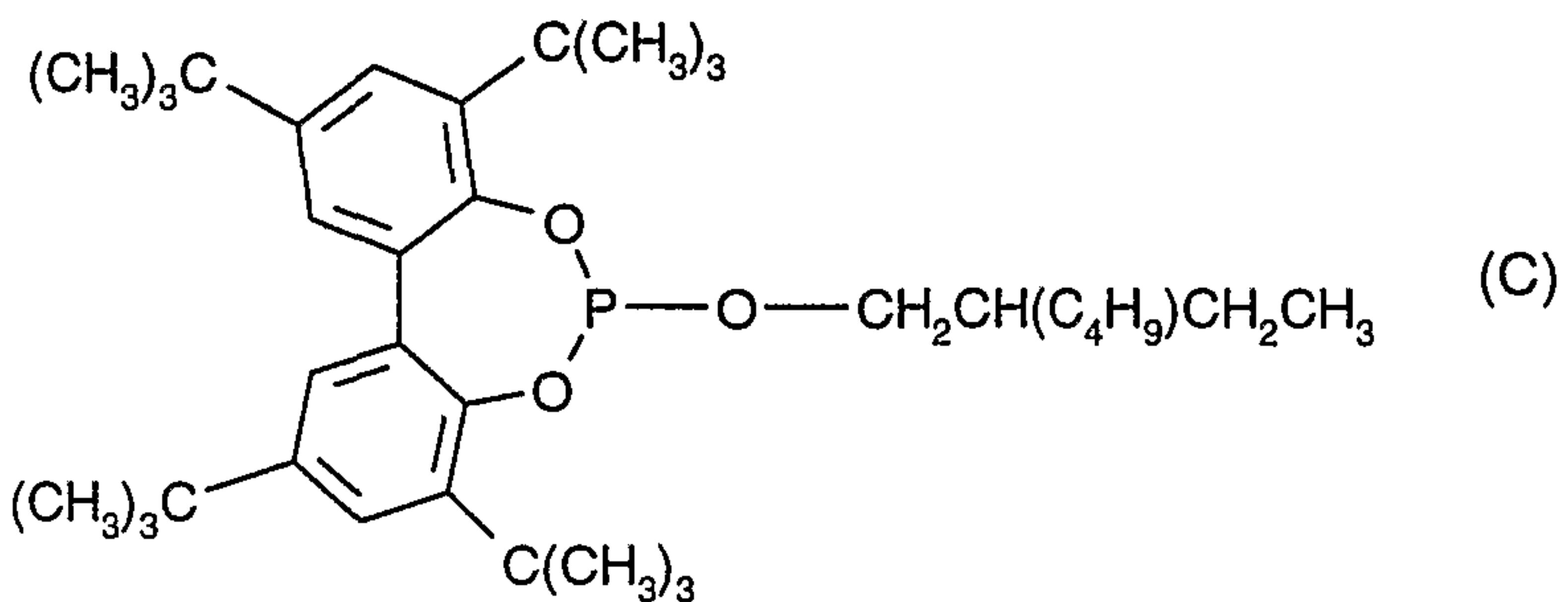
4. Phosphites and phosphonites, for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, bis(2,4-di-cumylphenyl)pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite, diisodecyloxy pentaerythritol 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-12H-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, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 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, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

The following phosphites are especially preferred:

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



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5. Hydroxylamines, for example N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-diethylhydroxylamine, 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. Nitrone, for example N-benzyl-alpha-phenylnitrone, N-ethyl-alpha-methylnitrone, N-octyl-alpha-heptylnitrone, N-lauryl-alpha-undecylnitrone, N-tetradecyl-alpha-tridecylnitrone, N-hexadecyl-alpha-pentadecylnitrone, N-octadecyl-alpha-heptadecylnitrone, N-hexadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-pentadecylnitrone, N-heptadecyl-alpha-heptadecylnitrone, N-octadecyl-alpha-hexadecylnitrone, 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-mercaptopbenzimidazole, 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 zinc 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). Especially preferred are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyldibenzylidene)sorbitol, and 1,3:2,4-di(benzylidene)sorbitol.

12. Fillers and reinforcing agents, for example calcium carbonate, silicates, glass fibres, glass beads, 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.

The co-stabilizers, with the exception of the benzofuranones listed under 14, are added for example in concentrations of 0.01 to 10%, relative to the total weight of the material to be stabilized.

Further preferred compositions comprise, in addition to components (a) and (b) further additives, in particular phenolic antioxidants, light stabilizers or processing stabilizers.

Particularly preferred additives are phenolic antioxidants (item 1 of the list), sterically hindered amines (item 2.6 of the list), phosphites and phosphonites (item 4 of the list), UV absorbers (item 2 of the list) and peroxide-destroying compounds (item 8 of the list).

Additional additives (stabilizers) which are also particularly preferred are benzofuran-2-ones, such as described, for example, in US-A-4 325 863, US-A-4,338 244 or US-A-5175312.

A most preferred phenolic antioxidant is neopentanetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate), n-octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 2,6-di-tert-butyl-p-cresol or 2,2'-ethylidene-bis(4,6-di-tert-butylphenol).

The instant composition can additionally contain a UV absorber selected from the group consisting of the benzotriazoles (preferred compounds listed above under 2.1), s-triazines (preferred compounds listed above under 2.8), the oxamides (preferred compounds listed above under 2.7), the hydroxybenzophenones (preferred compounds listed above under 2.2), benzoates (preferred compounds listed above under 2.3) and the α -cyanoacrylates (preferred compounds listed above under 2.4).

The alkyd resin lacquers which can be stabilized against the action of light and moisture in accordance with the instant invention are the conventional stoving lacquers which are used in particular for coating automobiles (automobile finishing lacquers), for example lacquers based on alkyd/melamine resins and alkyd/acrylic/melamine resins (see H. Wagner and H. F. Sarx, "Lackkunstharze" (1977), pages 99-123). Other crosslinking agents include glycouril resins, blocked isocyanates or epoxy resins.

The lacquers stabilized in accordance with the invention are suitable both for metal finish coatings and solid shade finishes, especially in the case of retouching finishes, as well as various coil coating applications. The lacquers stabilized in accordance with the invention are preferably applied in the conventional manner by two methods, either by the single-coat method or by the two-coat method. In the latter method, the pigment-containing base coat is applied first and then a covering coat of clear lacquer over it.

It is also to be noted that the compounds of the present invention are applicable for use in non-acid catalyzed thermoset resins such as epoxy, epoxy-polyester, vinyl, alkyd, acrylic and polyester resins, optionally modified with silicon, isocyanates or isocyanurates. The epoxy and epoxy-polyester resins are crosslinked with conventional crosslinkers such as acids, acid anhydrides, amines and the like. Correspondingly, the epoxide may be utilized as the crosslinking agent for various acrylic or polyester resin systems that have been modified by the presence of reactive groups on the backbone structure.

When used in two-coat finishes, the compounds of the instant invention can be incorporated in the clear coat or both in the clear coat and in the pigmented base coat.

When water-soluble, water miscible or water dispersible coating are desired ammonium salts of acid groups present in the resin are formed. Powder coating composition can be prepared by reacting glycidyl methacrylate with selected alcohol components.

While the instant compounds are particularly suited for automotive coating applications, it is contemplated that they will also be especially useful in other applications where their enhanced durability is required such as in solar films and the like.

The compounds of Examples 4 and 6, namely the cis and trans isomers of 1-(2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine and 1-(3-phenyl-2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine, are novel.

Still another embodiment of the instant invention is a composition which comprises

- (a) candle wax which is white and scented, white and unscented, dyed and scented, dyed and unscented, dipped and scented or dipped and unscented, and
- (b) an effective stabilizing amount of a compound of formula I, II or III as described above.

It should be noted that candles contain a host of various components. The base materials may be made up of the following:

- paraffin wax,
- natural oils,
- polyamide plus fatty acid/ester,
- fatty acids such as stearin,
- opacifiers,
- beeswax,
- glycerides plus oxidized wax,
- alcohols, and
- ethylene oligomers.

Candles also contain a number of additives such as the following:

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mold release agents,
fragrances,
insect repellants or insecticides,
hardeners,
crystal modifiers,
clarifiers,
guttering reducers,
colorants,
f.p. control agents,
stretchability improvers,
gelling agents,
extrusion aids, and
vortex reducers.

Each of the various components are meant to control or modify the properties of the candle to insure proper burning, reduce channelling, aid in uniform melting, and the like. The colorants and fragrances obviously are there to provide the proper color, scent or other aesthetic appeal.

Of increasing importance are the transparent gel candles which look like clear glass, but which burn like a classical candle. As is discussed in detail in United States Patent No. 5,879,694, these gel candles usually contain a copolymer selected from the group consisting of a triblock, radial block, diblock or multiblock copolymer classically made up of at least two thermodynamically incompatible segments containing both hard and soft segments. Typical of such block copolymers is KRATON® (Shell Chemical Co.) which consists of block segments of styrene monomer units and rubber monomer or comonomer units. The most common structure found in KRATON® D series is a linear ABA block with styrene-butadiene-styrene (SBS) or styrene-isoprene-styrene (SIS).

The following examples are for illustrative purposes only and are not to be construed to limit the scope of the invention in any manner whatsoever.

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Example 1

1-(2,3-Dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine

To a solution of 1.95 g (12.5 mmol) of 1-oxyl-2,2,6,6-tetramethylpiperidine, 3.1 g (30 mmol) of tert-butyl nitrite and 7.5 mg (0.012 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) in 100 mL of pyridine at 65°-70°C under a nitrogen atmosphere is added dropwise over 20 minutes a solution of 5.6 g (25 mmol) of 2-allyloxyaniline in 20 mL of pyridine. The evolution of gas is observed during the addition of the 2-allyloxy-aniline. After the addition is complete, the reaction mixture is kept at 65°-70°C for an additional forty minutes until gas evolution subsided. After cooling to ambient temperature, the reaction mixture is then concentrated. The residue obtained is purified by vacuum flash chromatography (heptane) to give 2.3 g of a viscous liquid in 63.7% yield. The structure is confirmed by ¹Hnmr and elemental analyses.

¹Hnmr (C₆D₆) (300.08 MHz) 1.15 (s, CH₃, 6H), 1.45 (s, CH₃, 6H), 1.64, 1.42, 1.29 (overlapping m, CH₂, 6H), 3.71 (q, CH, 1H), 3.89 (dd, CH, 1H, ²J_{HH}=9.90Hz, ³J_{HH}=7.65Hz), 3.99 (dd, CH, ²J_{HH}=9.23Hz, ³J_{HH}=7.43Hz), 4.40 (dd, CH, 1H, ²J_{HH}=8.92Hz, ³J_{HH}=6.59Hz), 4.63 (dd, CH, 1H, ²J_{HH}=10.01Hz, ³J_{HH}=8.93Hz), 6.80 (d, 1H, ³J_{HH}=6.87Hz), 6.85 (t, 1H, ³J_{HH}=5.72Hz), 7.14 (t, 1H, ³J_{HH}=7.18Hz), 7.25 (d, 1H, ³J_{HH}=7.44Hz).

Analysis:

Calcd for C₁₈H₂₇NO₂: C, 74.7; H, 9.4; N, 4.8.

Found: C, 74.5; H, 9.1; N, 4.9.

Example 2

1-(2,3-Dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine

The procedure of Example 1 is repeated using 1.95 g (12.5 mmol) of 1-oxyl-2,2,6,6-tetra-methyl-4-hydroxypiperidine, 3.10 g (30 mmol) of tert-butyl nitrite, 7.5 mg (0.012 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) mmol) in 100 mL of chlorobenzene and 5.60 g (25 mmol) of 2-allyloxyaniline in 20 mL of chlorobenzene. The crude product obtained is purified by vacuum flash chromatography (25% ethyl acetate/heptane) to give 2.22 g of a viscous liquid in 61.5% yield.

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Example 3

1-(2,3-Dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine

The procedure of Example 1 is repeated using 1.95 g (12.5 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 3.10 g (30 mmol) of tert-butyl nitrite, 2.4 g (25 mmol) of pyridine, 7.5 mg (0.012 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) mmol) in 100 mL of chlorobenzene and 5.60 g (25 mmol) of 2-allyloxyaniline in 20 mL of chlorobenzene. The crude product obtained is purified by vacuum flash chromatography (25% ethyl acetate/heptane) to give 2.13 g of a viscous liquid in 59.0% yield.

Example 4

The cis and trans isomers of 1-(2,3-Dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine

The procedure of Example 1 is repeated using 3.0 g (19 mmol) of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine, 4.64 g (45 mmol) of tert-butyl nitrite, 11.45 mg (0.019 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) mmol) in 80 mL of pyridine and 6.27 g (38 mmol) of 2-(1-methylallyloxyaniline in 10 mL of pyridine. The crude product obtained is purified by vacuum flash chromatography (25% ethyl acetate/heptane) to give 5.31 g of a viscous liquid in 92.4% yield. The cis and trans isomers can be further separated by chromatography. The structures are confirmed by ¹Hnmr analysis.

¹Hnmr (C₆D₆) (499.85 MHz):

trans isomer: 1.13 (d, CH₃, 6H), 1.05 (s, CH₃, 6H), 1.11 (s, CH₃, 6H), 1.48 (overlapping m, CH₂, 6H), 3.35 (dt, CH, 1H, ³J_{HH}=9.34Hz, ³J_{HH'}=5.24Hz), 4.01 (q, CH, 1H, ²J_{HH}=12.50Hz, ³J_{HH'}=6.44Hz), 4.26 (t, CH, 1H, ³J_{HH}=9.00Hz), 4.40 (dd, CH, 1H, ²J_{HH}=9.09Hz, ³J_{HH'}=4.98Hz), 6.82 (td, 1H, ³J_{HH}=7.46Hz, ⁴J_{HH'}=1.02Hz), 6.89 (d, 1H, ³J_{HH}=7.99Hz), 7.02 (t, 1H, ³J_{HH'}=7.71Hz), 7.29 (d, 1H, ³J_{HH'}=7.43Hz).

cis isomer: 1.03 (d, CH₃, 3H), 1.05 (s, CH₃, 6H), 1.11 (s, CH₃, 6H), 1.20 (overlapping m, CH₂, 6H), 3.68 (dt, CH, 1H, ³J_{HH}=9.11Hz, ³J_{HH'}=4.69Hz), 4.15 (q, CH, 1H, ²J_{HH}=6.54Hz, ³J_{HH'}=4.90Hz), 4.28 (t, CH, 1H, ³J_{HH}=9.04Hz), 4.51 (dd, CH, 1H, ²J_{HH}=9.11Hz, ³J_{HH'}=4.70Hz),

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6.77 (td, 1H, $^3J_{HH}=7.39$ Hz, $^4J_{HH}=0.99$ Hz), 6.88 (d, 1H, $^3J_{HH}=7.81$ Hz), 7.00 (t, 1H, $^3J_{HH}=7.92$ Hz), 7.11 (d, 1H, $^3J_{HH}=7.40$ Hz).

Example 5

N,N-Di-tert-butyl-O-(2,3-dihydro-benzofuran-3-ylmethyl)hydroxylamine

The procedure of Example 1 is repeated using 1.8 g (12.5 mmol) of di-tert-butyl nitroxide, 3.09 g (30 mmol) of tert-butyl nitrite, 7.6 mg (0.0125 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) mmol) in 100 mL of pyridine and 5.62 g (25 mmol) of 2-allyloxyaniline in 10 mL of pyridine. The crude product obtained is purified by dry column flash chromatography (25% ethyl acetate/heptane) to give 2.43 g g of a viscous liquid in 85.9% yield. The structure is confirmed by 1 Hnmr and mass spectrographic analyses.

1 Hnmr (C_6D_6) (300.08 MHz) 1.11 (s, CH_3 , 9H), 1.13 (s, CH_3 , 9H), 3.36 (q, CH , 1H), 3.73 (dd, CH , 1H, $^2J_{HH}=9.09$ Hz, $^3J_{HH}=8.05$ Hz), 3.86 (dd, CH , 1H, $^2J_{HH}=8.90$ Hz, $^3J_{HH}=6.54$ Hz), 4.40 (dd, CH , 1H, $^2J_{HH}=8.99$ Hz, $^3J_{HH}=6.07$ Hz), 4.63 (dd, CH , 1H, $^2J_{HH}=9.00$ Hz, $^3J_{HH}=8.79$ Hz), 6.73 (dt, 1H, $^3J_{HH}=7.41$ Hz, $^4J_{HH}=1.08$ Hz), 6.82 (t, 1H, $^3J_{HH}=7.63$ Hz), 6.95 (t, 1H, $^3J_{HH}=7.70$ Hz), 7.11 (d, 1H, $^3J_{HH}=6.63$ Hz); MS [M+1] = 277.

Example 6

1-(3-Phenyl-2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine

The procedure of Example 1 is repeated using 3.9 g (25 mmol) of 1-oxyl-2,2,6,6-tetra-methyl-4-hydroxypiperidine, 6.18 g (60 mmol) of tert-butyl nitrite, 15 mg (0.025 mmol) of (S,S)-(+)-N,N-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) mmol) in 100 mL of pyridine and 11.25 g (50 mmol) of 2-(2-phenylallyloxy)aniline in 20 mL of pyridine. The crude product obtained is purified by liquid chromatography (2.5% ethyl acetate/heptane) to give 2.5 g of an off-white oil in 27.4% yield. MS [M+1] 366

Raw Materials

Wax samples are supplied by the Candle-Lite Corporation. These samples contain dyes and fragrances.

The UV absorbers and hindered amine stabilizers are obtained from the Ciba Speciality Chemicals Corporation.

Sample Preparation

The wax samples obtained from the Candle-Lite Corporation already contain a dye and a fragrance (scent). In these cases, the wax is melted and the appropriate stabilizer(s) is (are) added and dissolved in the molten wax. The stabilized wax is then poured into five (5) 44 mm diameter aluminum pans giving five (5) wax disks.

Sample Exposure

Triuplicate samples of each disk are exposed under a bank of six (6) cool-white fluorescent lamps (40 watts) or under a bank of six (6) UV lamps having a wavelength of 368 nm with the test samples being twelve (12) inches (30.48 cm) below the lamps.

Dye color fade (or color change) is measured by a Macbeth ColorEye Spectrophotometer with a 6 inch integrating sphere. The conditions are: 10 degree observer; D65 illuminant and 8 degree viewing angle.

Initial color measurements are taken using the above parameters. The L, a and b values are calculated using the CIE system from the reflectance values. YI is calculated from the L, a and b values. Subsequent measurements are taken at specified intervals. Delta L, a, b and YI values are simply the difference between the initial values and the values at each interval. Delta(Δ) E is calculated as follows:

$$[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} = \Delta E.$$

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Example 7

Color Fade of White Scented Candle Wax under Fluorescent Lamp Exposure

A variety of different stabilizers are evaluated in white scented candle wax obtained from the Candle-Lite Corporation under fluorescent lamp exposure. The ΔE values represent the change in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after <u>5.9 days</u>	ΔE after <u>11.8 days</u>	ΔE after <u>35 days</u>
Sample* (wt% add)			
Blank (no add)	42.90	45.50	45.14
A (0.15%) +			
B (0.15%)	24.48	26.36	27.80
C (0.15%) +			
D (0.15%)	13.34	15.26	18.16
C (0.15% +			
E (0.15%)	8.12	10.57	12.75

*A is 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, TINUVIN® 329, CIBA.

B is bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, TINUVIN® 292, CIBA.

C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA.

D is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate. TINUVIN® 123, CIBA.

E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

These data show that the instant compound of Example 1 protects white scented candle from discoloring better than do conventional stabilizer systems.

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Example 8

Color Fade of Gray Scented Candle Wax under Fluorescent Lamp Exposure

A variety of different stabilizers are evaluated in gray scented candle wax obtained from the Candle-Lite Corporation under fluorescent lamp exposure. The ΔE values represent the change in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after <u>4.9 days</u>	ΔE after <u>15.5 days</u>	ΔE after <u>33.9 days</u>
Sample* (wt% add)			
Blank (no add)	9.66	14.07	16.01
C (0.15%) +			
E (0.15%)	1.06	1.75	3.22

*C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA. E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

Example 9

Color Fade of Pink Potpourri Scented Candle Wax under Fluorescent Lamp Exposure

An instant compound is evaluated in pink potpourri scented candle wax obtained from the Candle-Lite Corporation under fluorescent lamp exposure. The ΔE values represent the change in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after <u>5.9 days</u>	ΔE after <u>11.8 days</u>	ΔE after <u>35 days</u>
Sample* (wt% add)			
Blank (no add)	42.90	45.50	45.14
C (0.15%) +			
E (0.15%)	2.83	5.09	7.03

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*C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA. E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

These data show that the instant compound of Example 1 provides the pink potpouri scented candle good protection from discoloring.

Example 10

Color Fade of White Scented Candle Wax under UV Lamp Exposure

A variety of different stabilizers are evaluated in white scented candle wax obtained from the Candle-Lite Corporation under UV lamp exposure. The ΔE values represent the change in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after <u>4 days</u>	ΔE after <u>10.1 days</u>	ΔE after <u>33 days</u>
Blank (no add)	27.56	32.71	34.68
C (0.15%) +			
D (0.15%)	5.16	6.68	10.27
C (0.15%) +			
E (0.15%)	2.26	4.49	7.71

C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA.

D is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate. TINUVIN® 123, CIBA.

E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

These data show that the instant compound of Example 1 protects white scented candle from discoloring far better than do conventional stabilizer systems.

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Example 11

Color Fade of Gray Scented Candle Wax under UV Lamp Exposure

A variety of different stabilizers are evaluated in gray scented candle wax obtained from the Candle-Lite Corporation under UV lamp exposure. The ΔE values represent the change in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after 2.8 days	ΔE after 8.9 days	ΔE after 22.6 days
Sample* (wt% add)	2.8	8.9	22.6
Blank (no add)	22.2	28.98	30.07
C (0.15%) +			
D (0.15%)	1.70	3.47	5.11
C (0.15%) +			
E (0.15%)	1.22	2.71	4.06

*C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA.

D is bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate. TINUVIN® 123, CIBA.

E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

These data show that the instant compound of Example 1 protects gray scented candle from discoloring better than do conventional stabilizer systems.

Example 12

Color Fade of Pink Potpourri Scented Candle Wax under UV Lamp Exposure

An instant compound is evaluated in pink potpourri scented candle wax obtained from the Candle-Lite Corporation under fluorescent lamp exposure. The ΔE values represent the change

in color after the indicated days of exposure. A low ΔE value indicates less change in color and is highly desired.

	ΔE after <u>7.6 days</u>	ΔE after <u>18.4 days</u>	ΔE after <u>36.7 days</u>
Sample* (wt% add)			
Blank (no add)	16.16	17.47	20.27
C (0.15%) +			
E (0.15%)	5.55	6.16	8.06

*C is octyl 3-(benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, TINUVIN® 384, CIBA. E is 1-(2,3-dihydrobenzofuran-3-yl-methoxy)-2,2,6,6-tetramethylpiperidine, the compound of Example 1.

These data show that the instant compound of Example 1 provides the pink potpouri scented candle good protection from discoloring.

Example 13

Molding grade polypropylene is dry blended with test additives and then melt compounded into pellets. The pelletized fully formulated resin is then injection molded into test specimens using a Boy 50M laboratory model injection molder.

Test plaques are mounted in metal frames and exposed in an Atlas Ci65 Xenon Arc Weather-Ometer with intermittent light/dark cycles and water spray following ASTM G26 test procedure. Specimens are tested at periodic intervals for changes in tensile properties. Failure in this test is determined by the observation of the loss of tensile properties. The longer it takes for the loss in properties to occur, the more effective is the stabilizer system.

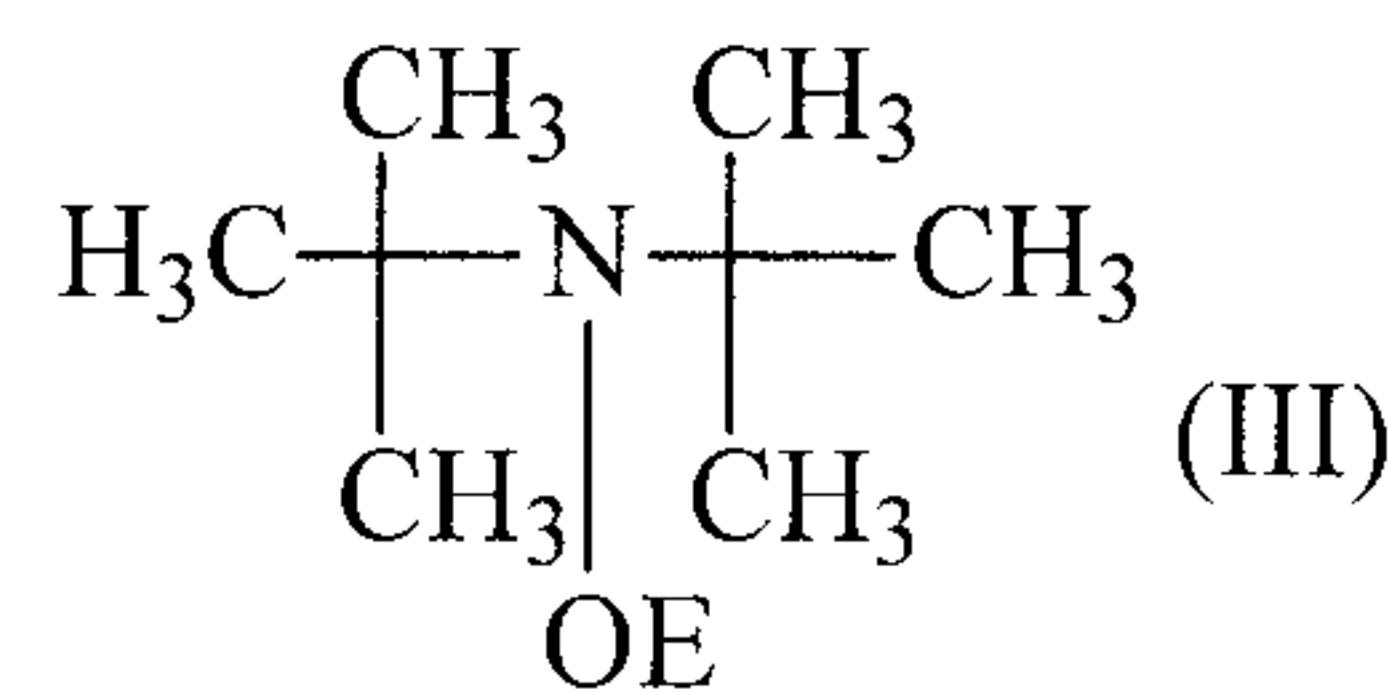
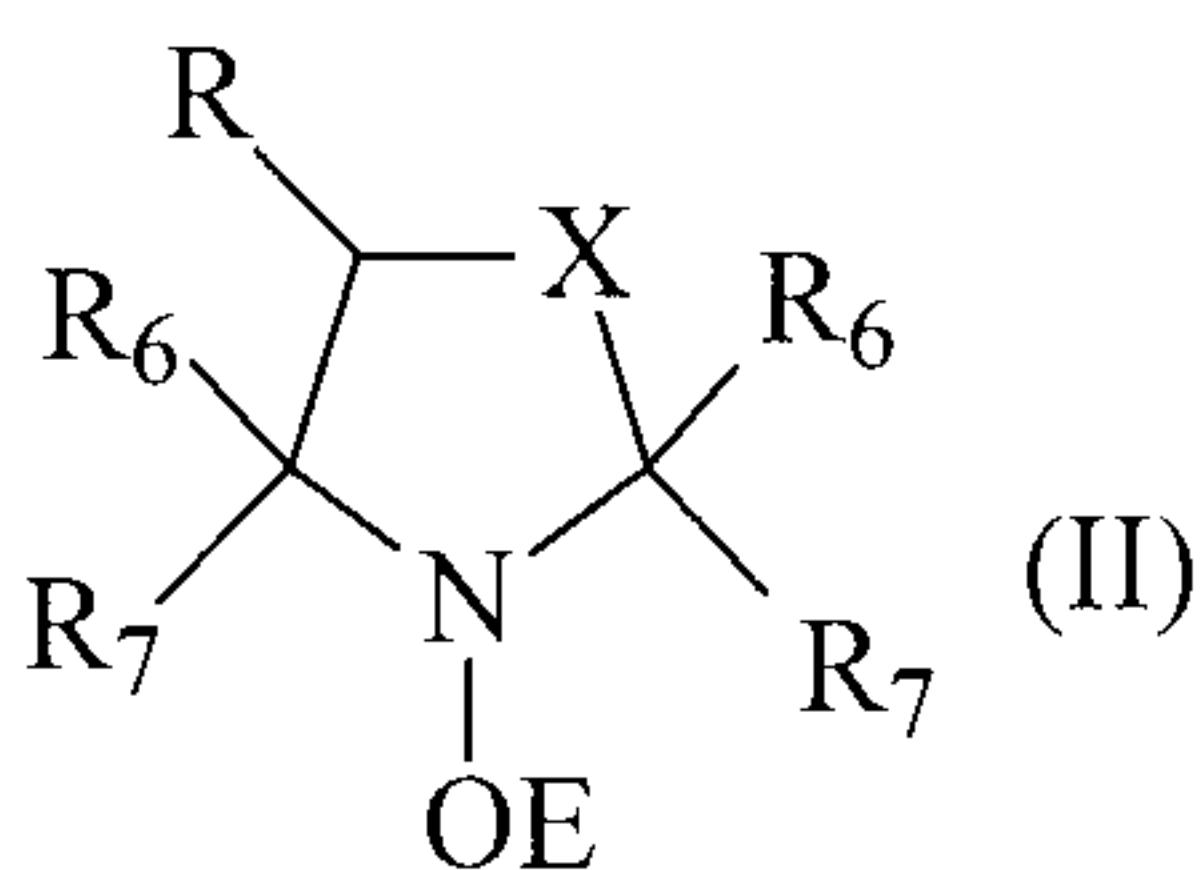
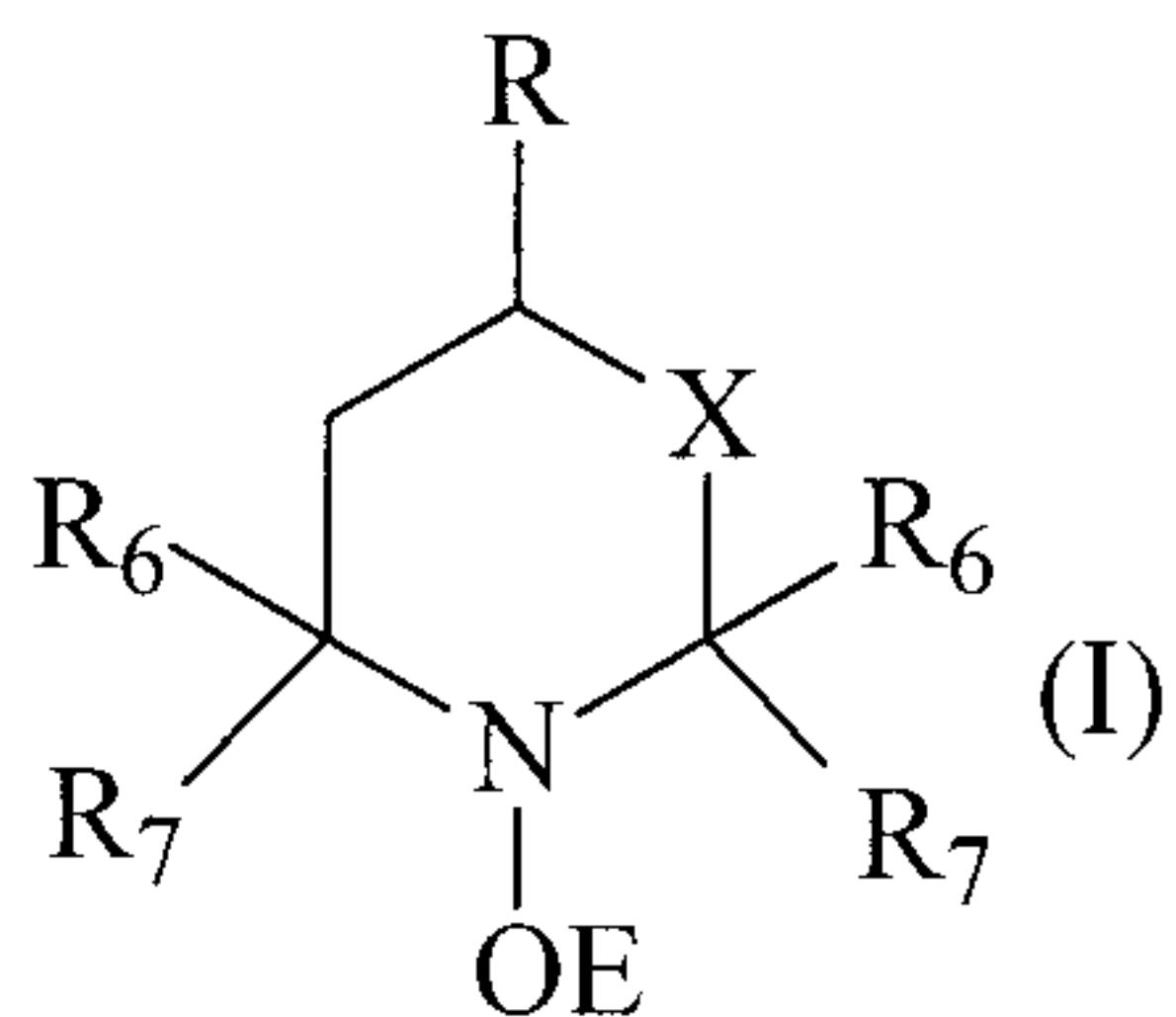
The test samples containing the instant compounds of Examples 1, 4, 5 and 6 exhibit good light stabilization properties.

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CLAIMS:

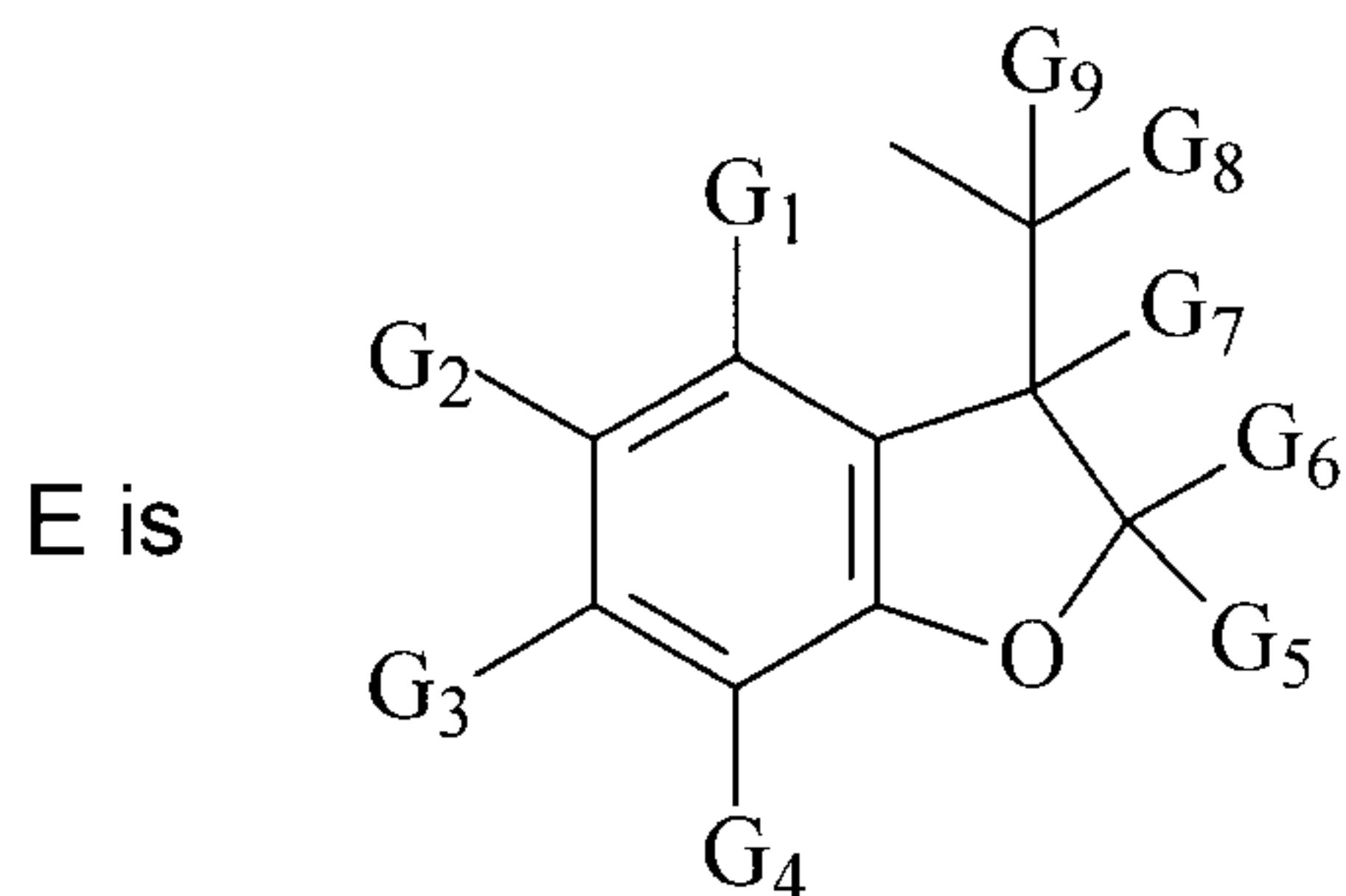
1. A compound which is 1-(3-phenyl-2,3-dihydrobenzofuran-3-ylmethoxy)-2,2,6,6-tetramethylpiperidine.
2. A composition stabilized which comprises
 - 5 (a) an organic material subject to degradation by heat, light or oxygen, which is a natural, semi-synthetic, or synthetic polymer, or a candle wax which is white and scented, white and unscented, dyed and scented, dyed and unscented, dipped and scented, or dipped and unscented,
 - (b) a compound of formula I, II or III



wherein

X is $-\text{CH}_2-$, $-\text{O}-$, $-\text{S}-$ or $-\text{NR}_8-$ where R_8 is hydrogen or alkyl of 1 to 12 carbon atoms,

15 R_6 and R_7 are independently alkyl of 1 to 8 carbon atoms, or R_6 and R_7 together are tetramethylene or pentamethylene,



R is hydrogen, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, hydroxyl, carboxyl, amino, alkylamino

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of 1 to 18 carbon atoms, dialkylamino of 2 to 36 carbon atoms, oxo, alkylthio of 1 to 18 carbon atoms, alkoxy of 1 to 18 carbon atoms, aryloxy of 7 to 15 carbon atoms, alkylcarbonyloxy of 2 to 18 carbon atoms or alkylcarbonylamino of 2 to 18 carbon atoms,

5 G_1 to G_4 are independently hydrogen, halogen, nitro, cyano, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms, hydroxyl, carboxyl, alkylthio of 1 to 18 carbon atoms, alkoxy of 1 to 18 carbon atoms, aryloxy of 7 to 15 carbon atoms, alkylcarbonyloxy of 1 to 18 carbon atoms, alkylsulfonyl of 1 to 18 carbon atoms, arylsulfonyl of 6 to 15 carbon atoms,
10 sulfo or phosphono, or any two vicinal substituents connected together to form a mono or polycyclic ring, and

G_5 to G_9 are independently hydrogen, alkyl of 1 to 18 carbon atoms, aralkyl of 7 to 15 carbon atoms or aryl of 6 to 10 carbon atoms.

3. A composition according to claim 2, wherein component (a) is candle
15 wax which is white and scented, white and unscented, dyed and scented, dyed and unscented, dipped and scented or dipped and unscented.

4. A composition according to claim 2, which additionally comprises a UV absorber.