

Description

The present invention relates to a stabilizer system containing two high-molecular polyalkylpiperidines, the use thereof for stabilizing synthetic polymers and the synthetic polymer which has been protected by means of the stabilizer system mentioned against degradation induced by light.

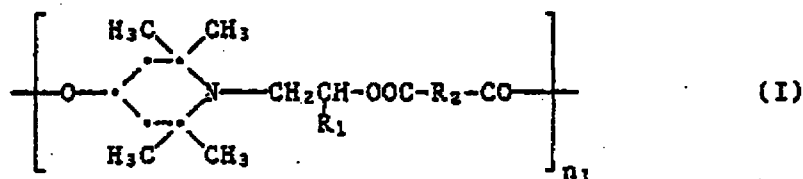
A number of high-molecular polyalkylpiperidines suitable for use as light stabilizers are known. For example, condensation and addition polymers containing sterically hindered piperidine groups are described in US-A 4,233,412, and triazine polymers containing piperidine groups are disclosed in US-A 4,086,204 and 4,331,586.

Mixtures of low-molecular and high-molecular polyalkylpiperidines are described in EP-A 80,431 as a stabilizer system for organic material.

Stabilized polyolefin compositions containing formamidines and polyalkylpiperidines are described in JP-A 85-115,644. Stabilized polyolefin compositions containing polyalkylpiperidines, sterically hindered phenols and phosphites are disclosed in JP-A 85-124,642.

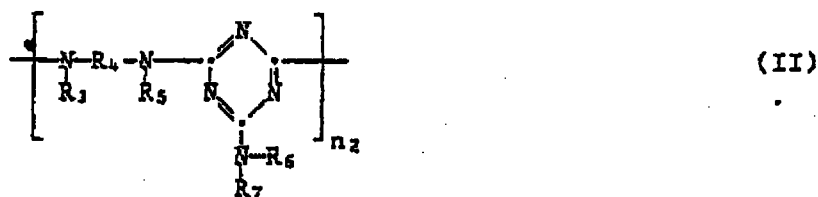
The present invention relates to a stabilizer system containing

a) at least one polyalkylpiperidine of the formula I



in which R_1 is hydrogen or methyl, R_2 is a direct bond or $\text{C}_1\text{-C}_{10}$ alkylene and n_1 is an integer from 2 to 100, and

b) at least one polyalkylpiperidine of the formula II



in which R_3 , R_5 and R_6 independently of one another are hydrogen, C_1 - C_4 alkyl, phenyl, phenyl which is substituted by -OH and/or C_4 - C_8 alkyl, benzyl or benzyl which is substituted by -OH and/or C_4 - C_8 alkyl or are a group of the formula III



in which R_8 is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkyl which is substituted by -OH, or is benzyl, allyl, acetyl or crotonyl, subject to the condition that the C atom attached to the nitrogen atom of the piperidyl group is a primary carbon atom, R_4 is C_2 - C_8 alkylene and R_7 is hydrogen, C_1 - C_{10} alkyl, phenyl, phenyl which is substituted by -OH and/or C_4 - C_8 alkyl, benzyl or benzyl which is substituted by -OH and/or C_4 - C_8 alkyl, or is a group of the formula III, or the radicals R_6 and R_7 , together with the nitrogen atom to which they are attached, form a 6-membered heterocyclic ring, n_2 is an integer from 2 to 100, and at least one of the radicals R_3 , R_5 , R_6 and R_7 is a group of the formula III.

Examples of R_2 as C_1 - C_{10} alkylene are 1,2-ethylene, 1,3-propylene, 1,2-propylene, tetramethylene, pentamethylene, 2,2-dimethyl-1,3-propylene, hexamethylene, heptamethylene, octamethylene or decamethylene. Linear C_1 - C_4 alkylene is preferred and ethylene is particularly preferred.

Examples of R_3 , R_5 and R_6 as C_1 - C_4 alkyl are methyl, ethyl, propyl, isopropyl, n-butyl or tert-butyl.

Examples of R_3 , R_5 , R_6 and R_7 as phenyl which is substituted by -OH and/or C_4 - C_8 alkyl are tert-butylphenyl or 3,5-di-tert-butyl-4-hydroxyphenyl. 3,5-di-tert-butyl-4-hydroxyphenyl is particularly

preferred.

Examples of R_3 , R_5 , R_6 and R_7 as benzyl which is substituted by -OH and/or C_4 - C_8 alkyl are tert-butylbenzyl or 3,5-di-tert-butyl-4-hydroxybenzyl. 3,5-di-tert-butyl-4-hydroxybenzyl is particularly preferred.

Examples of R_4 as C_2 - C_8 alkylene are 1,2-ethylene, 1,3-propylene, 1,2-propylene, tetramethylene, pentamethylene, 2,2-dimethyl-1,3-propylene, hexamethylene, heptamethylene or octamethylene. Hexamethylene is particularly preferred.

Examples of R_7 as C_1 - C_{10} alkyl are methyl, ethyl, propyl, isopropyl, n-butyl, tert-butyl, pentyl, hexyl, octyl, 1,1,3,3-tetramethylbutyl, nonyl or decyl. 1,1,3,3-tetramethylbutyl is particularly preferred.

Examples of R_8 as C_1 - C_4 alkyl which can if appropriate be substituted by -OH are methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, 2-hydroxyethyl or 2-hydroxypropyl. Especially preferred are methyl, 2-hydroxymethyl and 2-hydroxypropyl.

The radicals R_3 and R_5 are preferably a group of the formula III in which R_8 is preferably hydrogen.

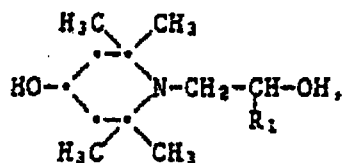
The radicals R_6 and R_7 , together with the nitrogen atom to which they are attached, preferably form a 6-membered heterocyclic ring, for example pyrrolidin-1-yl, piperidino, piperazin-1-yl, 4-methylpiperazin-1-yl or morpholino. Morpholino is particularly preferred.

The meanings of the end groups which saturate the free valencies in the compounds of the formulae I and II depend on the processes used for their preparation.

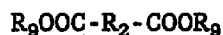
The compounds of the formulae I and II are known (in some cases commercially available) and can be prepared by known processes, for example as described in US-A 4,233,412 and 4,086,204.

If the preparation of the compounds of the formula I is effected, for

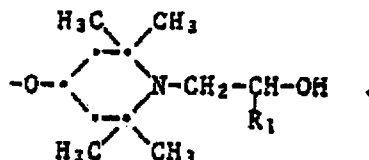
example, by reacting a compound of the formula



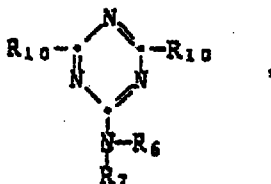
in which R_1 is hydrogen or methyl with a dicarboxylic acid diester of the formula



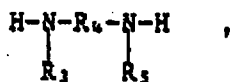
in which R_9 is, for example, methyl, ethyl or propyl and R_2 is as defined above, the end group attached to the 2,2,6,6-tetramethyl-4-oxypiperidin-1-yl radical is hydrogen or $-\text{CO}-\text{R}_2-\text{COOR}_9$, and the end group attached to the diacyl radical is $-\text{O}-\text{R}_9$ or



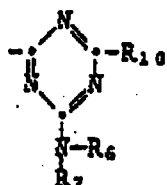
If the preparation of the compounds of the formula II is effected, for example, by reacting a compound of the formula



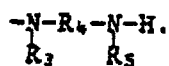
in which R_{10} is, for example, chlorine and R_6 and R_7 are as defined above with a compound of the formula



in which R_3 , R_4 and R_5 are as defined above, the end group attached to the diamino radical is hydrogen or



and the end group attached to the triazine radical is $-\text{R}_{10}$ or



If R_{10} is a halogen, for example chlorine, it is advantageous to replace this halogen, for example by -OH or an amino group, when the reaction is complete. The following may be mentioned as examples of amino groups: -NH_2 , $\text{-NH}(\text{C}_1\text{-C}_8\text{alkyl})$, $\text{-N}(\text{C}_1\text{-C}_8\text{alkyl})_2$, pyrrolidin-1-yl and morpholino.

A stabilizer mixture containing a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II in which R_3 and R_5 are a group of the formula III is also preferred.

R_3 is particularly preferably hydrogen or methyl.

A stabilizer mixture which is of interest contains a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II in which R_6 is hydrogen and R_7 is $\text{C}_1\text{-C}_{10}\text{alkyl}$, or R_6 and R_7 , together with the nitrogen atom to which they are attached, form the group



n_1 and n_2 are each preferably an integer from 2 to 35, in particular 2 to 20, for example 5 to 10.

A stabilizer mixture which is particularly preferred contains a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II in which R_3 and R_5 are a group of the formula III, R_4 is hexamethylene, R_6 and R_8 are hydrogen and R_7 is 1,1,3,3-tetramethylbutyl or R_6 and R_7 , together with the nitrogen atom to which they are attached, form a group



A stabilizer mixture which is of interest contains a) at least one polyalkylpiperidine of the formula I in which R_1 is hydrogen and R_2 is $\text{C}_1\text{-C}_4\text{alkylene}$, preferably ethylene, and b) at least one polyalkylpiperidine of the formula II.

Stabilizer mixtures consisting of a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II are preferred.

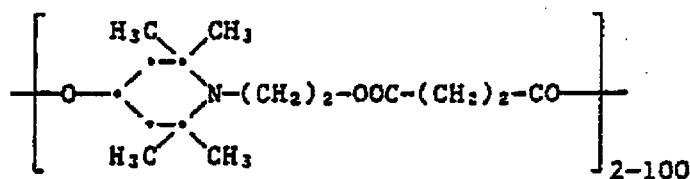
Stabilizer mixtures containing 1 to 3, preferably 1 to 2, compounds of the formula I and 1 to 3, preferably 1 to 2, compounds of the formula II are of interest.

Stabilizer systems containing one compound of the formula I and two compounds of the formula II are also of interest.

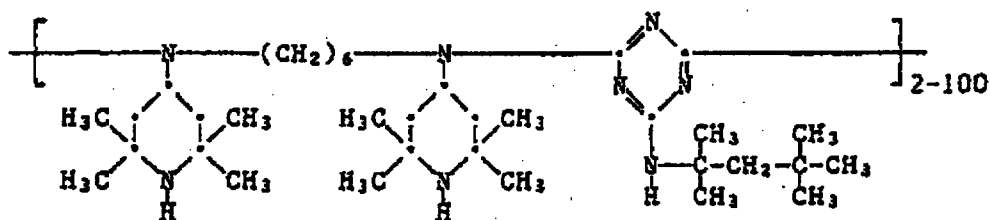
Stabilizer mixtures containing one compound of the formula I and one compound of the formula II are of particular interest.

The following are examples of compounds of the formulae I and II:

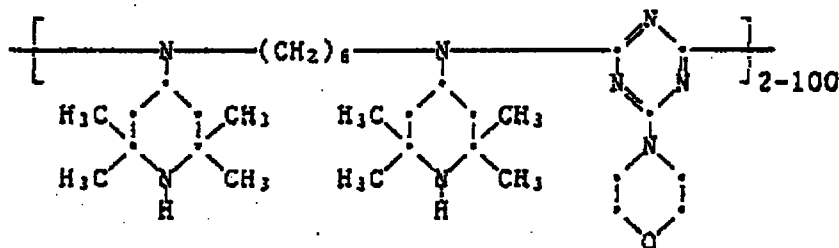
Compound 1:



Compound 2:



Compound 3:



Stabilizer mixtures containing a combination of compounds 1 and 2 or 1 and 3 or 1, 2 and 3 are particularly advantageous.

The stabilizer mixture according to the invention is suitable for stabilizing synthetic polymers against degradation induced by light. The following are examples of synthetic polymers:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, polymethylpent-1-ene, polyisoprene or polybutadiene, and polymers of cycloolefins, for example of cyclopentene or norbornene; and also polyethylene (which can, if appropriate, be crosslinked), for example high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear, low-density polyethylene (LLDPE).

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

3. Copolymers of monoolefins and diolefins with one another or with other vinyl monomers, for example, ethylene/propylene copolymers, linear, low-density polyethylene (LLDPE) and mixtures of the latter 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 or ethylene/acrylic acid copolymers and salts thereof (ionomers), and also terpolymers of ethylene with propylene and a diene, such as hexadiene, dicyclopentadiene or ethylidene norbornene; and also mixtures of such copolymers with one another and with the polymers mentioned under 1), for example polypropylene-ethylene/propylene copolymers, LDPE-ethylene/vinyl acetate copolymers, LDPE-ethylene/acrylic acid copolymers, LLDPE-ethylene/vinyl acetate copolymers and LLDPE-ethylene/acrylic acid copolymers.

3a. Hydrocarbon resins (for example C_5 - C_9), including hydrogenated modifications thereof (for example tackifier resins).

4. Polystyrene, poly-(p-methylstyrene) and poly-(α -methylstyrene).
5. Copolymers of styrene or α -methylstyrene with dienes or acrylic derivatives, such as, for example, styrene/butadiene, styrene/acrylonitrile, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate; mixtures of high impact strength composed of styrene copolymers and another polymer, for example a polyacrylate, a diene polymer or an ethylene/propylene/diene terpolymer; and block copolymers of styrene, for example styrene/butadiene/styrene, styrene/isoprene/styrene, styrene/ethylene-butylene/styrene or styrene/ethylene-propylene/styrene.
6. Graft copolymers of styrene or α -methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene/styrene or polybutadiene/acrylonitrile copolymers or 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 alkyl methacrylates on polybutadiene, styrene and acrylonitrile on ethylene/propylene/diene terpolymers, styrene and acrylonitrile on polyalkylacrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymers, and mixtures thereof with the copolymers mentioned under 5, such as are known, for example, as so-called ABS, MBS, ASA or AES polymers.
7. Polymers containing halogens, for example polychloroprene, chlorinated rubber, chlorinated or chlorosulfonated polyethylene, epichlorohydrin homopolymers and copolymers, especially polymers formed from halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride or polyvinylidene fluoride; and copolymers thereof, such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate.
8. Polymers derived from α,β -unsaturated acids and derivatives thereof, such as polyacrylates and polymethacrylates, polyacrylamides and polyacrylonitriles.

9. Copolymers from the monomers mentioned under 8) with one another or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/-alkoxyalkyl acrylate copolymers, acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.
10. Polymers derived from unsaturated alcohols and amines or acyl derivatives or acetals thereof, such as polyvinyl alcohol, polyvinyl acetate, stearate, benzoate or maleate, polyvinyl butyral, polyallyl phthalate or polyallylmelamine; and copolymers thereof with olefins mentioned in item 1.
11. Homopolymers and copolymers of cyclic ethers, such as polyalkylene glycols, polyethylene oxide or polypropylene oxide, or copolymers thereof with bisglycidyl ethers.
12. Polyacetals, such as polyoxymethylene and also polyoxymethylenes containing comonomers, for example ethylene oxide; and polyacetals which have been modified with thermoplastic polyurethanes, acrylates or MBS.
13. Polyphenylene oxides and sulfides and mixtures thereof with styrene polymers or polyamides.
14. Polyurethanes derived on the one hand from polyethers, polyesters and polybutadienes having terminal hydroxyl groups and, on the other hand, from aliphatic or aromatic polyisocyanates, and precursors thereof.
15. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, such as polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12 or 4/6, polyamide 11 or polyamide 12, aromatic polyamides obtained from m-xylene, a diamine and adipic acid; polyamides prepared from hexamethylenediamine and isophthalic and/or terephthalic acid and, if appropriate, an elastomer as modifier, for example poly-2,4,4-trimethylhexamethyleneterephthalamide or poly-m-phenyleneisophthalamide. Block copolymers of the polyamides mentioned above with polyolefins, olefin copolymers, ionomers or chemically linked or grafted elastomers;

or with polyethers, for example polyethylene glycol, polypropylene glycol or polytetramethylene glycol. Also polyamides or copolyamides which have been modified with EPDM or ABS; and polyamides which have been subjected to condensation during processing ("RIM polyamide systems").

16. Polyureas, polyimides, polyamide-imides and polybenzimidazoles.

17. Polyesters derived from dicarboxylic acids and dialcohols and/or hydroxycarboxylic acids or the corresponding lactones, such as polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylolcyclohexane terephthalate or polyhydroxybenzoates, and block polyether-esters derived from polyethers having hydroxyl end groups; and also polyesters which have been modified with polycarbonates or MBS.

18. Polycarbonates and polyester-carbonates.

19. Polysulfones, polyether-sulfones and polyether-ketones.

20. Crosslinked polymers derived on the one hand from aldehydes and, on the other hand, from phenols, urea or melamine, such as phenol/formaldehyde, urea/formaldehyde and melamine/formaldehyde resins.

21. Drying and non-drying alkyd resins.

22. Unsaturated polyester resins derived from copolyesters of saturated and unsaturated dicarboxylic acids with polyhydric alcohols, and also vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low combustability.

23. Crosslinkable acrylic resins derived from substituted acrylic acid esters, for example epoxyacrylates, urethane-acrylates or polyester-acrylates.

24. Alkyd resins, polyester resins and acrylate resins which have been crosslinked with melamine resins, urea resins, polyisocyanates or epoxide resins.

25. Crosslinked epoxide resins derived from polyepoxides, for example bisglycidyl ethers or cycloaliphatic diepoxides.

26. Polymer-homologous chemically modified derivatives of natural polymers, such as cellulose, natural rubber or gelatin. Examples are cellulose acetates, propionates and butyrates, and the cellulose ethers, such as methylcellulose.

27. Mixtures (polyblends) of the abovementioned polymers, 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 or PA/PPO.

28. Aqueous emulsions of synthetic rubbers, for example latices of carboxylated styrene/butadiene copolymers.

The invention also relates, therefore, to compositions containing a synthetic polymer and the stabilizer mixture according to the invention.

The synthetic polymer is in particular a polymer belonging to the groups indicated above. Polyolefins are preferred and polypropylene, polyethylene and copolymers thereof are particularly preferred.

The components a) and b) of the stabilizer system according to the invention can be added to the synthetic polymer to be stabilized on their own or mixed with one another. In this regard, the components a) and b) can be employed independently of one another in amounts from 0.01 to 4.99%, subject to the condition that the total amount of component a) plus component b) is 0.05 to 5%, preferably 0.05-2%, relative to the total weight of the material to be stabilized.

The stabilized polymer compositions of the invention can, in addition, also contain various conventional additives, 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-i-butylphenol, 2,6-di-cyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-di-octadecyl-4-methylphenol, 2,4,6-tri-cyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol and 2,6-dinonyl-4-methylphenol.

1.2. Alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butyl-hydroquinone, 2,5-di-tert-amyl-hydroquinone and 2,6-diphenyl-4-octadecyloxyphenol.

1.3. Hydroxylated thiodiphenyl ethers, for example 2,2'-thio-bis-(6-tert-butyl-4-methylphenol), 2,2'-thio-bis-(4-octylphenol), 4,4'-thio-bis-(6-tert-butyl-3-methylphenol) and 4,4'-thio-bis-(6-tert-butyl-2-methylphenol).

1.4. Alkylidene-bisphenols, for example 2,2'-methylene-bis-(6-tert-butyl-4-methylphenol), 2,2'-methylene-bis-(6-tert-butyl-4-ethylphenol), 2,2'-methylene-bis-[4-methyl-6-(α -methylcyclohexyl)-phenol], 2,2'-methylene-bis-(4-methyl-6-cyclohexylphenol), 2,2'-methylene-bis-(6-nonyl-4-methylphenol), 2,2'-methylene-bis-(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis-(4,6-di-tert-butylphenol), 2,2'-ethylidene-bis-(6-tert-butyl-4-isobutylphenol), 2,2'-methylene-bis-[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylene-bis-[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylene-bis-(2,6-di-tert-butylphenol), 4,4'-methylene-bis-(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-dodecylmercapto-butane, ethylene glycol bis-[3,3-bis-(3'-tert-butyl-4'-hydroxyphenyl)-butyrate], bis-(3-tert-butyl-4-hydroxy-5-methylphenyl)-dicyclopentadiene and bis-[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate.

1.5. Benzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis-(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, isooctyl 3,5-di-tert-butyl-4-

hydroxybenzylmercaptoacetate, bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)-dithiol terephthalate, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, the calcium salt of monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate and 1,3,5-tris-(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.6. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, 2,4-bis-(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-s-triazine and octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate.

1.7. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example, with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl) isocyanurate and N,N'-bis-(hydroxyethyl)-oxamide.

1.8. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)-propionic acid with monohydric or polyhydric alcohols, for example, with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl) isocyanurate and N,N'-bis-(hydroxyethyl)-oxamide.

1.9. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)-propionic acid with monohydric or polyhydric alcohols, for example, with methanol, octadecanol, 1,6-hexanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris-(hydroxyethyl) isocyanurate and N,N'-bis-(hydroxyethyl)-oxamide.

1.10. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid, for example N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexamethylenediamine, N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-trimethylenediamine and N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)-benzotriazole, for example the 5'-methyl, 3',5'-di-tert-butyl, 5'-tert-butyl, 5'-(1,1,3,3-tetramethylbutyl), 5-chloro-3',5'-di-tert-butyl, 5-chloro-3'-tert-butyl-5'-methyl, 3'-sec-butyl-5'-tert-butyl, 4'-octoxy, 3',5'-di-tert-amyl or 3',5'-bis-(α,α -dimethylbenzyl) derivative.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octoxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy or 2'-hydroxy-4,4'-dimethoxy derivative.

2.3. Esters of optionally substituted benzoic acids, for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis-(4-tert-butylbenzoyl)-resorcinol, benzoyl-resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate and hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl or isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl or 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'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)-phenol], such as the 1:1 or 1:2 complex, if appropriate containing additional ligands, such as n-butylamine, triethanolamine or N-cyclohexyl-diethanolamine, nickel dibutyldithiocarbamate, nickel salts of monoalkyl esters of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, such as the methyl or ethyl ester, nickel complexes of ketoximes such as of 2-hydroxy-4-methyl-phenyl-undecyl ketone oxime and nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, if appropriate containing additional ligands.

2.6. Sterically hindered amines, for example bis-(2,2,6,6-tetramethylpiperidyl) sebacate, 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 condensation product formed from 1-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensation product formed from N,N'-bis-(2,2,6,6-tetramethyl-

4-piperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-s-triazine, tris-(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate, tetrakis-(2,2,6,6-tetramethyl-4-piperidyl) 1,2,3,4-butane-tetraoate and 1,1'-(1,2-ethanediyl)-bis-(3,3,5,5-tetramethyl-piperazinone).

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butyloxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butyl-oxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis-(3-dimethylamino-propyl)-oxamide, 2-ethoxy-5-tert-butyl-2'-ethyloxanilide and a mixture thereof with 2-ethoxy-2'-ethyl-5,4'-di-tert-butyloxanilide and mixtures of o- and p-methoxy-disubstituted and o- and p-ethoxy-disubstituted oxanilides.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloylhydrazine, N,N'-bis-(salicyloyl)-hydrazine, N,N'-bis-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazine, 3-salicyloylamino-1,2,4-triazole and bis-(benzylidene)-oxalic acid 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, tristearyl sorbitol triphosphite, tetrakis-(2,4-di-tert-butylphenyl) 4,4'-biphenylene-diphosphonite and 3,9-bis-(2,4-di-tert-butylphenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane.

5. Compounds which destroy peroxides, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole, the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide and pentaerythritol tetrakis-(β -dodecylmercapto)-propionate.

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

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

8. Nucleating agents, for example 4-tert-butyl-benzoic acid, adipic acid and 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 and graphite.

10. Other additives, for example plasticizers, lubricants, emulsifiers, pigments, fluorescent whitening agents, fire-retarding agents, anti-static agents and blowing agents.

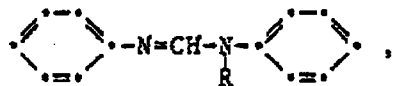
The ratio by weight of stabilizer mixture according to the invention to additional additives can be, for example, 1:0.5 to 1:5.

The incorporation of the stabilizer mixture according to the invention or of the individual components into the synthetic polymer is effected by known methods, for example before or during shaping or by applying the compounds, in solution or in dispersion, to the synthetic polymer, with or without subsequent removal of the solvent by evaporation. The individual components of the stabilizer system according to the invention can also be added to the materials to be stabilized in the form of a master-batch containing these components in a concentration of, for example, 2.5 to 25% by weight.

The mixtures according to the invention and their components can also be added before or during polymerization or before crosslinking.

The materials thus stabilized can be used in a very wide variety of shapes, for example as sheeting, fibres, tapes, moulding materials or profiles or as binders for lacquers, adhesives or putties.

A preferred embodiment of the invention is constituted by compositions containing the stabilizer system according to the invention and a synthetic polymer, wherein the compositions do not contain sterically hindered formamidines, in particular formamidines containing the structural unit



in which R is alkyl or phenyl.

The invention also relates to the use of a stabilizer system containing a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II, for stabilizing synthetic polymers against degradation induced by light.

The following examples illustrate the invention further. All percentages are by weight, unless stated otherwise.

Example 1: Light stabilizing action in polypropylene fibres

1,000 parts of unstabilized polypropylene powder (melt flow index at 230°C and a testing force of 2.16 kp: approx. 15 g/10 minutes) are mixed in a high-speed mixer with 0.5 part of calcium monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, 0.5 part of tris-(2,4-di-tert-butylphenyl) phosphite, 2.5 parts of titanium dioxide, 1 part of calcium stearate and 3 parts of the light stabilizer listed in Table 1, and are then extruded and granulated at 220°C in an extruder. The resulting granules are spun in a laboratory melt-spinning machine at a maximum temperature of 270°C at a rate of 10 m/s to give a multifilament of 12.1 decitex. This filament is stretched and twisted by means of a draw-twister. The stretching ratio is 1:3.2, so that multifilaments of 3.9 decitex are finally obtained. These multifilaments are mounted on white cardboard, subjected to treatment at 120°C in an oven for 20 minutes (simulation of "tentering") and are then exposed to light in a Xenotest 1200.

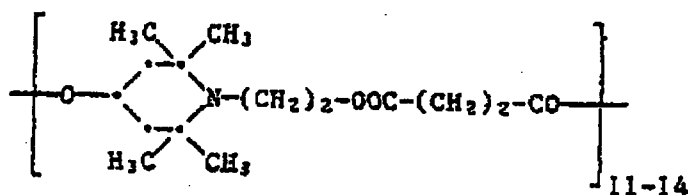
The exposure time required to reach a 50% loss of ultimate tensile strength is taken as a measure of the stabilizing action.

The results are summarized in Table 1.

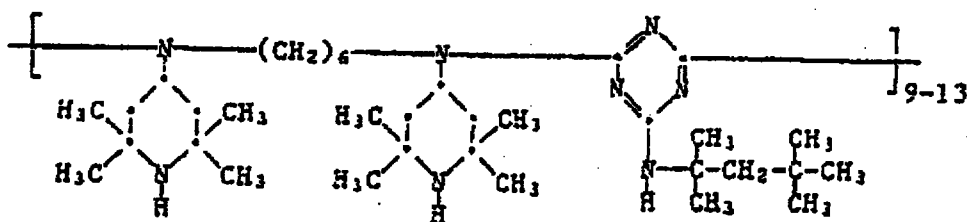
Table 1: Light stabilizing action in polypropylene multifilament (3.9 decitex)

Light stabilizer	Hours in Xenotest 1200 until 50% of residual ultimate tensile strength is reached
None	450
0.3% of compound 1	3,200
0.3% of compound 2	3,600
0.15% of compound 1 and 0.15% of compound 2	4,500

Compound 1:



Compound 2:



Example 2: Light stabilizing action in high-pressure polyethylene film

1,000 parts of polyethylene (density 0.918 g/cm³; melt flow index at 190°C and a testing force of 2.16 kp: approx. 2 g/10 minutes) are mixed with 0.3 part of n-octadecyl-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-propionate and 1.5 parts of the light stabilizer listed in Table 2 in a high-speed mixer, and the mixture is then extruded and granulated at 200°C. Tubular films 200 μm thick are blown from the granules thus obtained (blow head temperature 200°C; blow-up ratio 1:1.8). Sections

measuring 55 x 9 mm² are punched out of these films and exposed to light in an exposure apparatus (SAIREM-SEPAP 12.24). The test specimens are taken out of the exposure apparatus at regular intervals and their carbonyl content is checked in an IR spectrophotometer. The increase in the carbonyl extinction during exposure is a measure of the photo-oxidative degradation of the polymer (see L. Blaban et al., J. Polymer Sci. Part C, 22, 1059-1071 (1969); J.F. Heacock, J. Polymer Sci. Part A-1, 22, 2921-2934 (1969); D.J. Carlsson and D.M. Wiles, Macromolecules 2, 587-606 (1969)) and, according to experience, is associated with a falling off in the mechanical properties of the polymer.

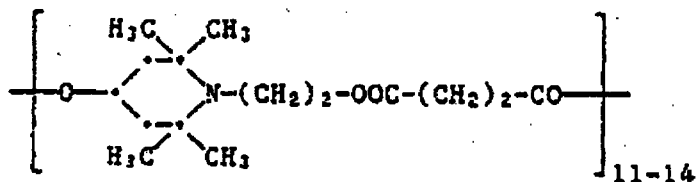
The time required to reach a carbonyl extinction of 0.100 is taken as a measure of the stabilizing action.

The results are summarized in Table 2.

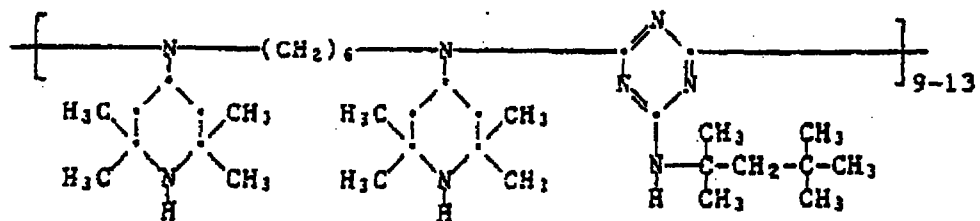
Table 2: Light stabilizing action in high-pressure polyethylene films

Light stabilizer	Hours in SAIREM-SEPAP 12.24 until a carbonyl extinction of 0.1 is reached
None	120
0.15% of compound 1	1,640
0.15% of compound 2	1,960
0.075% of compound 1 and 0.075% of compound 2	2,180

Compound 1:



Compound 2:

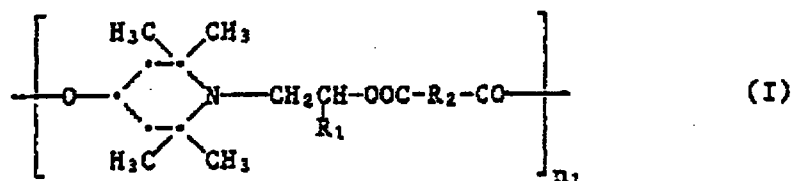


Examples 1 and 2 show clearly that the mixture of specific high-molecular polyalkylpiperidines displays a pronounced synergism in providing protection against the degradation, induced by light, of organic material.

Patent claims

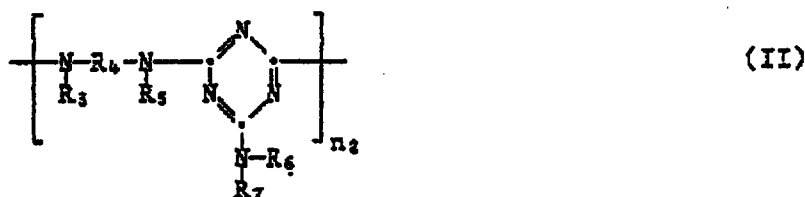
1. A stabilizer mixture containing

a) at least one polyalkylpiperidine of the formula I



in which R_1 is hydrogen or methyl, R_2 is a direct bond or C_1 - C_{10} alkylene and n_1 is an integer from 2 to 100, and

b) at least one polyalkylpiperidine of the formula II



in which R_3 , R_5 and R_6 independently of one another are hydrogen, C_1 - C_4 alkyl, phenyl, phenyl which is substituted by -OH and/or C_4 - C_8 alkyl, benzyl or benzyl which is substituted by -OH and/or C_4 - C_8 alkyl or are a group of the formula III



in which R_8 is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 alkyl which is substituted by -OH, or is benzyl, allyl, acetyl or crotonyl, subject to the condition that the C atom attached to the nitrogen atom of the piperidyl group is a primary carbon atom, R_4 is C_2 - C_8 alkylene and R_7 is hydrogen, C_1 - C_{10} alkyl, phenyl, phenyl which is substituted by -OH and/or C_4 - C_8 alkyl, benzyl or benzyl which is substituted by -OH and/or C_4 - C_8 alkyl, or is a group of the formula III, or the radicals R_6 and R_7 , together with the nitrogen atom to which they are attached, form a 6-membered heterocyclic



ring, n_2 is an integer from 2 to 100, and at least one of the radicals R_3 , R_5 , R_6 and R_7 is a group of the formula III.

2. A stabilizer mixture according to claim 1, in which R_3 and R_5 are a group of the formula III.

3. A stabilizer mixture according to claim 1, in which R_6 is hydrogen or methyl.

4. A stabilizer mixture according to claim 1, in which R_6 is hydrogen and R_7 is C_1 - C_{10} alkyl, or R_6 and R_7 , together with the nitrogen atom to which they are attached, form the group



5. A stabilizer mixture according to claim 4, in which the radicals R_6 and R_7 , together with the nitrogen atom to which they are attached, form the group



6. A stabilizer mixture according to claim 1, in which n_1 and n_2 independently of one another are integers from 2 to 35.

7. A stabilizer mixture according to claim 1, in which R_3 and R_5 are a group of the formula III, R_4 is hexamethylene, R_6 and R_8 are hydrogen and R_7 is 1,1,3,3-tetramethylbutyl, or R_6 and R_7 , together with the nitrogen atom to which they are attached, form a group



8. A stabilizer mixture according to claim 1, in which R_2 is C_1 - C_4 alkylene and R_1 is hydrogen.

9. A stabilizer mixture according to claim 8, in which R_2 is ethylene.

10. A stabilizer mixture according to claim 1, consisting of a) at least one polyalkylpiperidine of the formula I and b) at least one

polyalkylpiperidine of the formula II.

11. A composition containing a synthetic polymer and a stabilizer mixture according to claim 1.

12. A composition according to claim 11, wherein the synthetic polymer is a polyolefin.

13. Use of a stabilizer mixture according to claim 1 for stabilizing synthetic polymers against degradation induced by light.

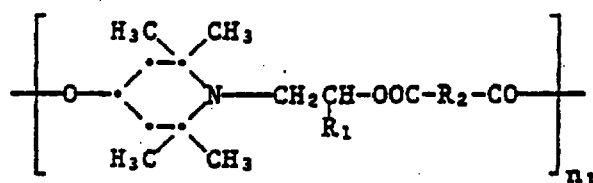


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Claims

1. A stabilizer mixture containing
 - a) at least one polyalkyl piperidine of the formula I



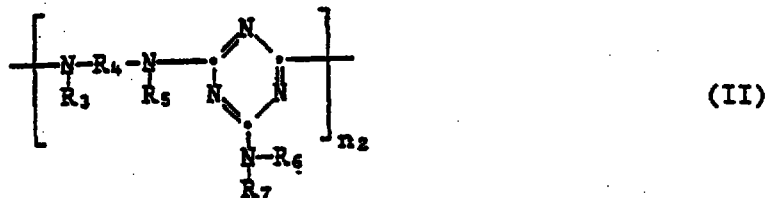
(I)



* C L N S *

in which R₁ is hydrogen or methyl, R₂ is a direct bond or C₁-C₁₀alkylene and n₁ is an integer from 2 to 100, and

b) at least one polyalkylpiperidine of the formula II



in which R₃, R₅ and R₆ independently of one another are hydrogen, C₁-C₄alkyl, phenyl, phenyl which is substituted by -OH and/or C₄-C₈alkyl, benzyl or benzyl which is substituted by -OH and/or C₄-C₈alkyl or are a group of the formula III



in which R₈ is hydrogen, C₁-C₄alkyl, C₁-C₄alkyl which is substituted by -OH, or is benzyl, allyl, acetyl or crotonyl, subject to the condition that the C atom attached to the nitrogen atom of the piperidyl group is a primary carbon atom, R₄ is C₂-C₈alkylene and R₇ is hydrogen, C₁-C₁₀alkyl, phenyl, phenyl which is substituted by -OH and/or C₄-C₈alkyl, benzyl or benzyl which is substituted by -OH and/or C₄-C₈alkyl, or is a group of the formula III, or the radicals R₆ and R₇, together with the nitrogen atom to which they are attached, form a 6-membered heterocyclic ring, n₂ is an integer from 2 to 100, and at least one of the radicals R₃, R₅, R₆ and R₇, is a group of the formula III.

2. A stabilizer mixture according to claim 1, in which R₃ and R₅ are a group of the formula III.
3. A stabilizer mixture according to claim 1, in which R₆ is hydrogen or methyl.
4. A stabilizer mixture according to claim 1, in which R₆ is hydrogen and R₇ is C₁-C₁₀alkyl, or R₆ and R₇, together with the nitrogen atom to which they are attached, form the group



5. A stabilizer mixture according to claim 4, in which the radicals R₆ and R₇, together with the nitrogen atom to which they are attached, form the group



6. A stabilizer mixture according to claim 1, in which n₁ and n₂ independently of one another are integers from 2 to 35.
7. A stabilizer mixture according to claim 1, in which R₃ and R₅ are a group of the formula III, R₄ is hexamethylene, and R₆ are hydrogen and R₇ is 1,1,3,3-tetramethylbutyl, or R₆ and R₇, together with the nitrogen atom to which they are attached, form a group



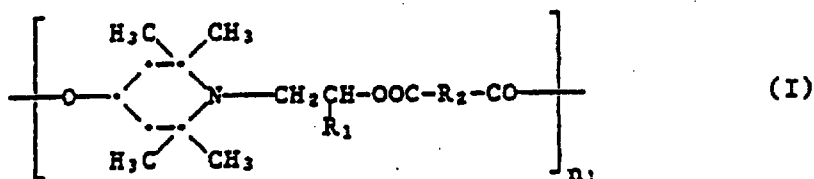
8. A stabilizer mixture according to claim 1, in which R_2 is C_1 - C_4 alkylene and R_1 is hydrogen.
9. A stabilizer mixture according to claim 8, in which R_2 is ethylene.
10. A stabilizer mixture according to claim 1, consisting of a) at least one polyalkylpiperidine of the formula I and b) at least one polyalkylpiperidine of the formula II.
11. A composition containing a synthetic polymer and a stabilizer mixture according to claim 1.
12. A composition according to claim 11, wherein the synthetic polymer is a polyolefin.
13. Use of a stabilizer mixture according to claim 1 for stabilizing synthetic polymers against degradation induced by light.

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Revendications

1. Mélange stabilisant qui contient :

a) au moins une polyalkyl-pipéridine répondant à la formule I:

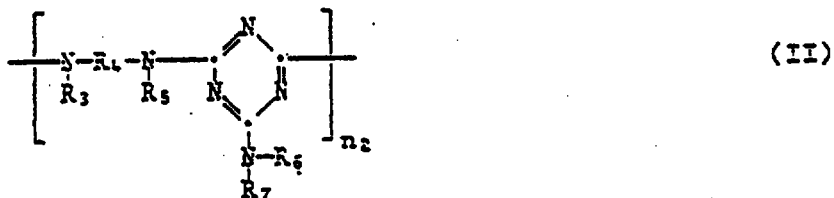


dans laquelle

R_1 représente l'hydrogène ou un méthyle,

R_2 représente une liaison directe ou un alkylène en C_1 - C_{10} et

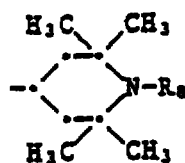
n_1 représente un nombre entier de 2 à 100, et b) au moins une polyalkyl-pipéridine répondant à la formule II:



dans laquelle

R_3 , R_5 et R_6 représentent chacun, indépendamment les uns des autres, l'hydrogène, un alkyle en C_1 - C_4 , un phényle, un phényle porteur d'un -OH et/ou d'un alkyle en C_4 - C_8 , un benzyle, un benzyle porteur d'un -OH et/ou d'un alkyle en C_4 - C_8 ou un radical répondant à la formule III:





(III)

dans laquelle R8 représente l'hydrogène, un alkyle en C₁-C₄, un alkyle en C₁-C₄ porteur d'un -OH, d'un benzyle, un allyle, un acétyle ou un crotonyle, avec la condition que l'atome de carbone lié à l'atome d'azote du radical pipéridyle soit un atome de carbone primaire,

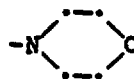
R₄ représente un alkylène en C₂-C₈,

R₇ représente l'hydrogène, un alkyle en C₁-C₁₀, un phényle, un phényle porteur d'un -OH et/ou d'un alkyle en C₄-C₈, un benzyle, un benzyle porteur d'un -OH et/ou d'un alkyle en C₄-C₈, ou un radical de formule III, ou

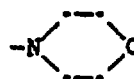
R₆ et R₇ forment ensemble, et avec l'atome d'azote auquel ils sont liés, un hétérocycle à six maillons, et

n₂ représente un nombre entier de 2 à 100, au moins un des symboles R₃, R₅, R₆ et R₇ représentant un radical de formule III.

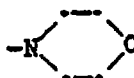
2. Mélange stabilisant selon la revendication 1 dans lequel R₃ et R₅ représentent chacun un radical de formule III.
3. Mélange stabilisant selon la revendication 1 dans lequel R₈ représente l'hydrogène ou un méthyle.
4. Mélange stabilisant selon la revendication 1 dans lequel R₆ représente l'hydrogène et R₇ un alkyle en C₁-C₁₀, ou R₆ et R₇ forment ensemble, et avec l'atome d'azote auquel ils sont liés, un radical



5. Mélange stabilisant selon la revendication 4 dans lequel R₆ et R₇ forment ensemble et avec l'atome d'azote auquel ils sont liés, un radical



6. Mélange stabilisant selon la revendication 1 dans lequel n₁ et n₂ représentent chacun, indépendamment l'un de l'autre, un nombre entier de 2 à 35.
7. Mélange stabilisant selon la revendication 1 dans lequel R₃ et R₅ représentent chacun un radical de formule III, R₄ représente un radical hexaméthylène, R₆ et R₈ représentent chacun l'hydrogène et R₇ représente un radical tétraméthyl-1,1,3,3 butyle, ou R₆ et R₇ forment ensemble, et avec l'atome d'azote auquel ils sont liés, un radical



8. Mélange stabilisant selon la revendication 1 dans lequel R₂ représente un alkylène en C₁-C₄ et R₁ l'hydrogène.
9. Mélange stabilisant selon la revendication 8 dans lequel R₂ représente un radical éthylène.



10. Mélange stabilisant selon la revendication 1 qui est constitué a) d'au moins une polyalkyl-pipéridine de formule I et b) d'au moins une polyalkyl-pipéridine de formule II.
11. Composition contenant un polymère synthétique et un mélange stabilisant selon la revendication 1.
12. Composition selon la revendication 11 caractérisée en ce que le polymère synthétique est une polyoléfine.
13. Application d'un mélange stabilisant selon la revendication 1 à la stabilisation de polymères synthétiques contre la dégradation induite par la lumière.

