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(54) Title: ALPHA CRYSTALLINE MODIFICATION OF 2,2',2"-NITRIL[O]TRIETHYL-TRIS-(3,3',5,5'-TETRA-TERT-BUTYL-1,1'-BIPHENYL-2,2'-DIYL)PHOSPHITE] (57) Abstract This invention pertains to an alpha crystalline modification of 2,2',2"-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], to a process for preparing said modification and the use thereof for stabilizing organic materials against oxidative, thermal or light-induced degradation.		

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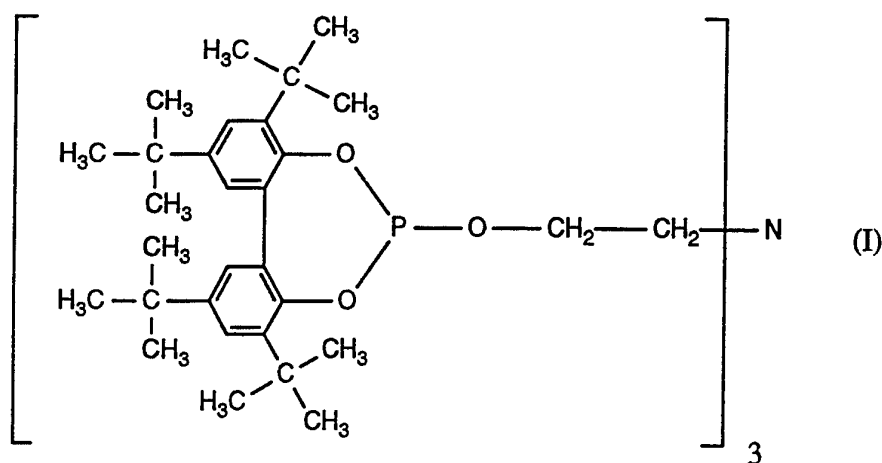
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Alpha Crystalline Modification of 2,2',2''-Nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite]

This invention pertains to a novel crystalline modification of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], to a process for preparing said modification and the use thereof for stabilizing organic materials against oxidative, thermal or light-induced degradation.

2,2',2''-Nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] is a compound having the formula I



This compound of formula I is useful as a processing stabilizer for organic materials as taught in US-A-4 318 845 and US-A-4 374 219. The compound of formula I is disclosed as being a white powder melting at 121-134°C. As such, the powdery product has defects in terms of handling and apparent density, exhibiting poor flowability, meterability, storage stability and hydrolytic stability.

It has now been found that the compound of formula I can be obtained in a different crystalline modification as purified crystalline particles which exhibit acceptable properties in respect to handling, apparent density, flowability, meterability, storage stability and hydrolytic stability.

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The new modification is characterized by a monoclinic crystalline form, melting in the range of 145-165°C as given by the peak temperature of the endotherm recorded by differential scanning calorimetry (DSC); and by an X-ray diffraction pattern obtained using Cu-K α which exhibits diffraction angles (2θ) of relative intensity given in the Table 1 below.

Table 1:

Diffraction Angle (2θ)	Relative Intensity (%)	Diffraction Angle (2θ)	Relative Intensity (%)	Diffraction Angle (2θ)	Relative Intensity (%)
5.2	100	11.6	18	18.7	20
5.8	38	12.7	7	19.6	20
6.3	13	13.6	20	20.0	17
6.5	15	14.2	23	20.2	17
7.2	14	14.9	18	20.8	17
8.0	30	15.7	30	21.1	18
8.7	31	16.2	31	22.6	18
8.9	36	16.6	48	22.7	18
10.0	35	17.0	28	22.9	18
10.1	31	17.4	58	23.1	16
10.7	41	18.2	37		

The X-ray diffraction pattern thus shows angles (2θ) lines of very high intensity at 5.2; lines of high intensity at 10.7, 16.6 and 17.4; lines of medium intensity at 5.8, 8.0, 8.9, 10.0, 10.1, 10.7, 15.7, 16.2 and 18.2; lines of weak intensity at 6.3, 6.5, 7.2, 11.6, 12.7, 13.6, 14.2, 14.9, 17.0, 18.7 and 19.6; and a relative absolute configuration of the three stereo axes of the dibenzo[d,f][1,3,2]dioxaphosphepin rings of R*,R*,R*.

R* follows the customary convention when the absolute configuration of a molecule is unknown. The nomenclature adopted here is based on recent Chemical Abstracts Service

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practice as described by L. C. Cross and W. Kyle, Pure Appl. Chem. 45, 11-30 (1976).

The instant invention also relates to a process for the preparation of this novel alpha crystalline form of the compound of formula I, which comprises crystallizing or recrystallizing said compound from a mixture of an aromatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms; from an ether solvent; from an ester solvent; or from a mixture of a halogenated aliphatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms.

Examples of aromatic hydrocarbon solvents useful in the instant process are benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, ethylbenzene, cumene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene, m-diisopropylbenzene, p-diisopropylbenzene, and mixtures of such aromatic hydrocarbon solvents.

Examples of lower carbon chain alkanols of 1 to 3 carbon atoms are methanol, ethanol, 1-propanol, isopropanol and mixtures of such lower alkanols.

Examples of ester solvents are methyl formate, ethyl formate, methyl acetate, ethyl acetate, n-butyl acetate, isobutyl acetate, amyl acetate and the like.

Examples of ether solvents are diethyl ether, diisopropyl ether, methyl tert-butyl ether and the like.

Examples of halogenated aliphatic hydrocarbon solvents are methylene chloride, chloroform, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane and the like.

The preferred process for preparing the novel alpha crystalline modification is by crystallizing or recrystallizing the compound of formula I from a mixture of an aromatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms.

The preferred process for preparing the novel alpha crystalline modification is also by crystallizing or recrystallizing the compound of formula I from a mixture of benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, ethylbenzene, cumene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene or m-diisopropylbenzene and an alkanol of 1 to 3 carbon atoms; from methyl formate, ethyl formate, methyl acetate, ethyl acetate, n-butyl acetate,

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isobutyl acetate or amyl acetate; from diethyl ether, diisopropyl ether or methyl tert-butyl ether; or from a mixture of methylene chloride, chloroform, 1,2-dichloroethane or 1,1,2,2-tetrachloroethane and an alkanol of 1 to 3 carbon atoms.

An especially preferred process for preparing the novel alpha crystalline modification is by crystallizing or recrystallizing the compound of formula I from a mixture of benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, ethylbenzene, cumene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene, or m-diisopropylbenzene and an alkanol of 1 to 3 carbon atoms.

Of interest is also a process for preparing the novel alpha crystalline modification by crystallizing or recrystallizing the compound of formula I from a mixture of toluene and methanol; xylene and methanol; toluene and isopropanol; or, xylene and isopropanol.

Of special interest is a process for preparing the novel alpha crystalline modification by crystallizing or recrystallizing the compound of formula I from ethyl acetate or diethyl ether or from a mixture of isopropanol and dichloromethane.

A preferred embodiment of the instant process involves isolating the crystalline mass from any of the above processes and drying it under vacuum at elevated temperature.

The instant invention relates also to the alpha, monoclinic crystalline form of 2,2',2''-nitriolo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], characterized by melting in the range of 145-165°C and by an X-ray diffraction pattern exhibiting lines of very high intensity at 5.2; lines of high intensity at 10.7, 16.6 and 17.4; lines of medium intensity at 5.8, 8.0, 8.9, 10.0, 10.1, 10.7, 15.7, 16.2 and 18.2; lines of weak intensity at 6.3, 6.5, 7.2, 11.6, 12.7, 13.6, 14.2, 14.9, 17.0, 18.7 and 19.6; and a relative configuration of the three dibenzo[d,f][1.3.2]dioxaphosphepin rings of R*, R*, R*, obtainable by crystallizing or recrystallizing said compound from a mixture of an aromatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms; from an ether solvent; from an ester solvent; or from a mixture of a halogenated aliphatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms.

The alpha, monoclinic crystalline form of formula I according to the invention is highly suitable for stabilizing organic materials against oxidative, thermal or light-induced degra-

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dation.

Examples of such organic materials 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), 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).
 - 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,

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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. 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,

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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.

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 sty-

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rene 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, 4/5, 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 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.

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23. Unsaturated polyester resins derived from copolyesters 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.

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.

Accordingly, the invention also relates to compositions comprising (a) an organic material subjected to oxidative, thermal or light-induced degradation and (b) the alpha, monoclinic

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crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite].

Preferably, the organic materials to be protected are natural, semi-synthetic or, preferably, synthetic organic materials. Particular preference is given to thermoplastic polymers, in particular PVC or polyolefins, especially polyethylene and polypropylene.

The action of the compounds according to the invention against thermal and oxidative degradation, especially under thermal stress, such as occurs during processing of thermoplastics, may be mentioned in particular. Accordingly, the compounds according to the invention are highly suitable for use as processing stabilizers.

Preferably, the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] according to the invention is added to the material to be stabilized in amounts of 0.01 to 10%, for example 0.01 to 5%, preferably 0.05 to 3%, in particular 0.05 to 1%, relative to the weight of the organic material to be stabilized.

The compositions according to the invention can contain, in addition to the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], further co-stabilizers, for example the following:

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, 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-di-phenyl-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. 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.

1.5. 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-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)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-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.6. 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, tris-(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithio-terephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.7. 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.

nate, 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.

1.8. 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.

1.9. 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.

1.10. 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.

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

1.12. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, 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.

1.13. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, 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 -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, 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 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, 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. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

2. UV absorbers and light stabilisers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonyl]ethyl)-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyl-

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oxycarbonylethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonylethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonylethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_n$, where R = 3'-tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl.

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-tertbutylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tertbutylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

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

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

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-piperidyl)succinate, bis(1,2,2,6,6-pentamethylpiperidyl)sebacate, bis(1,2,2,6,6-pentamethylpiperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succi-

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nic acid, the condensate 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, the condensate 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)pyrrolidin-2,5-dione.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethoxanilide, 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 and mixtures of ortho- and para-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine.

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 di-

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hydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl 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, 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, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphite.

5. 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.

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

7. 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 tin pyrocatecholate.

8. Nucleating agents, for example, 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid.

9. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite.

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10. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

11. Benzofuranones and indolinones, for example those disclosed in US-A-4 325 863, US-A-4 338 244 or US-A-5 175 312, 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.

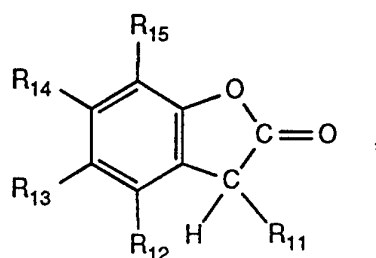
The co-stabilizers, with the exception of the benzofuranones listed under 11, are added for example in concentrations of 0.01 to 10%, relative to the total weight of the material to be stabilized.

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) and peroxide-destroying compounds (item 5.) 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-5 175 312.

Examples of such benzofuran-2-ones are compounds of the formula



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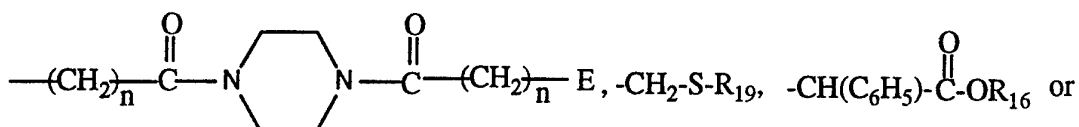
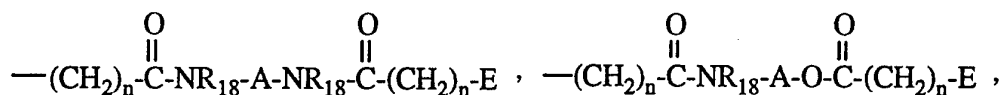
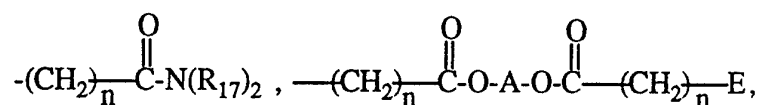
in which

R_{11} is phenyl or phenyl which is substituted by 1 to 3 alkyl radicals together having at most 18 carbon atoms, alkoxy having 1 to 12 carbon atoms, alkoxycarbonyl having 2 to 18 carbon atoms or chlorine;

R_{12} is hydrogen;

R_{14} is hydrogen, alkyl having 1 to 12 carbon atoms, cyclopentyl, cyclohexyl or chlorine;

R_{13} has the meaning of R_{12} or R_{14} or is a radical of the formula $-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-OR_{16}$,



-D-E,

in which

R_{16} is hydrogen, alkyl having 1 to 18 carbon atoms, alkyl having 2 to 18 carbon atoms which is interrupted by oxygen or sulfur, dialkylaminoalkyl having a total of 3 to 16 carbon atoms, cyclopentyl, cyclohexyl, phenyl or phenyl which is substituted by 1 to 3 alkyl radicals together having at most 18 carbon atoms;

n is 0, 1 or 2;

the substituents R_{17} , independently of one another, are hydrogen, alkyl having 1 to 18 carbon atoms, cyclopentyl, cyclohexyl, phenyl, phenyl which is substituted by 1 or 2 alkyl radicals together having at most 16 carbon atoms, a radical of the formula $-C_2H_4OH$,

$-C_2H_4-O-C_mH_{2m+1}$ or $-C_2H_4-O-\overset{\overset{O}{\parallel}}{C}-R_{20}$ or together with the nitrogen atom to which they are attached form a piperidine or morpholine radical;

m is 1 to 18;

R_{20} is hydrogen, alkyl having 1 to 22 carbon atoms or cycloalkyl having 5 to 12 carbon atoms;

A is alkylene having 2 to 22 carbon atoms which may be interrupted by nitrogen, oxygen or sulfur;

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R_{18} is hydrogen, alkyl having 1 to 18 carbon atoms, cyclopentyl, cyclohexyl, phenyl, phenyl which is substituted by 1 or 2 alkyl radicals together having at most 16 carbon atoms, or is benzyl;

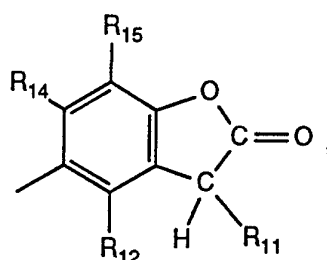
R_{19} is alkyl having 1 to 18 carbon atoms;

D is -O-, -S-, -SO-, -SO₂- or -C(R₂₁)₂-;

the substituents R_{21} , independently of one another, are hydrogen, C₁-C₁₆alkyl, the two R_{21} together containing 1 to 16 carbon atoms, R_{21} is furthermore phenyl or a radical of the

formula $-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-OR_{16}$ or $-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-N(R_{17})_2$, in which n, R_{16} and R_{17} are as defined above;

E is a radical of the formula



in which R_{11} , R_{12} and R_{14} are as defined above; and

R_{15} is hydrogen, alkyl having 1 to 20 carbon atoms, cyclopentyl, cyclohexyl, chlorine or a

radical of the formula $-\overset{\overset{O}{\parallel}}{C}-OR_{16}$ or $-\overset{\overset{O}{\parallel}}{C}-N(R_{17})_2$, in which R_{16} and R_{17} are as defined above, or R_{15} together with R_{14} forms a tetramethylene radical.

Preference is given to those benzofuran-2-ones in which R_{13} is hydrogen, alkyl having 1 to 12 carbon atoms, cyclopentyl, cyclohexyl, chlorine or a radical of the formula

$-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-OR_{16}$, $-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-N(R_{17})_2$ or -D-E, in which n, R_{16} , R_{17} , D and E are as defined above, R_{16} is in particular hydrogen, alkyl having 1 to 18 carbon atoms, cyclopentyl or cyclohexyl.

Preference is given furthermore to those benzofuran-2-ones in which R_{11} is phenyl or phenyl which is substituted by 1 or 2 alkyl radicals together having at most 12 carbon atoms; R_{12} is hydrogen; R_{14} is hydrogen or alkyl having 1 to 12 carbon atoms; R_{13} is

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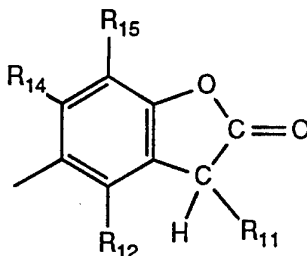
hydrogen, alkyl having 1 to 12 carbon atoms, $-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-OR_{16}$,

$-(CH_2)_n-\overset{\overset{O}{\parallel}}{C}-N(R_{17})_2$ or -D-E; R_{15} is hydrogen, alkyl having 1 to 20 carbon atoms,

$-CH_2-\overset{\overset{O}{\parallel}}{C}-OR_{16}$ or $-CH_2-\overset{\overset{O}{\parallel}}{C}-N(R_{17})_2$, or R_{15} together with R_{14} forms a tetramethylene radical, n, R_{16} , R_{17} , D and E being as defined at the beginning.

Of particular interest are also those benzofuran-2-ones in which R_{11} is phenyl; R_{13} is hydrogen, alkyl having 1 to 12 carbon atoms or -D-E; R_{12} and R_{14} , independently of one another, are hydrogen or alkyl having 1 to 4 carbon atoms; and R_{15} is alkyl having 1 to 20 carbon atoms, D and E being as defined at the beginning.

Of special interest are finally also those benzofuran-2-ones in which R_{11} is phenyl; R_{13} is alkyl having 1 to 4 carbon atoms or -D-E; R_{12} and R_{14} are hydrogen; and R_{15} is alkyl having 1 to 4 carbon atoms, cyclopentyl or cyclohexyl, D being a group $-C(R_{21})_2-$ and E being a radical of the formula



the substituents R_{21} being identical to or different from one another and each being alkyl having 1 to 4 carbon atoms, and R_{11} , R_{12} , R_{14} and R_{15} being as defined.

The amount of additional additives, in particular stabilizers, for example of the benzofuran-2-ones mentioned, can vary within wide limits. For example, 0.0005 to 10, preferably 0.001 to 5, in particular 0.01 to 2, % by weight thereof can be present in the compositions according to the invention.

Incorporation of the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] and, if desired, further addi-

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tives in the polymer organic material is carried out by known methods, for example before or during moulding or by applying the dissolved or dispersed compounds to the polymer organic material, if appropriate with subsequent slow evaporation of the solvent. The alpha, monoclinic crystalline form according to the invention can also be added to the materials to be stabilized in the form of a masterbatch containing them, for example, in a concentration of 2.5 to 25% by weight.

The alpha, monoclinic crystalline modification according to the invention can also be added before or during polymerization or before crosslinking.

The alpha, monoclinic crystalline modification according to the invention can be incorporated in the material to be stabilized in pure form or encapsulated in waxes, oils or polymers.

The alpha, monoclinic crystalline modification according to the invention can also be sprayed onto the polymer to be stabilized. They are capable of diluting other additives (for example the abovementioned customary additives) or their melts, thus enabling them to be sprayed onto the polymer to be stabilized also together with these additives. Addition by spraying during deactivation of the polymerization catalysts is particularly advantageous, it being possible, for example, for the steam used for deactivation to be used for spraying.

In the case of bead polymerized polyolefins, it may be advantageous, for example, to apply the alpha, monoclinic crystalline modification according to the invention, if desired together with other additives, by spraying.

The materials thus stabilized can be used in a wide range of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or cements.

As already mentioned, the organic materials to be protected are preferably organic, in particular synthetic, polymers. Of these, the materials being protected are particularly advantageously thermoplastic materials, in particular polyolefins. The excellent efficiency of the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] as processing stabilizer (thermal stabilizer) should be mentioned in particular. To this end, it is advantageously added to the polymer before or during its processing. It is however also possible to stabilize other polymers (for example

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elastomers) or lubricants or hydraulic fluids against degradation, for example light-induced or thermal-oxidative degradation. For elastomers, see the above list of possible organic materials.

Suitable lubricants and hydraulic fluids are based, for example, on mineral or synthetic oils or mixtures thereof. Lubricants are known to one skilled in the art and described in the relevant technical literature, for example in Dieter Klamann, "Schmierstoffe und verwandte Produkte" (Verlag Chemie, Weinheim 1982), in Schewe-Kobek, "Das Schmiermittel-Taschenbuch" (Dr. Alfred Hüthig-Verlag, Heidelberg, 1974) and in "Ullmanns Enzyklopädie der technischen Chemie" vol. 13, pages 85-94 (Verlag Chemie, Weinheim, 1977).

Accordingly, a preferred embodiment of the present invention is the use of the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] for stabilizing organic materials against oxidative, thermal or light-induced degradation.

The alpha, monoclinic crystalline modification according to the invention is preferably used as processing stabilizer (thermal stabilizer) of thermoplastic polymers.

The present invention also provides a process for stabilizing an organic material against oxidative, thermal or light-induced degradation, which comprises incorporating therein or applying thereto the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite].

Differential scanning calorimetry (DSC) measurements are obtained on a TA Instrument Inc., 910 differential scanning calorimeter, with a 100 ml/min nitrogen purge, aligned aluminum pan, temperature scan at 5°C/min to 230°C.

X-ray diffraction patterns are recorded on a Philips Norelco X-ray Diffractometer unit, using Cu-K α radiation with a nickel filter.

The examples which follow further illustrate the invention. The parts or percentages given are by weight.

Example 1:

The compound of formula I, 2,2',2''-nitrido[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-bi-phenyl-2,2'-diyl) phosphite], is prepared according to procedure of Example 4 of U.S. Patent No. 4,318,845. The product obtained is recrystallized from the following solvent systems to obtain the novel alpha, crystalline modification of the instant invention. The results are summarized in Table 2.

Table 2:

Solvent (wt/wt)	Compound/Solvent Ratio (weight/weight)	Melting Point ^{a)} (°C)	Yield (%)
ethyl acetate	1 / 3.8	160	74
toluene / isopropanol (1 / 6)	1 / 7	158	75
xylene / isopropanol (1 / 1)	1.2 / 1	159	91
xylene / methanol (1.8 / 1)	1.5 / 1	159	97
toluene / methanol (1 / 1)	1 / 2	159	91
toluene / methanol (1.1 / 1)	1 / 8.3	159	50
diethyl ether	1 / 3.5	165	25
isopropanol/dichloromethane (1.2 / 1)	1 / 7.25	161	38
xylene / 1-propanol (1 / 1)	1.2 / 1	163	93

a) Melting point is determined by differential scanning calorimetry and the peak temperature in the endotherm is recorded as the melting point.

Suitable crystals for X-ray analysis are grown from ethyl acetate. For the structure determination, a thick hexagonal plate is selected and broken to reduce the largest dimension to

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less than 1 mm. Intensity data are measured on a Siemens R3MV four circle diffractometer as described in Table 3 below. The structure is solved by direct methods using Siemens SHELXTL PLUS (VMS). Full-matrix least-square refinements are carried out. The relative absolute configuration is determined to be R*, R*, R*.

Table 3

Crystal and Data Collection Parameters

Formula	C ₉₀ H ₁₃₂ NO ₉ P ₃
Formula weight (g•mol ⁻¹)	1464.96
Color; Habit	Colorless Hexagonal Prism
Crystal System	Monoclinic
Space group	P2 ₁ /n
Z	4
Cell parameters	a = 20.0700 (10) Å b = 17.477 (2) Å c = 27.620 (3) Å β = 93.050 (10) deg
Volume	v = 9674.5 (14) Å ³
d _{calc}	1.006
Absorption Coefficient	0.926 mm ⁻¹
Crystal Size	0.3 x 0.3 x 0.6 mm
F(000)	3184
Temperature	23° C
Diffractometer Type	Siemens R3m/V
Radiation	CuKα (λ = 1.54178 Å)
Monochromator	Orientated graphite crystal
2θ Range	3.15 to 115.0 deg
Scan Type	2θ-θ
Scan Range (w)	0.50° plus Kα separation
Reflections Collected	14042
No. of observed reflections	9094 (F > 3.0 σ (F))
R	0.1159
R _w	0.1690

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Example 2: Flowability Properties

This example illustrates the superior flowability properties of the new alpha crystalline modification of the compound of formula I prepared in Example 1 as compared to the flow properties of the compound of formula I as prepared according to the procedure of Example 4 of US-A-4 318 845.

The angle of repose is measured according to the procedure reported by G. Gold et al. in J. Pharm. Sci., 55, 1291 (1966). A smaller angle of repose indicated a superior flowing solid product. The results are summarized in Table 4.

Table 4:

Compound	Angle of Repose (degrees)
Polypropylene (control)	38
Example 1 (alpha crystalline form)	38
Example 4 of US-A-4 318 845	43

Example 3: Process Stabilization of Polypropylene at 274°C.

The base formulation comprises unstabilized, high yield/high selectivity catalyzed polypropylene (PROFAX[®] 6501, Batch No. BD07155, produced by Himont) containing 0.075% by weight of calcium stearate. The test additives are incorporated into the polypropylene by dry blending or, when the additive is a liquid, using a minimum amount of methylene chloride solvent. The solvent is then removed by evaporation under reduced pressure. The stabilized resin formulation is extruded at 90 rpm from a 2.54 cm diameter extruder at 274°C with a residence time of 90 seconds. After each of the first, third and fifth extrusions, the melt flow rate (in grams/10 minutes) is determined by ASTM method D1238 on the pellets obtained from the extruder. The melt flow rate is a measure of the molecular weight of the polymer and indicates whether thermal degradation is occurring during melt processing by extrusion. A minimum change in melt flow rate is favored and

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indicates good melt processing stabilization. A substantial increase in the melt flow denotes pronounced chain degradation, i.e. poor stabilization. The results are given in Table 5 below.

Table 5:

Additive	Concentration (% by weight)	Melt Flow after Extrusion		
		1st	3rd	5th
Calcium stearate	0.075	13.5	24.0	45.2
Calcium stearate plus AO A	0.075 0.075	8.1	12.9	17.5
Calcium stearate plus AOA plus Compound of Example 1 (alpha crystalline form)	0.075 0.075 0.075	5.6	6.8	7.4

AO A is neopentetetrayl tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate).

Example 4: Comparison of the X-ray diffraction data of the alpha, monoclinic crystalline form of formula I according to the invention (compound A) and the compound of formula I as prepared according to the procedure of Example 4 of US-A-4 318 845 (compound B).

The alpha, monoclinic crystalline form of 2,2',2"-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] was prepared in accordance with instant Example 1. The product was recrystallized from ethyl acetate (compound A). The state of the art modification of formula I was prepared according to the procedure of Example 4 of US-A-4 318 845 and recrystallized from a mixture of acetonitrile and toluene (compound B). The results are summarized in Table 6.

Table 6:

Property	Compound A	Compound B
Melting Point	160°C	134-140°C
Unit Cell Dimensions		
a	20.0700 Å	20.308 Å
b	17.477 Å	17.615 Å
c	27.620 Å	27.918 Å
β	93.050°	93.730°
Volume	9674.5 Å ³	9966 Å ³
Density (calc.)	1.006 Mg/m ³	0.986 Mg/m ³

The procedure for the X-ray analysis performed is the same as provided in instant Example 1. Comparison of the data readily shows a difference in structure between the instant alpha, crystalline form (compound A) and the state of the art compound (compound B).

The unit cell of compound B contains an entrapped molecule of toluene. This was not recognized by the authors of US-A-4 318 845 or they failed to mention it. In constrast, the crystal cell of compound A of the instant invention does not contain a molecule of solvent from any of the claimed recrystallization solvent systems.

The above fact is clearly reflected in the large difference in melting points between the alpha crystalline form (compound A) and the prior art material (compound B). Additionally, this fact is seen in comparing the difference between the cell dimensions, volume and density. In particular, a significant difference can be seen by comparing the volumes of the alpha crystalline form (9674.5 Å³) and the prior art material (9966 Å³).

WHAT IS CLAIMED IS:

1. The alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], characterized by melting in the range of 145-165°C and by an X-ray diffraction pattern exhibiting lines of very high intensity at 5.2; lines of high intensity at 10.7, 16.6 and 17.4; lines of medium intensity at 5.8, 8.0, 8.9, 10.0, 10.1, 10.7, 15.7, 16.2 and 18.2; lines of weak intensity at 6.3, 6.5, 7.2, 11.6, 12.7, 13.6, 14.2, 14.9, 17.0, 18.7 and 19.6; and a relative configuration of the three dibenzo[d,f]-[1.3.2]dioxaphosphepin rings of R*, R*, R*.
2. A process for the preparation of the alpha, monoclinic crystalline form of the compound 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] which comprises crystallizing or recrystallizing said compound from a mixture of an aromatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms; from an ether solvent; from an ester solvent; or from a mixture of a halogenated aliphatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms.
3. A process according to claim 2 wherein the crystallizing or recrystallizing is from a mixture of an aromatic hydrocarbon solvent and an alkanol of 1 to 3 carbon atoms.
4. A process according to claim 2 wherein the crystallizing or recrystallizing is from a mixture of benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, ethylbenzene, cumene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene or m-diisopropylbenzene and an alkanol of 1 to 3 carbon atoms; from methyl formate, ethyl formate, methyl acetate, ethyl acetate, n-butyl acetate, isobutyl acetate or amyl acetate; from diethyl ether, diisopropyl ether or methyl tert-butyl ether; or from a mixture of methylene chloride, chloroform, 1,2-dichloroethane or 1,1,2,2-tetrachloroethane and an alkanol of 1 to 3 carbon atoms.
5. A process according to claim 2 wherein the crystallizing or recrystallizing is from a mixture of benzene, toluene, o-xylene, m-xylene, p-xylene, 1,2,3-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,4,5-tetramethylbenzene, ethylbenzene, cumene, o-cymene, m-cymene, p-cymene, o-diisopropylbenzene, or m-diisopropylbenzene and an alkanol of 1 to 3 carbon atoms.

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6. A process according to claim 5 wherein the crystallizing or recrystallizing is from a mixture of toluene and methanol; xylene and methanol; toluene and isopropanol; or, xylene and isopropanol.
7. A process according to claim 2 wherein the crystallizing or recrystallizing is from ethyl acetate or diethyl ether or from a mixture of isopropanol and dichloromethane.
8. A process according to claim 2 wherein the isolated crystalline mass is dried under vacuum at an elevated temperature.
9. The alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] obtainable by the process of claim 2.
10. A composition comprising
 - a) an organic material subjected to oxidative, thermal or light-induced degradation, and
 - b) the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] as defined in claim 1 and 9.
11. A composition according to claim 10, additionally comprising, apart from components (a) and (b), further additives.
12. A composition according to claim 11, comprising, as further additives, phenolic anti-oxidants, light stabilizers or processing stabilizers.
13. A composition according to claim 11, comprising, as the further additive, at least one compound of benzofuran-2-one type.
14. A composition according to claim 10, comprising, as component (a), natural, semi-synthetic or synthetic polymers.
15. A composition according to claim 10, comprising, as component (a), thermoplastic polymers.
16. A composition according to claim 10, comprising, as component (a), a polyolefin.

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17. A composition according to claim 10, comprising, as component (a), polyethylene or polypropylene.
18. Use of the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], as defined in claim 1 and 9, as stabilizer for organic materials against oxidative, thermal or light-induced degradation.
19. Use according to claim 18, in which the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite], as defined in claim 1 and 9, is used as processing stabilizer (thermal stabilizer) in thermoplastic polymers.
20. A process for stabilizing an organic material against oxidative, thermal or light-induced degradation, which comprises incorporating therein or applying thereto the alpha, monoclinic crystalline form of 2,2',2''-nitrilo[triethyl-tris-(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl) phosphite] as defined in claim 1 and 9.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 93/11327A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C07F9/6574 C08K5/527

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 5 C07F 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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 053 098 (CIBA-GEIGY AG) 2 June 1982 cited in the application see page 22; example 4 ---	1-20
A	EP,A,0 026 893 (HOECHST AG) 14 April 1981 see page 3, line 30 - line 34; claims 1-3 -----	1-20

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US 93/11327

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0053098	02-06-82	US-A- 4318845	09-03-82
		CA-A- 1159078	20-12-83
		JP-C- 1623667	18-11-91
		JP-B- 2049319	29-10-90
		JP-A- 57118593	23-07-82
		US-A- 4374219	15-02-83

EP-A-0026893	15-04-81	DE-A- 2940548	16-04-81
