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(54) **STABILIZED BIODIESEL FUEL
COMPOSITIONS**

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(57) **ABSTRACT**

Disclosed are stabilized biodiesel fuel compositions, which compositions comprise a biodiesel fuel, for example the methyl esters of the fatty acids of rapeseed or soy oil, and one or more additives selected from the group consisting of the 3-arylbenzofuranones and the hindered amine light stabilizers, and optionally, one or more hindered phenolic antioxidants.

STABILIZED BIODIESEL FUEL COMPOSITIONS

[0001] This application claims benefit under 35 USC 119(e) of U.S. provisional application No. 60/756,090, filed Jan. 4, 2006, the contents of which are hereby incorporated by reference.

[0002] The present invention is aimed at biodiesel fuel (or bio-fuel) compositions, stabilized against the deleterious effects of heat, light and oxygen by an effective amount of a stabilizer selected from the group consisting of the 3-aryl-benzofuranone stabilizers and the sterically hindered amine light stabilizers, or an effective amount of a stabilizer selected from the group consisting of the 3-arylbenzofuranone stabilizers and the sterically hindered amine light stabilizers in combination with a stabilizer selected from the group consisting of the hindered phenolic antioxidants.

BACKGROUND

[0003] WO2004055141 teaches the stabilization of fats, oils and food. The stabilizers are selected from the group consisting of the 3-arylbenzofuranones, long chain N,N-dialkylhydroxylamines, substituted hydroxylamines, nitrones and amine oxides.

[0004] U.S. Pat. No. 6,548,580, to Rohde, et al., teaches ethylene homo- and copolymers stabilized by sterically hindered amines or by N-hydroxy or N-oxyl derivatives to produce articles for the storage and transport of biodiesel fuel.

[0005] JP2004059720 discloses polyoxymethylene resin containing a hindered amine light stabilizer that is used in a part in direct contact with a bio-diesel fuel.

[0006] EP1170296 teaches a process for the preparation for 3-aryl-benzofuranones. Fuel additives are disclosed therein.

[0007] EP1486555, EP1484387 and EP1484388 disclose a low corrosive fuel composition for use in a blue flame burner or an optimized yellow flame burner of a boiler.

[0008] Biodiesel fuel is of increasing importance as a renewable fuel source. It may for example be employed as a fuel itself, or may be used in combination with diesel fuel.

SUMMARY

[0009] Disclosed are biodiesel fuel compositions stabilized against the deleterious effects of heat, light and oxygen, which compositions comprise

[0010] a biodiesel fuel and

[0011] an effective stabilizing amount of

[0012] one or more additives selected from the group consisting of the 3-arylbenzofuranone stabilizers and the hindered amine light stabilizers and

[0013] optionally, one or more additives selected from the group consisting of the hindered phenolic antioxidants.

[0014] Also disclosed is a process for the stabilization of a biodiesel fuel against the deleterious effects of heat, light and oxygen, which process comprises

[0015] incorporating into a biodiesel fuel

[0016] an effective stabilizing amount of

[0017] one or more additives selected from the group consisting of the 3-arylbenzofuranone stabilizers and the hindered amine light stabilizers and

[0018] optionally, one or more additives selected from the group consisting of the hindered phenolic antioxidants.

DETAILED DISCLOSURE

[0019] Biodiesel fuels are a renewable resource and are of increasing importance.

[0020] Biodiesel fuels typically comprise lower alkyl fatty acid esters, prepared for example by transesterifying triglycerides with lower alcohols, e.g. methanol or ethanol. A typical biodiesel fuel is the fatty acid methyl ester of rapeseed oil or of soy oil. Sources for biodiesel fuel include vegetable and animal sources. Recycled cooking oil may be a source of biodiesel fuel.

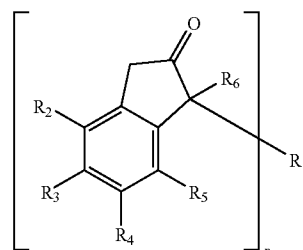
[0021] Biodiesel fuel and its preparation is taught for example in U.S. Pat. Nos. 5,578,090, 5,713,965, 5,891,203, 6,015,440, 6,174,501 and 6,398,707, the contents of which are hereby incorporated by reference.

[0022] Biodiesel fuel of the present invention for example comprises lower alkyl esters of a mixture of saturated and unsaturated straight chain fatty acids of from 12 to 22 carbon atoms, derived from vegetable or oleaginous seeds. The term "lower alkyl ester" means C₁-C₅ esters, in particular methyl and ethyl esters. The mixture of methyl esters of the saturated, monounsaturated and polyunsaturated C₁₆-C₂₂ fatty acids are what is typically known as "biodiesel" or "rapeseed methyl ester".

[0023] Biodiesel fuel according to the present invention is 100% lower alkyl fatty acid ester, or is a combination of a lower alkyl fatty acid ester with diesel fuel. The present biodiesel fuel is for example between about 5 and about 95 weight percent fatty acid ester and between about 95 and about 5 weight percent diesel fuel. For example, the present biodiesel fuel is between about 10 and about 90 weight percent fatty acid ester and between about 90 and about 10 weight percent diesel fuel. For instance, the present biodiesel fuel is between about 25 and about 75 weight percent fatty acid ester and between about 75 and about 25 weight percent diesel fuel.

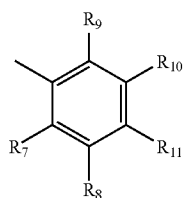
[0024] The 3-arylbenzofuranones antioxidants of the present invention are for example those disclosed in U.S. Pat. Nos. 4,325,863; U.S. Pat. No. 4,388,244; U.S. Pat. No. 5,175,312; U.S. Pat. No. 5,252,643; U.S. Pat. No. 5,216,052; U.S. Pat. No. 5,369,159; U.S. Pat. No. 5,488,117; U.S. Pat. No. 5,356,966; U.S. Pat. No. 5,367,008; U.S. Pat. No. 5,428,162; U.S. Pat. No. 5,428,177; and U.S. Pat. No. 5,516,920; which are hereby incorporated by reference.

[0025] Particularly suitable 3-arylbenzofuranones in the present invention are compounds of the formula I



in which, if n is 1,

[0026] R_1 is unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_1 - C_4 alkylthio-, hydroxyl-, halo-, amino-, C_1 - C_4 alkylamino-, phenylamino- or di(C_1 - C_4 alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizynyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizynyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinoxalinyl, cinnolinyl, pteridinyl, carbazolyl, β -carboline, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R_1 is a radical of the formula II



(II)

and

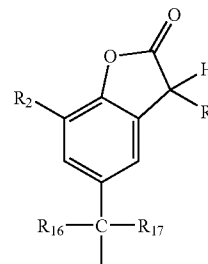
[0027] if n is 2,

[0028] R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxy-substituted phenylene or naphthylene; or is $-R_{12}-X-R_{13}-$,

[0029] R_2 , R_3 , R_4 and R_5 independently of one another are hydrogen, chlorine, hydroxyl, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_{25} alkanoyloxy, C_1 - C_{25} alkanoylamino, C_3 - C_{25} alkenoyloxy, C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or



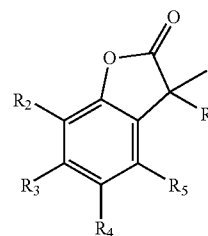
; C_6 - C_9 cycloalkylcarbonyloxy, benzoyloxy or C_1 - C_{12} alkyl-substituted benzoyloxy; or else the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5 , together with the carbon atoms to which they are attached, form a benzo ring, R_4 is additionally $-(CH_2)_p-COR_{15}$ or $-(CH_2)_qOH$ or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III



(III)

in which R_1 is defined as indicated above for $n=1$,

[0030] R_6 is hydrogen or a radical of the formula IV



(IV)

where R_4 is not a radical of the formula III and R_1 is defined as indicated above for $n=1$,

[0031] R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, halogen, hydroxyl, C_1 - C_{25} alkyl, C_2 - C_{25} alkyl interrupted by oxygen, sulfur or



; C_1 - C_{25} alkoxy, C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or



C_1 - C_{25} alkylthio, C_3 - C_{25} alkenyl, C_3 - C_{25} alkenylloxy, C_3 - C_{25} alkynyl, C_3 - C_{25} alkynylloxy, C_7 - C_9 phenylalkyl, C_7 - C_9 phenylalkoxy, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted phenoxy; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy; C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_{25} alkanoyl, C_3 - C_{25} alkanoyl interrupted by oxygen, sulfur or



C₁-C₂₅alkanoyloxy, C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or



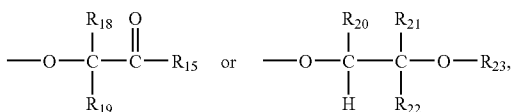
C₁-C₂₅alkanoylamino, C₃-C₂₅alkenoyl, C₃-C₂₅alkenoyl interrupted by oxygen, sulfur or



C₃-C₂₅alkenoyloxy, C₃-C₂₅alkenoyloxy interrupted by oxygen, sulfur or



C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy;



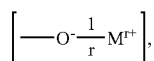
or else, in formula II, the radicals R₇ and

[0032] R₈ or the radicals R₈ and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,

[0033] R₁₂ and R₁₃ independently of one another are unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

[0034] R₁₄ is hydrogen or C₁-C₈alkyl,

[0035] R₁₅ is hydroxyl,



C₁-C₁₈alkoxy or



[0036] R₁₆ and R₁₇ independently of one another are hydrogen, CF₃, C₁-C₁₂alkyl or phenyl, or R₁₆ and R₁₇, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

[0037] R₁₈ and R₁₉ independently of one another are hydrogen, C₁-C₄alkyl or phenyl,

[0038] R₂₀ is hydrogen or C₁-C₄alkyl,

[0039] R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl, C₂-C₂₅alkyl interrupted by oxygen, sulfur or



C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl; C₇-C₂₅phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and interrupted by oxygen, sulfur or



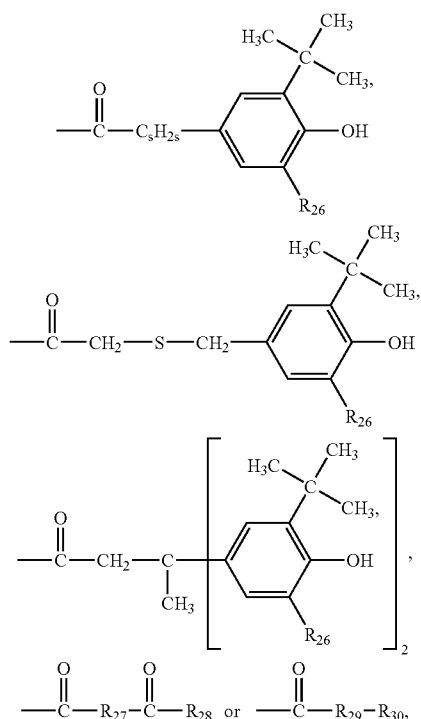
or else the radicals R₂₀ and R₂₁, together with the carbon atoms to which they are attached, form a C₅-C₁₂cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

[0040] R₂₂ is hydrogen or C₁-C₄alkyl,

[0041] R₂₃ is hydrogen, C₁-C₂₅alkanoyl, C₃-C₂₅alkenoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or



C₂-C₂₅alkanoyl substituted by a di(C₁-C₆alkyl)phosphonate group; C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl;



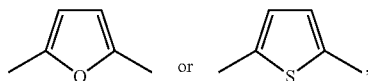
[0042] R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₈alkyl,

[0043] R₂₆ is hydrogen or C₁-C₈alkyl,

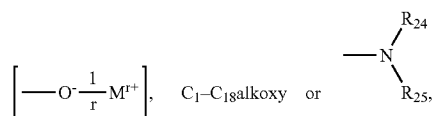
[0044] R₂₇ is a direct bond, C₁-C₁₈alkylene, C₂-C₁₈alkylene interrupted by oxygen, sulfur or



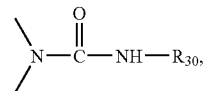
C₂-C₁₈alkenylene, C₂-C₂₀alkylidene, C₇-C₂₀phenylalkylidene, C₅-C₈cycloalkylene, C₇-C₈bicycloalkylene, unsubstituted or C₁-C₄alkyl-substituted phenylene, or



[0045] R₂₈ is hydroxyl,



[0046] R₂₉ is oxygen, —NH— or



[0047] R₃₀ is C₁-C₁₈alkyl or phenyl,

[0048] R₃₁ is hydrogen or C₁-C₁₈alkyl,

[0049] M is an r-valent metal cation,

[0050] X is a direct bond, oxygen, sulfur or —NR₃₁—,

[0051] n is 1 or 2,

[0052] p is 0, 1 or 2,

[0053] q is 1, 2, 3, 4, 5 or 6,

[0054] r is 1, 2 or 3, and

[0055] s is 0, 1 or 2.

[0056] Unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolizyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizyl, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl is, for example, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-phenoxathiinyl, 2,7-phenoxathiinyl, 2-pyrrolyl, 3-pyrrolyl, 5-methyl-3-pyrrolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 2-methyl-4-imidazolyl, 2-ethyl-4-imidazolyl, 2-ethyl-5-imidazolyl, 3-pyrazolyl, 1-methyl-3-pyrazolyl, 1-propyl-4-pyrazolyl, 2-pyrazinyl, 5,6-dimethyl-2-pyrazinyl, 2-indolizyl, 2-methyl-3-isoindolyl, 2-methyl-1-isoindolyl, 1-methyl-2-indolyl, 1-methyl-3-indolyl, 1,5-dimethyl-2-indolyl, 1-methyl-3-indazolyl, 2,7-dimethyl-8-purinyl, 2-methoxy-7-methyl-8-purinyl, 2-quinolizyl, 3-isoquinolyl, 6-isoquinolyl, 7-isoquinolyl, isoquinolyl, 3-methoxy-6-isoquinolyl, 2-quinolyl, 6-quinolyl, 7-quinolyl, 2-methoxy-3-quinolyl, 2-methoxy-6-quinolyl, 6-phthalazinyl, 7-phthalazinyl, 1-methoxy-6-phthalazinyl, 1,4-dimethoxy-6-phthalazinyl, 1,8-naphthyridin-2-yl, 2-quinoxalinyl, 6-quinoxalinyl, 2,3-dimethyl-6-quinoxalinyl, 2,3-dimethoxy-6-quinoxalinyl, 2-quinazolinyl, 7-quinazolinyl, 2-dimethylamino-6-

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[0057] Particular preference is given to unsubstituted or C_1 - C_4 alkyl-, C_1 - C_4 alkoxy-, C_1 - C_4 alkylthio-, hydroxyl-, phenylamino- or di(C_1 - C_4 alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, isoindolyl, indolyl, phenothiazinyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl such as, for example, 1-naphthyl, 2-naphthyl, 1-phenylamino-4-naphthyl, 1-methylnaphthyl, 2-methylnaphthyl, 1-methoxy-2-naphthyl, 2-methoxy-1-naphthyl, 1-dimethylamino-2-naphthyl, 1,2-dimethyl-4-naphthyl, 1,2-dimethyl-6-naphthyl, 1,2-dimethyl-7-naphthyl, 1,3-dimethyl-6-naphthyl, 1,4-dimethyl-6-naphthyl, 1,5-dimethyl-2-naphthyl, 1,6-dimethyl-2-naphthyl, 1-hydroxy-2-naphthyl, 2-hydroxy-1-naphthyl, 1,4-dihydroxy-2-naphthyl, 7-phenanthryl, 1-anthryl, 2-anthryl, 9-anthryl, 3-benzo[b]thienyl, 5-benzo[b]thienyl, 2-benzo[b]thienyl, 4-dibenzofuryl, 4,7-dibenzofuryl, 4-methyl-7-dibenzofuryl, 2-xanthenyl, 8-methyl-2-xanthenyl, 3-xanthenyl, 2-pyrrolyl, 3-pyrrolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl.

[0058] Halogen (halo) is, for example, chlorine, bromine or iodine. Preference is given to chlorine.

[0059] Alkanoyl having up to 25 carbon atoms is a branched or unbranched radical such as, for example, formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, eicosanoyl or docosanoyl. Preference is given to alkanoyl having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to acetyl.

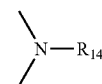
[0060] C_2 - C_{25} alkanoyl substituted by a di(C_1 - C_6 alkyl)phosphonate group is, for example, $(CH_3CH_2O)_2POCH_2CO-$, $(CH_3O)_2POCH_2CO-$, $(CH_3CH_2CH_2CH_2O)_2POCH_2CO-$, $(CH_3CH_2O)_2POCH_2CH_2CO-$, $(CH_3O)_2POCH_2CH_2CO-$, $(CH_3CH_2CH_2CH_2CH_2O)_2POCH_2CH_2CO-$, $(CH_3CH_2O)_2PO(CH_2)_4CO-$, $(CH_3CH_2O)_2PO(CH_2)_8CO-$ or $(CH_3CH_2O)_2PO(CH_2)_{17}CO-$.

[0061] Alkanoyloxy having up to 25 carbon atoms is a branched or unbranched radical such as, for example, formyloxy, acetoxo, propionyloxy, butanoyloxy, pentanoyloxy, hexanoyloxy, hepta-noyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octa-decanoyloxy, eicosanoyloxy or docosanoyloxy. Preference is given to alkanoyloxy hav-

ing 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms. Particular preference is given to acetoxo.

[0062] Alkenoyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propenoyl, 2-butenoyl, 3-butenoyl, isobutenoyl, n-2,4-pentadienoyl, 3-methyl-2-butenoyl, n-2-octenoyl, n-2-dodecenoyl, iso-dodecenoyl, oleoyl, n-2-octadecenoyl or n-4-octadecenoyl. Preference is given to alkenoyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

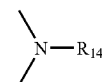
[0063] C_3 - C_{25} alkenoyl interrupted by oxygen, sulfur or



is, for example, $CH_3OCH_2CH_2CH=CHCO-$ or $CH_3OCH_2CH_2OCH=CHCO-$.

[0064] Alkenoyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propenoyloxy, 2-butenoyloxy, 3-butenoyloxy, isobutenoyloxy, n-2,4-pentadienoyloxy, 3-methyl-2-butenoyloxy, n-2-octenoyloxy, n-2-dodecenoyloxy, iso-dodecenoyloxy, oleoyloxy, n-2-octadecenoyloxy or n-4-octadecenoyloxy. Preference is given to alkenoyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

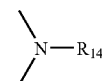
[0065] C_3 - C_{25} alkenoyloxy interrupted by oxygen, sulfur or



is, for example,

[0066] $CH_3OCH_2CH_2CH=CHCOO-$ or $CH_3OCH_2CH_2OCH=CHCOO-$.

[0067] C_3 - C_{25} alkanoyl interrupted by oxygen, sulfur or



is, for example, CH_3-O-CH_2CO- , CH_3-S-CH_2CO- , $CH_3-NH-CH_2CO-$, $CH_3-N(CH_3)-CH_2CO-$, $CH_3-O-CH_2CH_2-O-CO-$, $CH_3-(O-CH_2CH_2)_2O-CH_2CO-$, $CH_3-(O-CH_2CH_2)_3O-CH_2CO-$ or $CH_3-(O-CH_2CH_2)_4O-CH_2CO-$.

[0068] C_3 - C_{25} alkanoyloxy interrupted by oxygen, sulfur or



is, for example, $\text{CH}_3\text{—O—CH}_2\text{COO—}$, $\text{CH}_3\text{—S—CH}_2\text{COO—}$, $\text{CH}_3\text{—NH—CH}_2\text{COO—}$, $\text{CH}_3\text{—N(CH}_3\text{)—CH}_2\text{COO—}$, $\text{CH}_3\text{—O—CH}_2\text{CH}_2\text{—O—CH}_2\text{COO—}$, $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_2\text{O—CH}_2\text{COO—}$, $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_3\text{O—CH}_2\text{COO—}$ or $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_4\text{O—CH}_2\text{COO—}$.

[0069] $\text{C}_6\text{—C}_9$ cycloalkylcarbonyl is, for example, cyclopentylcarbonyl, cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. Cyclohexylcarbonyl is preferred.

[0070] $\text{C}_6\text{—C}_9$ cycloalkylcarbonyloxy is, for example, cyclopentylcarbonyloxy, cyclohexylcarbonyloxy, cycloheptylcarbonyloxy or cyclooctylcarbonyloxy. Cyclohexylcarbonyloxy is preferred.

[0071] $\text{C}_1\text{—C}_{12}$ alkyl-substituted benzoyl, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyl, 2,3-dimethylbenzoyl, 2,4-dimethylbenzoyl, 2,5-dimethylbenzoyl, 2,6-dimethylbenzoyl, 3,4-dimethylbenzoyl, 3,5-dimethylbenzoyl, 2-methyl-6-ethylbenzoyl, 4-tert-butylbenzoyl, 2-ethylbenzoyl, 2,4,6-trimethylbenzoyl, 2,6-dimethyl-4-tert-butylbenzoyl or 3,5-dimethyl-4-tert-butylbenzoyl. Preferred substituents are $\text{C}_1\text{—C}_8$ alkyl, especially $\text{C}_1\text{—C}_4$ alkyl.

[0072] $\text{C}_1\text{—C}_{12}$ alkyl-substituted benzoyloxy, which preferably carries 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylbenzoyloxy, 2,3-dimethylbenzoyloxy, 2,4-dimethylbenzoyloxy, 2,5-dimethylbenzoyloxy, 2,6-dimethylbenzoyloxy, 3,4-dimethylbenzoyloxy, 3,5-dimethylbenzoyloxy, 2-methyl-6-ethylbenzoyloxy, 4-tert-butylbenzoyloxy, 2-ethylbenzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-dimethyl-4-tert-butylbenzoyloxy. Preferred substituents are $\text{C}_1\text{—C}_8$ alkyl, especially $\text{C}_1\text{—C}_4$ alkyl.

[0073] Alkyl having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, n-pentyl, isopentyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetramethylpentyl, nonyl, decyl, undecyl, 1-methylundecyl, dodecyl, 1,1,3,3,5,5-hexamethylhexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl or docosyl. One of the preferred meanings of R_2 and R_4 is, for example, $\text{C}_1\text{—C}_{18}$ alkyl. A particularly preferred meaning of R_4 is $\text{C}_1\text{—C}_4$ alkyl.

[0074] Alkenyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, iso-dodecenyl, oleyl, n-2-octadecenyl or n-4-octadecenyl. Preference is given to alkenyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

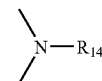
[0075] Alkenyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, pro-

penyloxy, 2-butenyloxy, 3-butenyloxy, isobutenyloxy, n-2, 4-pentadienyloxy, 3-methyl-2-butenyloxy, n-2-octenyloxy, n-2-dodecenyloxy, iso-dodecenyloxy, oleyloxy, n-2-octadecenyloxy or n-4-octadecenyloxy. Preference is given to alkenyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

[0076] Alkynyl having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propynyl ($\text{—CH}_2\text{—C}\equiv\text{CH}$), 2-butylnyl, 3-butylnyl, n-2-octynyl, or n-2-dodecynyl. Preference is given to alkynyl having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

[0077] Alkynyloxy having 3 to 25 carbon atoms is a branched or unbranched radical such as, for example, propynyloxy ($\text{—OCH}_2\text{—C}\equiv\text{CH}$), 2-butynyloxy, 3-butynyloxy, n-2-octynyloxy, or n-2-dodecynyloxy. Preference is given to alkynyloxy having 3 to 18, especially 3 to 12, for example 3 to 6, in particular 3 to 4 carbon atoms.

[0078] $\text{C}_2\text{—C}_{25}$ alkyl interrupted by oxygen, sulfur or

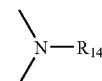


is, for example, $\text{CH}_3\text{—O—CH}_2\text{—}$, $\text{CH}_3\text{—S—CH}_2\text{—}$, $\text{CH}_3\text{—NH—CH}_2\text{—}$, $\text{CH}_3\text{—N(CH}_3\text{)—CH}_2\text{—}$, $\text{CH}_3\text{—O—CH}_2\text{—}$, $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_2\text{O—CH}_2\text{—}$, $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_3\text{O—CH}_2\text{—}$ or $\text{CH}_3\text{—(O—CH}_2\text{CH}_2\text{—)}_4\text{O—CH}_2\text{—}$.

[0079] $\text{C}_7\text{—C}_9$ phenylalkyl is, for example, benzyl, α -methylbenzyl, α,α -dimethylbenzyl or 2-phenylethyl. Benzyl and α,α -dimethylbenzyl are preferred.

[0080] $\text{C}_7\text{—C}_9$ phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by $\text{C}_1\text{—C}_4$ alkyl is, for example, benzyl, α -methylbenzyl, α,α -dimethylbenzyl, 2-phenylethyl, 2-methylbenzyl, 3-methylbenzyl, 4-methylbenzyl, 2,4-dimethylbenzyl, 2,6-dimethylbenzyl or 4-tert-butylbenzyl. Benzyl is preferred.

[0081] $\text{C}_7\text{—C}_{25}$ phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by $\text{C}_1\text{—C}_4$ alkyl and is interrupted by oxygen, sulfur or



is a branched or unbranched radical such as, for example, phenoxymethyl, 2-methylphenoxymethyl, 3-methylphenoxymethyl, 4-methylphenoxymethyl, 2,4-dimethylphenoxymethyl, 2,3-dimethylphenoxy-methyl, phenylthiomethyl, N-methyl-N-phenylmethyl, N-ethyl-N-phenylmethyl, 4-tert-butylphenoxymethyl, 4-tert-butylphenoxyethoxymethyl, 2,4-di-tert-butylphenoxymethyl, 2,4-di-tert-butylphenoxyethoxymethyl, phenoxyethoxyethoxyethoxymethyl, benzyloxymethyl, benzyloxy-ethoxymethyl, N-benzyl-N-ethylmethyl or N-benzyl-N-isopropylmethyl.

[0082] C_7 - C_9 phenylalkoxy is, for example, benzyloxy, α -methylbenzyloxy, α,α -dimethylbenzyloxy or 2-phenylethoxy. Benzyloxy is preferred.

[0083] C_1 - C_4 alkyl-substituted phenyl, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

[0084] C_1 - C_4 alkyl-substituted phenoxy, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenoxy, 2,3-dimethylphenoxy, 2,4-dimethylphenoxy, 2,5-dimethylphenoxy, 2,6-dimethylphenoxy, 3,4-dimethylphenoxy, 3,5-dimethylphenoxy, 2-methyl-6-ethylphenoxy, 4-tert-butylphenoxy, 2-ethylphenoxy or 2,6-diethylphenoxy.

[0085] Unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl is, for example, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. Preference is given to cyclohexyl and tert-butylcyclohexyl.

[0086] Unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkoxy is, for example, cyclopentoxo, methylcyclopentoxo, dimethylcyclopentoxo, cyclohexoxo, methylcyclohexoxo, dimethylcyclohexoxo, trimethylcyclohexoxo, tert-butylcyclohexoxo, cycloheptoxo or cyclooctoxo. Preference is given to cyclohexoxo and tert-butylcyclohexoxo.

[0087] Alkoxy having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy, octoxy, decyloxy, tetradecyloxy, hexadecyloxy or octadecyloxy. Preference is given to alkoxy having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

[0088] C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or



is, for example, $CH_3-O-CH_2CH_2O-$, $CH_3-S-CH_2CH_2O-$, $CH_3-NH-CH_2CH_2O-$, $CH_3-N(CH_3)-CH_2CH_2O-$, $CH_3-O-CH_2CH_2-O-CH_2CH_2O-$, $CH_3-(O-CH_2CH_2)_2O-CH_2CH_2CH_2O-$ or $CH_3-(O-CH_2CH_2)_4O-CH_2CH_2O-$.

[0089] Alkylthio having up to 25 carbon atoms is a branched or unbranched radical such as, for example, methylthio, ethylthio, propylthio, isopropylthio, n-butylthio, isobutylthio, pentylthio, isopentylthio, hexylthio, heptylthio, octylthio, decylthio, tetradecylthio, hexadecylthio or octadecylthio. Preference is given to alkylthio having 1 to 12, especially 1 to 8, for example 1 to 6 carbon atoms.

[0090] Alkylamino having up to 4 carbon atoms is a branched or unbranched radical such as, for example, methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutyl-amino or tert-butylamino.

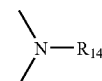
[0091] $Di(C_1-C_4alkyl)amino$ also means that the two radicals independently of one another are branched or unbranched, such as, for example, dimethylamino, methyl-ethylamino, diethylamino, methyl-n-propylamino, methyl-isopropylamino, methyl-n-butylamino, methylisobutylamino, ethylisopropylamino, ethyl-n-butylamino, ethylisobutylamino, ethyl-tert-butylamino, diethylamino, diisopropylamino, isopropyl-n-butylamino, isopropylisobutylamino, di-n-butylamino or diisobutylamino.

[0092] Alkanoylamino having up to 25 carbon atoms is a branched or unbranched radical such as, for example, formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, heptanoylamino, octanoylamino, nonanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino, hexadecanoylamino, heptadecanoylamino, octadecanoylamino, eicosanoylamino or doco-sanoylamino. Preference is given to alkanoylamino having 2 to 18, especially 2 to 12, for example 2 to 6 carbon atoms.

[0093] C_1 - C_{18} alkylene is a branched or unbranched radical such as, for example, methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene, dodecamethylene or octadecamethylene. Preference is given to C_1 - C_{12} alkylene, especially C_1 - C_8 alkylene.

[0094] A C_1 - C_4 alkyl-substituted C_5 - C_{12} cycloalkylene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals is, for example, cyclopentylene, methylcyclopentylene, dimethylcyclopentylene, cyclohexylene, methylcyclohexylene, dimethylcyclohexylene, trimethylcyclohexylene, tert-butylcyclohexylene, cycloheptylene, cyclooctylene or cyclodecylene. Preference is given to cyclohexylene and tert-butylcyclohexylene.

[0095] C_2 - Cl_8 alkylene interrupted by oxygen, sulfur or



is, for example, $-CH_2-O-CH_2-$, $-CH_2-S-CH_2-$, $-CH_2-NH-CH_2-$, $-CH_2-N(CH_3)-CH_2-$, $-CH_2-O-CH_2CH_2-O-CH_2-$, $-CH_2-(O-CH_2CH_2)_2O-CH_2-$, $-CH_2-(O-CH_2CH_2)_3O-CH_2-$, $-CH_2-(O-CH_2CH_2CH_2)_4O-CH_2-$ or $-CH_2CH_2-S-CH_2CH_2-$.

[0096] C_2 - C_{18} alkenylene is, for example, vinylene, methylvinylene, octenylethylene or dodecenylethylene. Preference is given to C_2 - C_8 alkenylene.

[0097] Alkylidene having 2 to 20 carbon atoms is, for example, ethylidene, propylidene, butylidene, pentylidene, 4-methylpentylidene, heptylidene, nonylidene, tridecylidene, nonadecylidene, 1-methylethylidene, 1-ethylpropylidene or 1-ethylpentylidene. Preference is given to C_2 - C_8 alkylidene.

[0098] Phenylalkylidene having 7 to 20 carbon atoms is, for example, benzyldiene, 2-phenylethylidene or 1-phenyl-2-hexylidene. Preference is given to C_7 - C_9 phenylalkylidene.

[0099] C₅-C₈cycloalkylene is a saturated hydrocarbon group having two free valencies and at least one ring unit and is, for example, cyclopentylene, cyclohexylene, cycloheptylene or cyclooctylene. Preference is given to cyclohexylene.

[0100] C₇-C₈bicycloalkylene is, for example, bicycloheptylene or bicyclooctylene.

[0101] Unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene is, for example, 1,2-, 1,3-, 1,4-phenylene, 1,2-, 1,3-, 1,4-, 1,6-, 1,7-, 2,6- or 2,7-naphthylene. 1,4-Phenylene is preferred.

[0102] A C₁-C₄alkyl-substituted C₅-C₈cycloalkylidene ring, which preferably contains 1 to 3, especially 1 or 2 branched or unbranched alkyl group radicals is, for example, cyclopentylidene, methylcyclopentylidene, dimethylcyclopentylidene, cyclohexylidene, methylcyclohexylidene, dimethylcyclohexylidene, trimethylcyclohexylidene, tert-butylcyclohexylidene, cycloheptylidene or cyclooctylidene. Preference is given to cyclohexylidene and tert-butylcyclohexylidene.

[0103] A mono-, di- or trivalent metal cation is preferably an alkali metal, alkaline earth metal or aluminium cation, for example, Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺ or Al⁺⁺⁺.

[0104] A particularly preferred composition of present invention contains at least one compound of formula 1, wherein, if n=1, R₁ is phenyl which is unsubstituted or substituted in para-position by C₁-C₁₈alkylthio or di(C₁-C₄alkyl)amino; mono- to penta-substituted alkyphenyl containing together a total of at most 18 carbon atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothizynyl or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, hydroxy or amino.

[0105] Preference is given to compounds of the formula I in which, if n is 2,

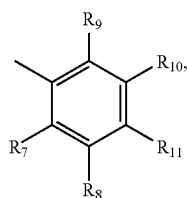
[0106] R₁ is —R₁₂—X—R₁₃—,

[0107] R₁₂ and R₁₃ are phenylene,

[0108] X is oxygen or —NR₃₁—, and

[0109] R₃₁ is C₁-C₄alkyl.

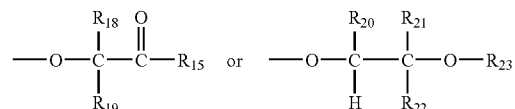
[0110] Preference is also given to compounds of the formula I in which, if n is 1, R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, thienyl, dibenzo-furyl, carbazolyl, fluorenyl or a radical of the formula II



(II)

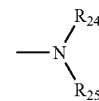
R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, chlorine, bromine, hydroxyl, C₁-C₁₈alkyl, C₂-C₁₈alkyl interrupted by oxygen or sulfur; C₁-C₁₈alkoxy, C₂-C₁₈alkoxy interrupted by oxygen or sulfur;

C₁-C₁₈alkylthio, C₃-C₁₂alkenylthio, C₃-C₁₂alkynylthio, C₇-C₉phenylalkyl, C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; phenoxy, cyclohexyl, C₅-C₈cycloalkoxy, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₁₂alkanoyl, C₃-C₁₂alkanoyl interrupted by oxygen or sulfur; C₁-C₁₂alkanoyloxy, C₃-C₁₂alkanoyloxy interrupted by oxygen or sulfur; C₁-C₁₂alkanoylamino, C₃-C₁₂alkenoyl, C₃-C₁₂alkenoyloxy, cyclohexylcarbonyl, cyclohexylcarbonyloxy, benzoyl or C₁-C₄alkyl-substituted benzoyl; benzoyloxy or C₁-C₄alkyl-substituted benzoyloxy;



or else in formula II the radicals R₇ and R₈ or the radicals R₈ and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,

[0111] R₁₅ is hydroxyl, C₁-C₁₂alkoxy or



[0112] R₁₈ and R₁₉ independently of one another are hydrogen or C₁-C₄alkyl,

[0113] R₂₀ is hydrogen,

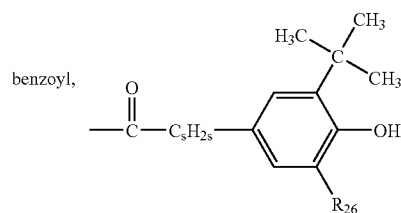
[0114] R₂₁ is hydrogen, phenyl, C₁-C₁₈alkyl, C₂-C₁₈alkyl interrupted by oxygen or sulfur;

[0115] C₇-C₉phenylalkyl, C₇-C₁₈-phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and is interrupted by oxygen or sulfur, or else the radicals R₂₀ and R₂₁, together with the carbon atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl,

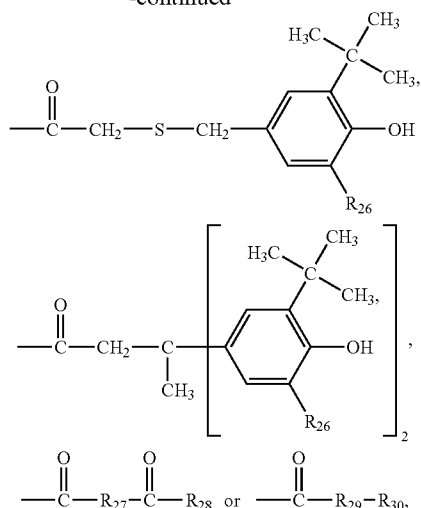
[0116] R₂₂ is hydrogen or C₁-C₄alkyl,

[0117] R₂₃ is hydrogen, C₁-C₁₈alkanoyl, C₃-C₁₈alkenoyl, C₃-C₁₂alkanoyl interrupted by oxygen or sulfur;

[0118] C₂-C₁₂alkanoyl substituted by a di(C₁-C₆alkyl)phosphonate group; C₆-C₉cycloalkylcarbonyl,



-continued



[0119] R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₂alkyl,

[0120] R₂₆ is hydrogen or C₁-C₄alkyl,

[0121] R₂₇ is C₁-C₁₂alkylene, C₂-C₈alkenylene, C₂-C₈alkylidene, C₇-C₁₂phenylalkylidene, C₆-C₈cycloalkylene or phenylene,

[0122] R₂₈ is hydroxyl, C₁-C₁₂alkoxy or

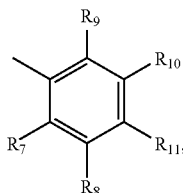


[0123] R₂₉ is oxygen or —NH—,

[0124] R₃₀ is C₁-C₁₈alkyl or phenyl, and

[0125] s is 1 or 2.

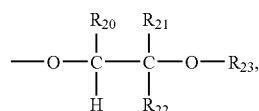
[0126] Preference is likewise given to compounds of the formula I in which, if n is 1, R₁ is phenanthryl, thienyl, dibenzofuryl, unsubstituted or C₁-C₄alkyl-substituted carbazolyl; or is fluorenyl; or R₁ is a radical of the formula II



(II)

[0127] R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, chlorine, hydroxyl,

[0128] C₁-C₁₈alkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₃-C₄alkenyloxy, C₃-C₄alkinyloxy, C₂-C₁₈alkanoyloxy, phenyl, benzoyl, benzoyloxy or



[0129] R_{20} is hydrogen,

[0130] R₂₁ is hydrogen, phenyl or C₁-C₁₈alkyl, or else the radicals R₂₀ and R₂₁, together with the carbon atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl.

[0131] R₂₂ is hydrogen or C₁-C₄alkyl, and

[0132] R₂₃ is hydrogen, C₁-C₁₈alkanoyl or benzoyl.

[0133] Particular preference is given to compounds of the formula I in which, if n is 1,

[0134] R₇, R₈, R₉, R₁₀ and R₁₁ independently of one another are hydrogen, C₁-C₄alkylthio or phenyl.

[0135] Of particular interest is a composition containing at least one compound of the formula I in which R₂, R₃, R₄ and R₅ independently of one another are hydrogen, chlorine, C₁-C₁₈alkyl, benzyl, phenyl, C₅-C₈cycloalkyl, C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₁₈alkanoyloxy, C₁-C₁₈alkanoylamino, C₃-C₁₈alkenoyloxy or benzoyloxy; or else the radicals R₂ and R₃ or the radicals R₃ and R₄ or the radicals R₄ and R₅, together with the carbon atoms to which they are attached, form a benzo ring, R₄ is additionally —(CH₂)_p—COR₁₅ or —(CH₂)_qOH, or, if R₃, R₅ and R₆ are hydrogen, R₄ is additionally a radical of the formula III,

[0136] R₁₅ is hydroxyl, C₁-C₁₂alkoxy or



[0137] R₁₆ and R₁₇ are methyl groups or, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl,

[0138] R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₂alkyl,

[0139] p is 1 or 2, and

[0140] q is 2, 3, 4, 5 or 6.

[0141] Also of particular interest is a composition containing at least one compound of the formula I in which at least two of the radicals R_2 , R_3 , R_4 and R_5 are hydrogen.

[0142] Of special interest is a composition containing at least one compound of the formula I in which R_3 and R_5 are hydrogen.

[0143] Of very special interest is composition containing at least one compound of the formula I in which

[0144] R₂ is C₁-C₄alkyl,

[0145] R₃ is hydrogen,

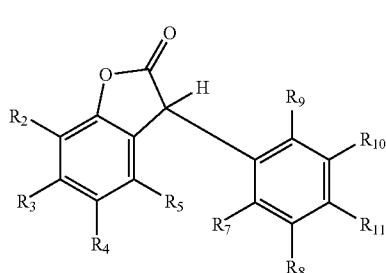
[0146] R_4 is C_1 - C_4 alkyl or, if R_6 is hydrogen, R_4 is additionally a radical of the formula III,

[0147] R_5 is hydrogen, and

[0148] R_{16} and R_{17} , together with the C atom to which they are attached, form a cyclohexylidene ring.

[0149] The following compounds are examples of the benzofuran-2-one type which are particularly suitable in the composition of the present invention: 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-butylbenzofuran-2-one; 3-(3,5-dimethyl-4-pivaloyloxy-phenyl)-5,7-di-tert-butyl-benzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-benzofuran-2-one; 5,7-di-tert-butyl-3-(2,3-dimethylphenyl)benzofuran-2-one.

[0150] Also of special interest is a composition containing at least one compound of the formula V



(V)

in which

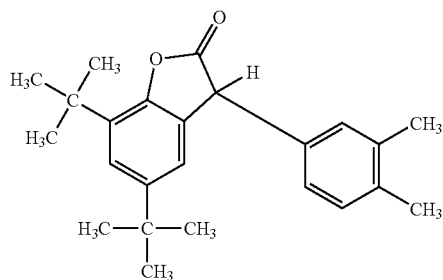
[0151] R_2 is hydrogen or C_1 - C_6 alkyl,

[0152] R_3 is hydrogen,

[0153] R_4 is hydrogen or C_1 - C_6 alkyl,

[0154] R_5 is hydrogen, R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, C_1 - C_4 alkyl or C_1 - C_4 alkoxy, with the proviso that at least two of the radicals R_7 , R_8 , R_9 , R_{10} or R_{11} are hydrogen.

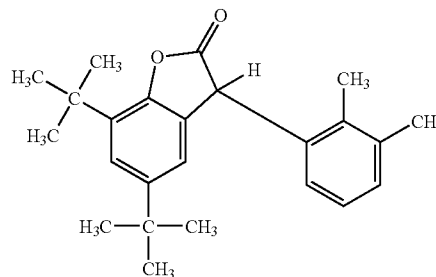
[0155] Very particular preference is given to a composition containing at least one compound of the formula Va or Vb



(Va)

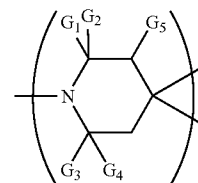
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(Vb)



or a mixture of the two compounds of the formula Va and Vb.

[0156] The present sterically hindered amine stabilizers contain at least one moiety of formula



where G_1 , G_2 , G_3 , G_4 and G_5 are independently alkyl of 1 to 8 carbon atoms or G_1 and G_2 or G_3 and G_4 together are pentamethylene.

[0157] The hindered amines are disclosed for example in U.S. Pat. Nos. 5,004,770, 5,204,473, 5,096,950, 5,300,544, 5,112,890, 5,124,378, 5,145,893, 5,216,156, 5,844,026, 5,980,783, 6,046,304, 6,117,995, 6,271,377, 6,297,299, 6,392,041, 6,376,584 and 6,472,456, and U.S. application Ser. Nos. 09/714,717, filed Nov. 16, 2000 and U.S. application Ser. No. 10/485,377, filed Aug. 6, 2002. The relevant disclosures of these patents and applications are hereby incorporated by reference.

[0158] U.S. Pat. Nos. 6,271,377, 6,392,041 and U.S. Pat. No. 6,376,584, cited above disclose hindered hydroxy-alkoxyamine stabilizers.

[0159] Suitable hindered amines include for example:

[0160] 1) 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine,

[0161] 2) bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

[0162] 3) bis(1-acetoxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

[0163] 4) bis(1,2,2,6,6-pentamethyl-4-yl) sebacate,

[0164] 5) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

[0165] 6) bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;

[0166] 7) bis(1-acyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

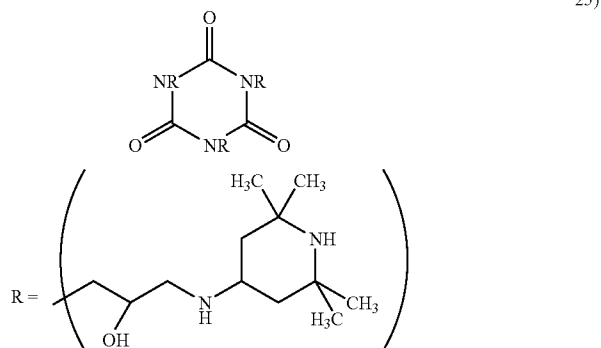
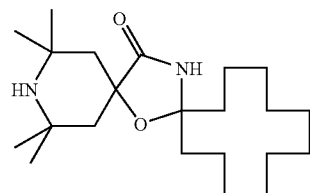
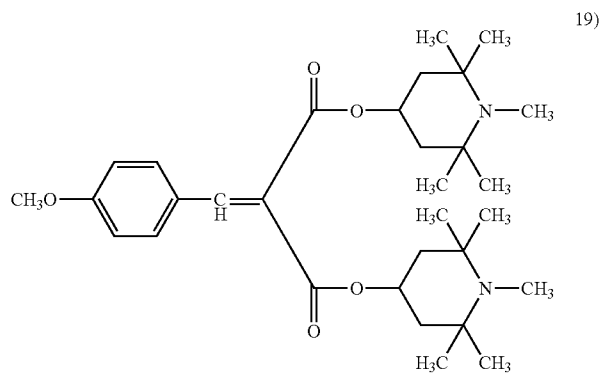
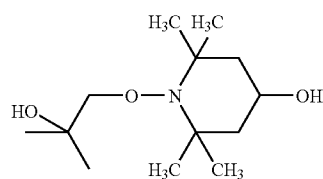
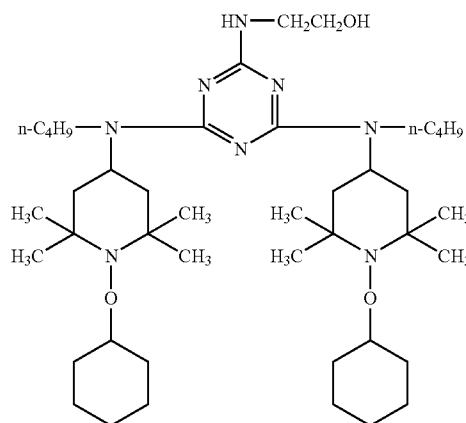
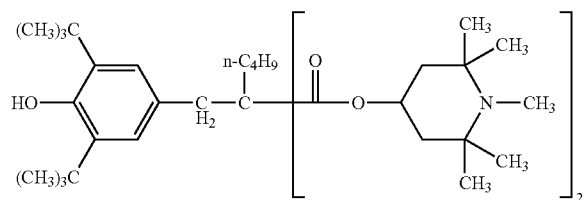
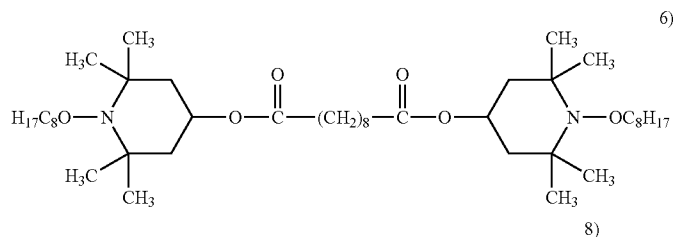
- [0167] 8) bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate
- [0168] 9) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxy-ethylamino-s-triazine),
- [0169] 10) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- [0170] 11) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine,
- [0171] 12) 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine,
- [0172] 13) 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine,
- [0173] 14) 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine,
- [0174] 15) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- [0175] 16) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- [0176] 17) 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine,
- [0177] 18) 4-benzoyl-2,2,6,6-tetramethylpiperidine,
- [0178] 19) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) p-methoxybenzylidenemalonate,
- [0179] 20) 4-stearyl-2,2,6,6-tetramethylpiperidine,
- [0180] 21) bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate,
- [0181] 22) 1,2,2,6,6-pentamethyl-4-aminopiperidine,
- [0182] 23) 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane,
- [0183] 24) tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate,
- [0184] 25) tris(2-hydroxy-3-(amino-(2,2,6,6-tetramethylpiperidin-4-yl)propyl) nitrilotriacetate,
- [0185] 26) tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- [0186] 27) tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- [0187] 28) 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone),
- [0188] 29) 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione,
- [0189] 30) 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione,
- [0190] 31) 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione,
- [0191] 32) 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione,
- [0192] 33) N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine,
- [0193] 34) the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine),
- [0194] 35) the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid,
- [0195] 36) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine,
- [0196] 37) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine,
- [0197] 38) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- [0198] 39) linear or cyclic condensates of N,N'-bis(1,2,2,6,6-pentamethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- [0199] 40) 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,
- [0200] 41) 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,
- [0201] 42) a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane and epichlorohydrin,
- [0202] 43) poly[methyl-(3-oxy-(2,2,6,6-tetramethylpiperidin-4-yl)propyl)] siloxane, CAS#182635-99-0,
- [0203] 44) reaction product of maleic acid anhydride-C₁₈-C₂₂- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine,
- [0204] 45) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- [0205] 46) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1,2,2,6,6-pentaamethylpiperidine) and 2,4-dichloro-6-[(1,2,2,6,6-pentaamethyl-piperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- [0206] 47) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1-propoxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-propoxy-2,2,6,6-tetra-methylpiperin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- [0207] 48) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1-acyloxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-acyloxy-2,2,6,6-tetra-methylpiperin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine and

[0208] 49) product obtained by reacting a product, obtained by reacting 1,2-bis(3-amino-propylamino) ethane with cyanuric chloride, with (2,2,6,6-tetramethylpiperidin-4-yl)butylamine.

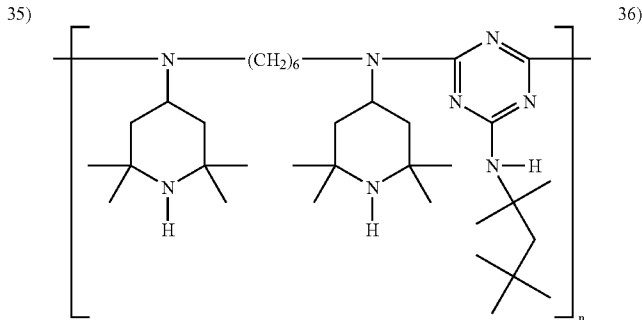
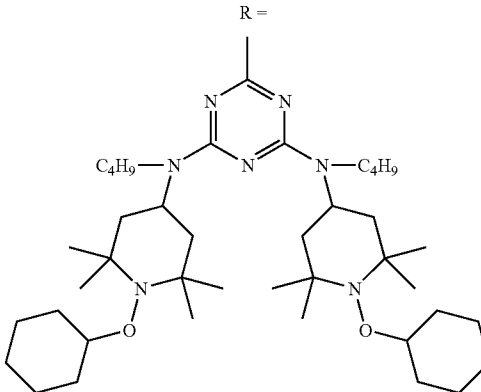
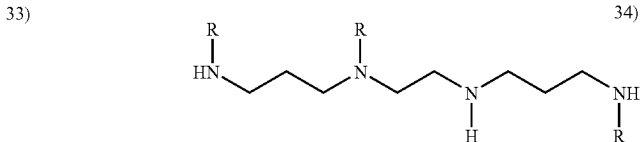
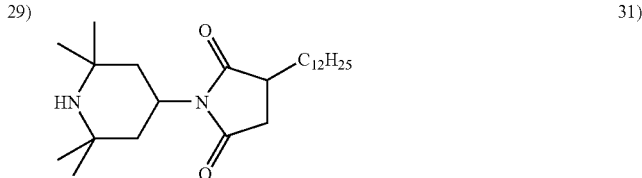
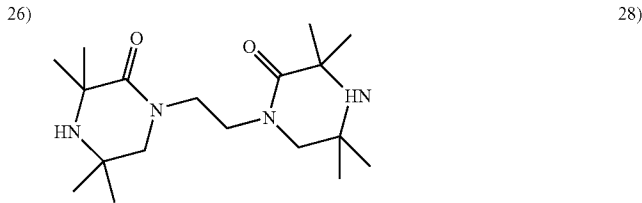
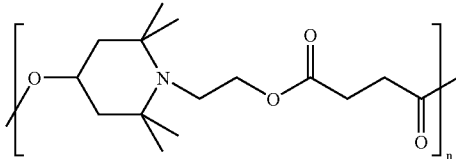
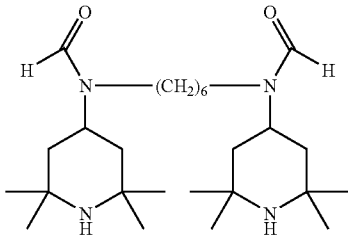
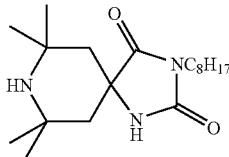
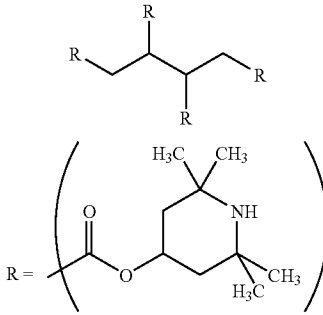
[0209] Also included are the sterically hindered N—H, N-methyl, N-methoxy, N-propoxy, N-octyloxy, N-cyclohexyloxy, N-acyloxy and N-(2-hydroxy-2-methylpropoxy)

analogues of any of the above mentioned compounds. For example, replacing an N—H hindered amine with an N-methyl hindered amine would be employing the N-methyl analogue in place of the N—H.

[0210] For illustrative purposes, some of the structures for the above-named compounds are shown below:

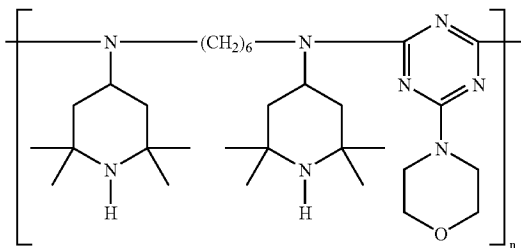


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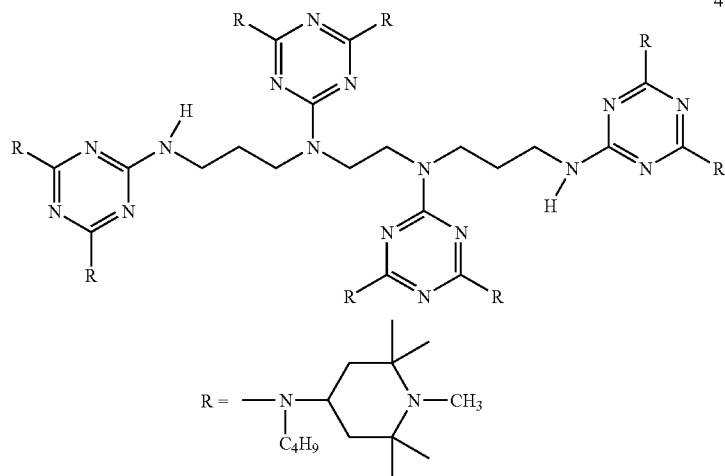


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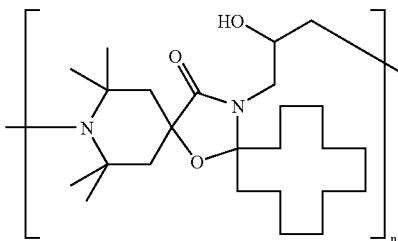
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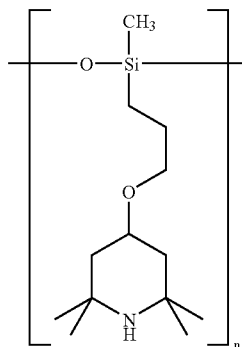
41)



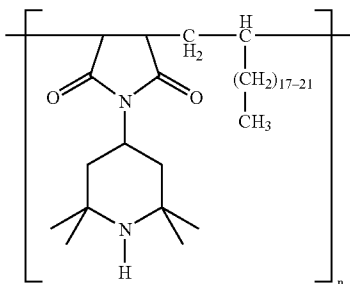
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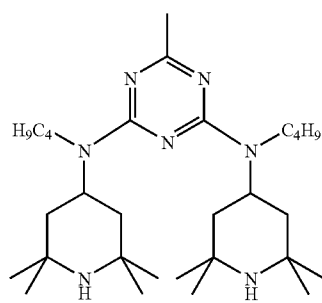
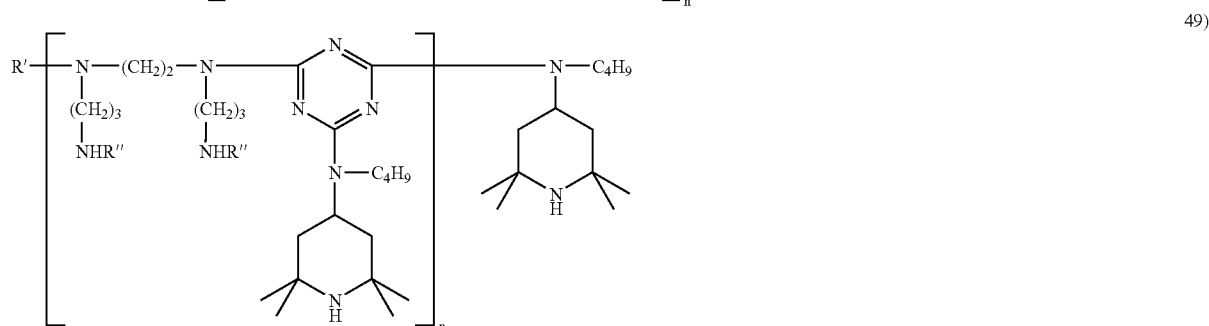
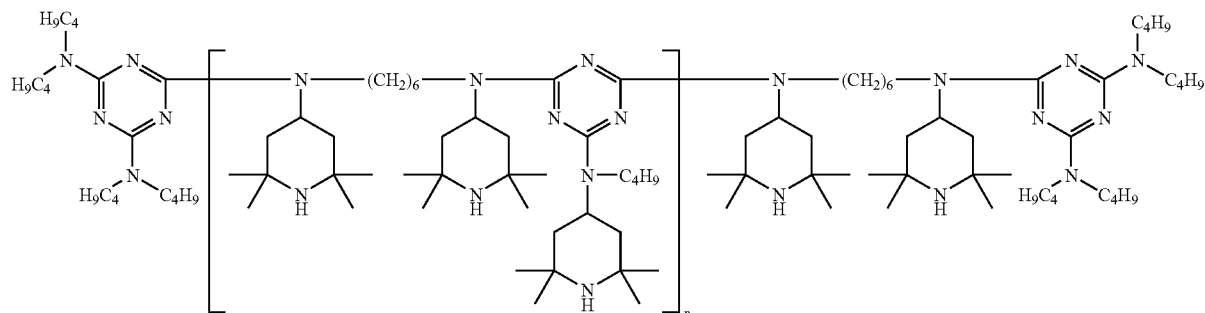
43)



44)



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where R' = R'' or H
and where R'' =

[0211] The hindered phenolic antioxidants are for example

[0212] 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1-methylundec-1-yl)phenol, 2,4-dimethyl-6-(1-methylheptadec-1-yl)phenol, 2,4-dimethyl-6-(1-methyltridec-1-yl)phenol and mixtures thereof.

[0213] 1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol.

[0214] 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-

butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl)adipate.

[0215] 1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

[0216] 1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide.

[0217] 1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-meth-

ylphenol), 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.

[0218] 1.7. Benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, 1,3,5-tri-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, di-(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide, 3,5-di-tert-butyl-4-hydroxybenzyl-mercapto-acetic acid isooctyl ester, bis-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithiol terephthalate, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris-(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dioctadecyl ester and 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid monoethyl ester, calcium-salt.

[0219] 1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-dodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

[0220] 1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

[0221] 1.10. Triazine compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxy-phenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

[0222] 1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-

di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

[0223] 1.12. Acylaminophenols, for example 4-hydroxy-lauric acid anilide, 4-hydroxy-stearic acid anilide, 2,4-bis-octylmercapto-6-(3,5-tert-butyl-4-hydroxyanilino)-s-triazine and octyl-N-(3,5-di-tert-butyl-4-hydroxyphenyl)-carbamate.

[0224] 1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

[0225] 1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

[0226] 1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

[0227] 1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

[0228] 1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Naugard®XL-1 supplied by Uniroyal).

[0229] Each of the 3-arylbenzofuranone and hindered amine light stabilizers, and the optional phenolic antioxidant, are employed at levels of about 5 ppm to about 5000

ppm, for example from about 50 ppm to about 5000 ppm, for example from about 100 to about 5000 ppm by weight, based on the weight of the biodiesel fuel. For example, each of the present additives are present from about 150 to about 4000 ppm, from about 200 to about 3000 ppm, or from about 250 to about 2500 ppm by weight, based on the weight of the biodiesel fuel. In certain instances, the levels may be as high as about 1%, about 2% or about 3% by weight, based on the weight of the biodiesel fuel.

[0230] The present stabilized biodiesel fuels exhibit increased storage stability vs. unstabilized samples. Degradation of biodiesel fuels under the conditions of heat, light or oxygen is observed by the formation of carboxylic acids, peroxides, aldehydes and alcohols.

EXAMPLES

[0231] The Rancimat test, developed by the food industry, is employed to test the oxidative stability of soy biodiesel (methyl ester of soy fatty acid). A 3.0 g sample of soy biodiesel is held at 111.7° C. and exposed to a bubbling stream of air (10 liters per hour). The sample vessel is vented to a secondary container, where the off-gases are bubbled through 60 mL of distilled water. The test measures the volatile oxidation decomposition products such as peroxides, alcohols, aldehydes and carboxylic acids. The volatile decomposition products (chiefly formic acid) are swept through the sample vessel and vented into the secondary container where they are trapped by the distilled water. The conductivity of the water is constantly monitored as a function of time through use of an electrode. The inflection point (not a specific value) of the conductivity curve is the measured induction time. It should be pointed out that some samples will be highly conductive before the inflection point is achieved, while others will only be slightly conductive. An increase of the induction time indicates an increase in oxidative stability. Results are in the table below. Levels of additive are in weight percent based on the weight of the biodiesel.

Rancimat Induction Time		
sample	additive	Induction Time (hours)
1 (control)	none	5.0
2	250 ppm A	6.6
3	2500 ppm A	8.8
4	2500 ppm B	12.7

Additive A is bis-(1,1,2,2,6,6-pentamethyl-4-piperidyl) sebacate; B is 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

[0232] A 6 hour induction time is necessary to meet the EN 14214 specification.

What is claimed is:

1. A biodiesel fuel composition stabilized against the deleterious effects of heat, light and oxygen, which composition comprises

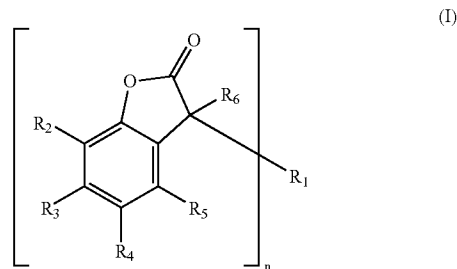
a biodiesel fuel and

an effective stabilizing amount of

one or more additives selected from the group consisting of the 3-arylbenzofuranone stabilizers and the hindered amine light stabilizers and

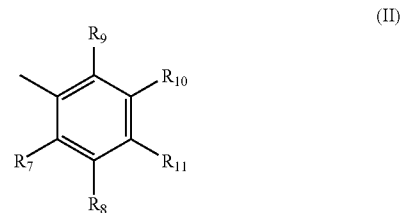
optionally, one or more additives selected from the group consisting of the hindered phenolic antioxidants.

2. A composition according to claim 1 comprising one or more 3-arylbenzofuranone stabilizers of formula I



in which, if n is 1,

R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, isindolyl, indolyl, indazolyl, purinyl, quinoliziny, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β-carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R₁ is a radical of the formula II



and

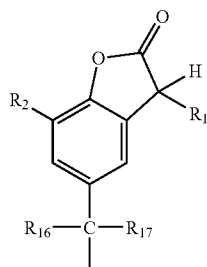
if n is 2,

R₁ is unsubstituted or C₁-C₄alkyl- or hydroxy-substituted phenylene or naphthylene; or is -R₁₂-X-R₁₃—,

R₂, R₃, R₄ and R₅ independently of one another are hydrogen, chlorine, hydroxyl, C₁-C₂₅alkyl, C₇-C₉ phenylalkyl, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; C₁-C₁₈alkoxy, C₁-C₁₈alkylthio, C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyloxy, C₁-C₂₅alkanoylamino,

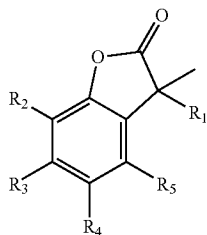
C₃-C₂₅alkenoyloxy, C₃-C₂₅alkanoyloxy which is interrupted by oxygen, sulfur or

C₆-C₉cycloalkylcarbonyloxy, benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy; or else the radicals R₂ and R₃ or the radicals R₃ and R₄ or the radicals R₄ and R₅, together with the carbon atoms to which they are attached, form a benzo ring, R₄ is additionally —(CH₂)_p—COR₁₅ or —(CH₂)_qOH or, if R₃, R₅ and R₆ are hydrogen, R₄ is additionally a radical of the formula III



(III)

in which R₁ is defined as indicated above for n=1, R₆ is hydrogen or a radical of the formula IV



(IV)

where R₄ is not a radical of the formula III and R₁ is defined as indicated above for n=1, R₇, R₈, R₉, R₁₀, and R₁₁ independently of one another are hydrogen, halogen, hydroxyl, C₁-C₂₅alkyl, C₂-C₂₅alkyl interrupted by oxygen, sulfur or

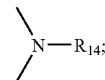


C₁-C₂₅alkoxy, C₂-C₂₅alkoxy interrupted by oxygen, sulfur or

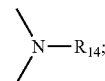


C₁-C₂₅alkylthio, C₃-C₂₅alkenyl, C₃-C₂₅alkenyloxy, C₃-C₂₅alkynyl, C₃-C₂₅alkynyloxy, C₇-C₉phenylalkyl,

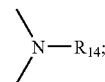
C₇-C₉phenylalkoxy, unsubstituted or C₁-C₄alkyl-substituted phenyl; unsubstituted or C₁-C₄alkyl-substituted phenoxy; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkyl; unsubstituted or C₁-C₄alkyl-substituted C₅-C₈cycloalkoxy; C₁-C₄alkylamino, di(C₁-C₄alkyl)amino, C₁-C₂₅alkanoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or



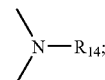
C₁-C₂₅alkanoyloxy, C₃-C₂₅alkanoyloxy interrupted by oxygen, sulfur or



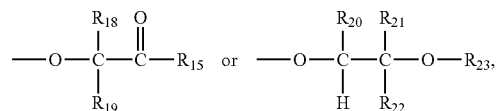
C₁-C₂₅alkanoylamino, C₃-C₂₅alkenoyl, C₃-C₂₅alkenoyl interrupted by oxygen, sulfur or



C₃-C₂₅alkenoyloxy, C₃-C₂₅alkenoyloxy interrupted by oxygen, sulfur or



C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy;



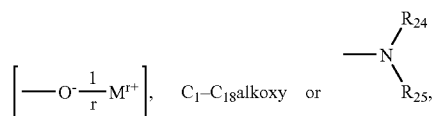
or else, in formula II, the radicals R₇ and

R₈ or the radicals R₈ and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,

R₁₂ and R₁₃ independently of one another are unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

R₁₅ is hydroxyl,



R_{16} and R_{17} independently of one another are hydrogen, CF_3 , C_1-C_{12} alkyl or phenyl, or R_{16} and

R_{17} , together with the C atom to which they are attached, form a C_5-C_8 cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C_1-C_4 alkyl;

R_{18} and R_{19} independently of one another are hydrogen, C_1-C_4 alkyl or phenyl,

R_{20} is hydrogen or C_1-C_4 alkyl,

R_{21} is hydrogen, unsubstituted or C_1-C_4 alkyl-substituted phenyl; C_1-C_{25} alkyl, C_2-C_{25} alkyl interrupted by oxygen, sulfur or



C_7-C_9 phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1-C_4 alkyl; C_7-C_{25} phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C_1-C_4 alkyl and interrupted by oxygen, sulfur or



or else the radicals R_{20} and R_{21} , together with the carbon atoms to which they are attached, form a C_5-C_{12} cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C_1-C_4 alkyl;

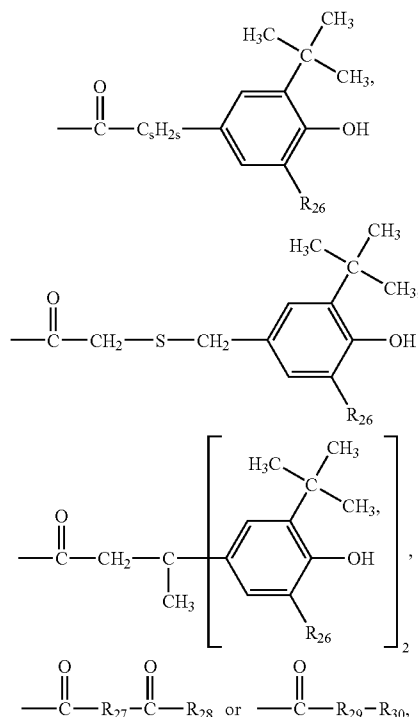
R_{22} is hydrogen or C_1-C_4 alkyl,

R_{23} is hydrogen, C_1-C_{25} alkanoyl, C_3-C_{25} alkenoyl, C_3-C_{25} alkanoyl interrupted by oxygen, sulfur or



C_2-C_{25} alkanoyl substituted by a di(C_1-C_6 alkyl)phosphonate group;

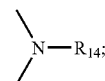
C_6-C_9 cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1-C_{12} alkyl-substituted benzoyl;



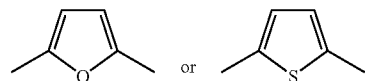
R_{24} and R_{25} independently of one another are hydrogen or C_1-C_{18} alkyl,

R_{26} is hydrogen or C_1-C_8 alkyl,

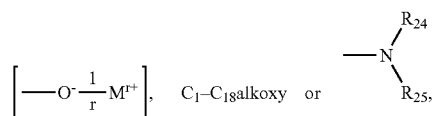
R_{27} is a direct bond, C_1-C_{18} alkylene, C_2-C_{18} alkylene interrupted by oxygen, sulfur or



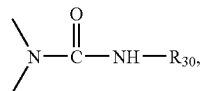
C_2-C_{18} alkenylene, C_2-C_{20} alkylidene, C_7-C_{20} phenylalkylidene, C_5-C_8 cycloalene, C_7-C_8 bicycloalkylene, unsubstituted or C_1-C_4 alkyl-substituted phenylene, or



R_{28} is hydroxyl,



R₂₉ is oxygen, —NH— or



R₃₀ is C₁-C₁₈alkyl or phenyl,

R₃₁ is hydrogen or C₁-C₁₈alkyl,

M is an r-valent metal cation,

X is a direct bond, oxygen, sulfur or **13** NR₃₁—,

n is 1 or 2,

p is 0, 1 or 2,

q is 1, 2, 3, 4, 5 or 6,

r is 1, 2, or 3, and

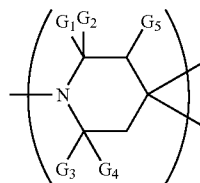
s is 0, 1 or 2.

3. A composition according to claim 2 wherein the 3-aryl-benzofuranones are of formula I wherein n=1, R₁ is phenyl which is unsubstituted or substituted in para-position by C₁-C₁₈alkylthio or di(C₁-C₄alkyl)amino; mono- to penta-substituted alkylphenyl containing together a total of at most 18 carbon atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazoyl, thienyl, pyrrolyl, phenothizynyl or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C₁-C₄alkyl, C₁-C₄alkoxy, C₁-C₄alkylthio, hydroxy or amino.

4. A composition according to claim 2 wherein the 3-aryl-benzofuranones are of formula I wherein n is 2, R₁ is —R₁₂—X—R₁₃—, R₁₂ and R₁₃ are phenylene, X is oxygen or —NR₃₁—, and R₃₁ is C₁-C₄alkyl.

5. A composition according to claim 2 wherein the 3-aryl-benzofuranones are selected from the group consisting of 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-butylbenzofuran-2-one; 3-(3,5-dimethyl-4-pivaloyloxy-phenyl)-5,7-di-tert-butylbenzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-benzofuran-2-one and 5,7-di-tert-butyl-3-(2,3-dimethylphenyl)-benzofuran-2-one.

6. A composition according to claim 1 comprising one or more hindered amine light stabilizers that contain at least one moiety of formula



where G₁, G₂, G₃, G₄ and G₅ are independently alkyl of 1 to 8 carbon atoms or G₁ and G₂ or G₃ and G₄ together are pentamethylene.

7. A composition according to claim 6 where the hindered amine stabilizers are selected from the group consisting of

- 1) 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine,
- 2) bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 3) bis(1-acetoxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 4) bis(1,2,2,6,6-pentamethyl-4-yl) sebacate,
- 5) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 6) bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- 7) bis(1-acyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 8) bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate
- 9) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxy-ethylamino)-s-triazine,
- 10) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- 11) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine,
- 12) 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine,
- 13) 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine,
- 14) 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine,
- 15) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 16) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- 17) 2,4-bis[N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butyl-amino]-6-(2-hydroxyethylamino)-s-triazine,
- 18) 4-benzoyl-2,2,6,6-tetramethylpiperidine,
- 19) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) p-methoxybenzylidenemalonate,
- 20) 4-stearyloxy-2,2,6,6-tetramethylpiperidine,
- 21) bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate,
- 22) 1,2,2,6,6-pentamethyl-4-aminopiperidine,
- 23) 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane,
- 24) tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate,
- 25) tris(2-hydroxy-3-(amino-(2,2,6,6-tetramethylpiperidin-4-yl)propyl) nitrilotriacetate,

- 26) tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- 27) tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- 28) 1,1'-(1,2-ethanedyl)-bis(3,3,5,5-tetramethylpiperazine),
- 29) 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione,
- 30) 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione,
- 31) 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione,
- 32) 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione,
- 33) N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine,
- 34) the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine),
- 35) the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid,
- 36) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine,
- 37) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine,
- 38) linear or cyclic condensates of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- 39) linear or cyclic condensates of N,N'-bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- 40) 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,
- 41) 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,
- 42) a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane and epichlorohydrin,
- 43) poly[methyl(3-oxy-(2,2,6,6-tetramethylpiperidin-4-yl)propyl)] siloxane, CAS#182635-99-0,
- 44) reaction product of maleic acid anhydride-C₁₈-C₂₂- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine,
- 45) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- 46) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1,2,2,6,6-

pentaamethylpiperidine) and 2,4-dichloro-6-[(1,2,2,6,6-pentaamethyl-piperidin-4-yl)butylamino]-s-triazine end -capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,

47) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1-propoxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-propoxy-2,2,6,6-tetra-methylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,

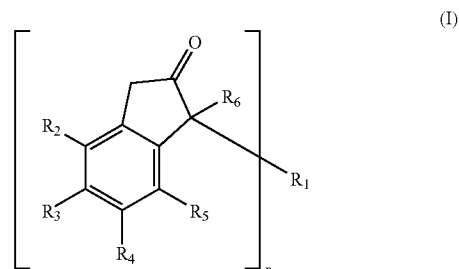
48) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1-acyloxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-acyloxy-2,2,6,6-tetra-methylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine and

49) product obtained by reacting a product, obtained by reacting 1,2-bis(3-amino-propylamino)ethane with cyanuric chloride, with (2,2,6,6-tetramethylpiperidin-4-yl)butylamine.

8. A composition according to claim 6 where the hindered amine is an N—H, N-methyl, N-methoxy, N-propoxy, N-octyloxy, N-cyclohexyloxy, N-acyloxy or an N-(2-hydroxy-2-methyl-propoxy) substituted amine.

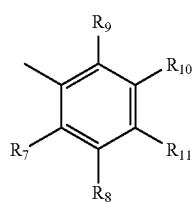
9. A composition according to claim 1 comprising one or more 3-arylbenzofuranone stabilizers and one or more hindered phenolic antioxidants.

10. A composition according to claim 9 where the 3-arylbenzofuranone stabilizers are of formula I

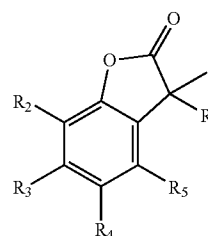


in which, if n is 1,

R₁ is unsubstituted or C₁-C₄alkyl-, C₁-C₄alkoxy-, C₁-C₄alkylthio-, hydroxyl-, halo-, amino-, C₁-C₄alkylamino-, phenylamino- or di(C₁-C₄alkyl)amino-substituted naphthyl, phenanthryl, anthryl, 5,6,7,8-tetrahydro-2-naphthyl, 5,6,7,8-tetrahydro-1-naphthyl, thienyl, benzo[b]thienyl, naphtho[2,3-b]thienyl, thianthrenyl, dibenzofuryl, chromenyl, xanthenyl, phenoxathiinyl, pyrrolyl, imidazolyl, pyrazolyl, pyrazinyl, pyrimidinyl, pyridazinyl, indoliziny, isindolyl, indolyl, indazolyl, purinyl, quinoliziny, isoquinolyl, quinolyl, phthalazinyl, naphthyridinyl, quinoxalinyl, quinazolinyl, cinnolinyl, pteridinyl, carbazolyl, β -carbolinyl, phenanthridinyl, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, isothiazolyl, phenothiazinyl, isoxazolyl, furazanyl, biphenyl, terphenyl, fluorenyl or phenoxazinyl, or R₁ is a radical of the formula II



(II)



(IV)

and

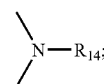
if n is 2,

R_1 is unsubstituted or C_1 - C_4 alkyl- or hydroxy-substituted phenylene or naphthylene; or is $-R_{12}-X-R_{13}-$,

R_2 , R_3 , R_4 and R_5 independently of one another are hydrogen, chlorine, hydroxyl, C_1 - C_{25} alkyl, C_7 - C_9 phenylalkyl, unsubstituted or C_1 - C_4 alkyl-substituted phenyl; unsubstituted or C_1 - C_4 alkyl-substituted C_5 - C_8 cycloalkyl; C_1 - C_{18} alkoxy, C_1 - C_{18} alkylthio, C_1 - C_4 alkylamino, di(C_1 - C_4 alkyl)amino, C_1 - C_{25} alkanoyloxy, C_1 - C_{25} alkanoylamino, C_3 - C_{25} alkenoyloxy, C_3 - C_{25} alkanoyloxy which is interrupted by oxygen, sulfur or

where R_4 is not a radical of the formula III and R_1 is defined as indicated above for $n=1$,

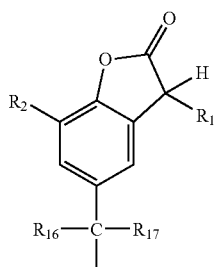
R_7 , R_8 , R_9 , R_{10} and R_{11} independently of one another are hydrogen, halogen, hydroxyl, C_1 - C_{25} alkyl, C_2 - C_{25} alkyl interrupted by oxygen, sulfur or



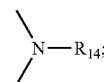
C_1 - C_{25} alkoxy, C_2 - C_{25} alkoxy interrupted by oxygen, sulfur or



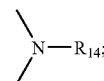
C_6 - C_9 cycloalkylcarbonyloxy, benzoyloxy or C_1 - C_{12} alkyl-substituted benzoyloxy; or else the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5 , together with the carbon atoms to which they are attached, form a benzo ring, R_4 is additionally $-(CH_2)_p-COR_{15}$ or $-(CH_2)_qOH$ or, if R_3 , R_5 and R_6 are hydrogen, R_4 is additionally a radical of the formula III



(III)



C_1 - C_{25} alkanoyloxy, C_3 - C_{25} alkanoyloxy interrupted by oxygen, sulfur or



in which R_1 is defined as indicated above for $n=1$,

R_6 is hydrogen or a radical of the formula IV

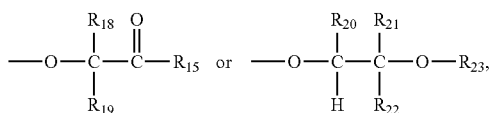
C_1 - C_{25} alkanoylamino, C_3 - C_{25} alkenoyl, C_3 - C_{25} alkenoyl interrupted by oxygen, sulfur or



C₃-C₂₅alkenoyloxy, C₃-C₂₅alkenoyloxy interrupted by oxygen, sulfur or



C₆-C₉cycloalkylcarbonyl, C₆-C₉cycloalkylcarbonyloxy, benzoyl or C₁-C₁₂alkyl-substituted benzoyl; benzoyloxy or C₁-C₁₂alkyl-substituted benzoyloxy;

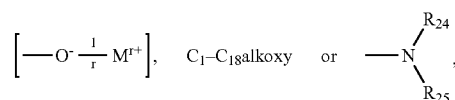


or else, in formula II, the radicals R₇ and R₈ or the radicals R₈ and R₁₁, together with the carbon atoms to which they are attached, form a benzo ring,

R₁₂ and R₁₃ independently of one another are unsubstituted or C₁-C₄alkyl-substituted phenylene or naphthylene,

R₁₄ is hydrogen or C₁-C₈alkyl,

R₁₅ is hydroxyl,



R₁₆ and R₁₇ independently of one another are hydrogen, CF₃, C₁-C₁₂alkyl or phenyl, or R₁₆ and

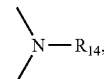
R₁₇, together with the C atom to which they are attached, form a C₅-C₈cycloalkylidene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

R₁₈ and R₁₉ independently of one another are hydrogen, C₁-C₄alkyl or phenyl, R₂₀ is hydrogen or C₁-C₄alkyl,

R₂₁ is hydrogen, unsubstituted or C₁-C₄alkyl-substituted phenyl; C₁-C₂₅alkyl, C₂-C₂₅alkyl interrupted by oxygen, sulfur or

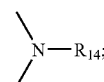


C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl; C₇-C₂₅phenylalkyl which is unsubstituted or substituted on the phenyl radical from 1 to 3 times by C₁-C₄alkyl and interrupted by oxygen, sulfur or

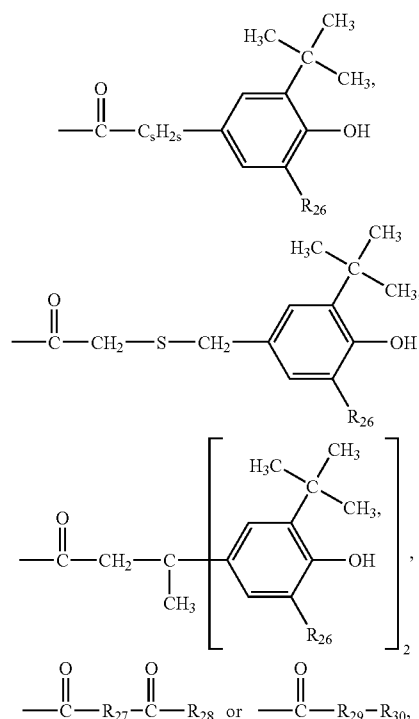


or else the radicals R₂₀ and R₂₁, together with the carbon atoms to which they are attached, form a C₅-C₁₂cycloalkylene ring which is unsubstituted or substituted from 1 to 3 times by C₁-C₄alkyl;

R₂₂ is hydrogen or C₁-C₄alkyl, R₂₃ is hydrogen, C₁-C₂₅alkanoyl, C₃-C₂₅alkenoyl, C₃-C₂₅alkanoyl interrupted by oxygen, sulfur or



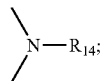
C₂-C₂₅alkanoyl substituted by a di(C₁-C₆alkyl)phosphonate group; C₆-C₉cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C₁-C₁₂alkyl-substituted benzoyl;



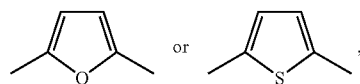
R₂₄ and R₂₅ independently of one another are hydrogen or C₁-C₁₈alkyl,

R₂₆ is hydrogen or C₁-C₈alkyl,

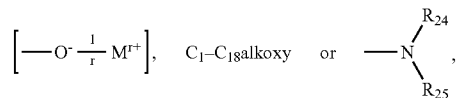
R_{27} is a direct bond, C_1 - C_{18} alkylene, C_2 - C_{18} alkylene interrupted by oxygen, sulfur or



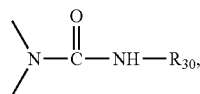
C_2 - C_{18} alkenylene, C_2 - C_{20} alkylidene, C_5 - C_8 cycloalkylene, C_7 - C_8 bicycloalkylene, unsubstituted or C_1 - C_4 alkyl-substituted phenylene, or



R_{28} is hydroxyl,



R_{29} is oxygen, $-NH-$ or



R_{30} is C_1 - C_{18} alkyl or phenyl,

R_{31} is hydrogen or C_1 - C_{18} alkyl,

M is an r -valent metal cation,

X is a direct bond, oxygen, sulfur or $-NR_{31}-$,

n is 1 or 2,

p is 0, 1 or 2,

q is 1, 2, 3, 4, 5 or 6,

r is 1, 2 or 3, and

s is 0, 1 or 2.

11. A composition according to claim 10 wherein the 3-arylbenzofuranones are of formula I wherein $n=1$, R_1 is phenyl which is unsubstituted or substituted in para-position by C_1 - C_{18} alkylthio or di(C_1 - C_4 alkyl)amino; mono- to penta-substituted alkylphenyl containing together a total of at most 18 carbon atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothizynyl or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C_1 - C_4 alkyl, C_1 - C_4 alkoxy, C_1 - C_4 alkylthio, hydroxy or amino.

12. A composition according to claim 10 wherein the 3-arylbenzofuranones are of formula I wherein n is 2, R_1 is

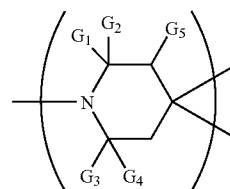
$-R_{12}-X-R_{13}-$, R_{12} and R_{13} are phenylene, X is oxygen or $-NR_{31}-$, and R_{31} is C_1 - C_4 alkyl.

13. A composition according to claim 10 wherein the 3-arylbenzofuranones are selected from the group consisting of 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-butylbenzofuran-2-one; 3-(3,5-dimethyl-4-pivaloyloxy-phenyl)-5,7-di-tert-butylbenzofuran-2-one; 5,7-di-tert-butyl-3-phenylbenzofuran-2-one; 5,7-di-tert-butyl-3-(3,4-dimethylphenyl)-benzofuran-2-one and 5,7-di-tert-butyl-3-(2,3-dimethylphenyl)benzofuran-2-one.

14. A composition according to claim 9 where the hindered phenolic antioxidants are selected from the group consisting of butylated hydroxytoluene, butylated hydroxyanisole, tocopherol, benzylphosphonates, esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols and esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols.

15. A composition according to claim 1 comprising one or more hindered amine light stabilizers and one or more hindered phenolic antioxidants.

16. A composition according to claim 15 where the hindered amine light stabilizers contain at least one moiety of formula



where G_1 , G_2 , G_3 , G_4 and G_5 are independently alkyl of 1 to 8 carbon atoms or G_1 and G_2 or G_3 and G_4 together are pentamethylene.

17. A composition according to claim 15 where the hindered amine stabilizers are selected from the group consisting of

- 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine,
- bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- bis(1-acetoxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- bis(1,2,2,6,6-pentamethyl-4-yl) sebacate,
- bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- bis(1-acyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,

- 8) bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate
- 9) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxy-ethylamino-s-triazine,
- 10) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- 11) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine,
- 12) 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine,
- 13) 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine,
- 14) 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine,
- 15) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate,
- 16) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate,
- 17) 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N -butyl-amino}-6-(2-hydroxyethylamino)-s-triazine,
- 18) 4-benzoyl-2,2,6,6-tetramethylpiperidine,
- 19) di-(1,2,2,6,6-pentamethylpiperidin-4-yl) p-methoxybenzylidenemalonate,
- 20) 4-stearyloxy-2,2,6,6-tetramethylpiperidine,
- 21) bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl) succinate,
- 22) 1,2,2,6,6-pentamethyl-4-aminopiperidine,
- 23) 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane,
- 24) tris(2,2,6,6-tetramethyl-4-piperidyl) nitrilotriacetate,
- 25) tris(2-hydroxy-3-(amino-(2,2,6,6-tetramethylpiperidin-4-yl)propyl) nitrilotriacetate,
- 26) tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- 27) tetrakis(1,2,2,6,6-pentamethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate,
- 28) 1,1'-(1,2-ethanedyl)-bis(3,3,5,5-tetramethylpiperazine),
- 29) 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione,
- 30) 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione,
- 31) 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-2,5-dione,
- 32) 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione,
- 33) N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine,
- 34) the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro -s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine),
- 35) the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid,
- 36) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine,
- 37) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine,
- 38) linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- 39) linear or cyclic condensates of N,N'-bis(1,2,2,6,6-pentamethyl-4-piperidyl)-hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine,
- 40) 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,
- 41) 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,
- 42) a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane and epichlorohydrin,
- 43) poly[methyl, (3-oxy-(2,2,6,6-tetramethylpiperidin-4-yl)propyl)] siloxane, CAS#182635-99-0,
- 44) reaction product of maleic acid anhydride-C₁₈-C₂₂- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine,
- 45) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2, 2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- 46) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1,2,2,6,6-pentaamethylpiperidine) and 2,4-dichloro-6-[(1,2,2,6,6-pentaamethyl-piperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- 47) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-1-propoxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-propoxy-2,2,6,6-tetra-methylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine,
- 48) the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis (amino-1-acyloxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-acyloxy-2,2,6,6-tetra-methylpiperidin -4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine and
- 49) product obtained by reacting a product, obtained by reacting 1,2-bis(3-amino-propylamino) ethane with cyanuric chloride, with (2,2,6,6-tetramethylpiperidin-4-yl)butylamine.

18. A composition according to claim 15 where the hindered amine is an N—H, N-methyl, N-methoxy, N-propoxy, N-octyloxy, N-cyclohexyloxy, N-acyloxy or an N-(2-hydroxy-2-methyl-propoxy) substituted amine.

19. A composition according to claim 15 where the hindered phenolic antioxidants are selected from the group consisting of butylated hydroxytoluene, butylated hydroxyanisole, tocopherol, benzylphosphonates, esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols and esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols.

20. A process for the stabilization of a biodiesel fuel against the deleterious effects of heat, light and oxygen, which process comprises

incorporating into a biodiesel fuel

an effective stabilizing amount of

one or more additives selected from the group consisting of the 3-arylbenzofuranone stabilizers and the hindered amine light stabilizers and

optionally, one or more additives selected from the group consisting of the hindered phenolic antioxidants.

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