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(71) Demandeur/Applicant:
CIBA HOLDING INC., CH

(72) Inventeurs/Inventors:
LI, NATALIE R., US;
HUGHES, DAVID ROYSTON, US;
CUSATIS, PATRICE, US;
OLENSKI, DAVID, US

(74) Agent: FETHERSTONHAUGH & CO.

(54) Titre : COMPOSITIONS STABILISEES DE COMBUSTIBLE BIODIESEL
(54) Title: STABILIZED BIODIESEL FUEL COMPOSITIONS

(57) Abrégé/Abstract:
Disclosed are stabilized biodiesel fuel compositions, which compositions comprise a bio- diesel 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 hin- dered amine light stabilizers, and optionally, one or more hindered phenolic antioxidants.

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60/756,090 4 January 2006 (04.01.2006) US

(71) Applicant *(for all designated States except US)*: **CIBA SPECIALTY CHEMICALS HOLDING INC.** [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **LI, Natalie R.** [US/US]; Bank Street Apt 121i, White Plains, New York 10606 (US). **HUGHES, David Royston** [US/US]; 2200 North Benson Road, Fairfield, Connecticut 06824 (US). **CUSATIS, Patrice** [US/US]; 44 Brandywine Crossing, Newburgh, New York 12550 (US). **OLENSKI, David** [US/US]; 12 Barger Hill Road, Putnam Valley, New York 10579 (US).

(74) Common Representative: **CIBA SPECIALTY CHEMICALS HOLDING INC.**; Patent Department, Klybeckstrasse 141, CH-4057 Basel (CH).

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(54) Title: STABILIZED BIODIESEL FUEL COMPOSITIONS

(57) Abstract: Disclosed are stabilized biodiesel fuel compositions, which compositions comprise a bio- diesel 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 hin- dered amine light stabilizers, and optionally, one or more hindered phenolic antioxidants.

Stabilized Biodiesel Fuel Compositions

The 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-arylbenzofuranone 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.

WO 2004055141 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.

U.S. Pat. No. 6,548,580 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.

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

EP 1 170296 teaches a process for the preparation for 3-aryl-benzofuranones. Fuel additives are disclosed therein.

EP 1 486 555, *EP1 484 387* and *EP1 484 388* disclose a low corrosive fuel composition for use in a blue flame burner or an optimized yellow flame burner of a boiler.

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.

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

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.

Also disclosed is 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.

Biodiesel fuels are a renewable resource and are of increasing importance.

Biodiesel fuels 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.

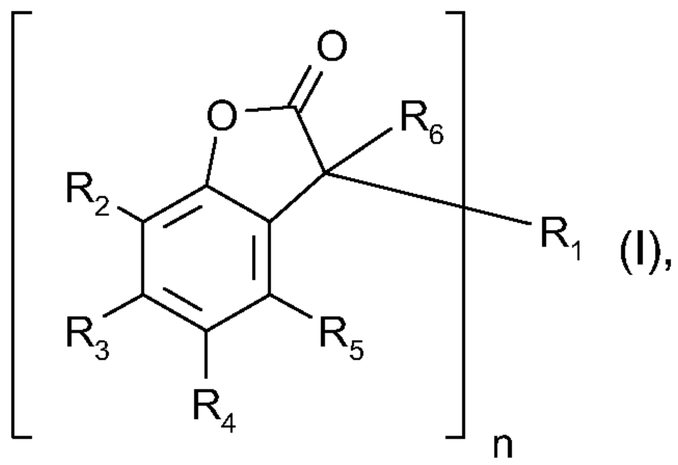
Biodiesel fuel and its preparation is disclosed, for example, in *U.S. Pat. Nos. 5,578,090, 5,713,965, 5,891,203, 6,015,440, 6,174,501* and *6,398,707*.

Biodiesel fuel of the invention for example comprises lower alkyl esters of a mixture of saturated and unsaturated straight chain fatty acids of from 12 to 22 C-atoms, derived from vegetable or oleaginous seeds. The term “lower alkyl ester” means C_1-C_5-esters, in particular methyl and ethyl esters. The mixture of methyl esters of the saturated, monounsaturated and polyunsaturated C_{16}-C_{22}-fatty acids are what is known as “biodiesel” or “rapeseed methyl ester”.

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

The 3-arylbenzofuranones antioxidants of the invention are for example those disclosed in *U.S. patent Nos. 4,325,863; U.S. 4,388,244; U.S. 5,175,312; U.S. 5,252,643; U.S. 5,216,052; U.S. 5,369,159; U.S. 5,488,117; U.S. 5,356,966; U.S. 5,367,008; U.S. 5,428,162; U.S. 5,428,177;* and *U.S. 5,516,920*.

Particularly suitable 3-arylbenzofuranones in the invention are compounds of the formula I

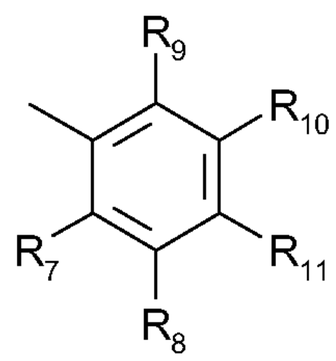


(I),

in which, if n is 1,

R_1 is 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, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, 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 any of these carbocyclic or heterocyclic groups substituted by C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4alkylthio-, hydroxyl-, halo-, amino-, C_1-C_4alkylamino-, phenylamino- or di(C_1-C_4alkyl)amino;

or R_1 is a radical of the formula II

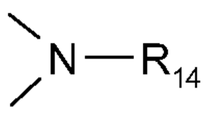


(II)

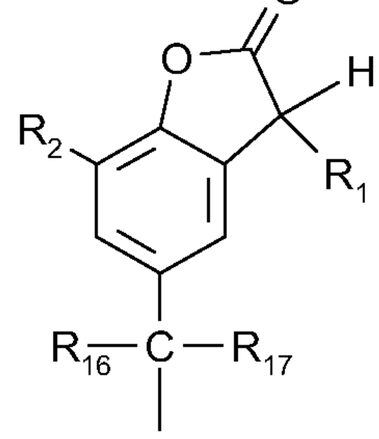
and

if n is 2,

R_1 is unsubstituted or C_1-C_4alkyl- 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_9phenylalkyl, unsubstituted or C_1-C_4alkyl-substituted phenyl; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl; C_1-C_{18}alkoxy, C_1-C_{18}alkylthio, C_1-C_4alkylamino, di(C_1-C_4alkyl)-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, sulphur or  ; C_6-C_9cycloalkylcarbonyloxy, benzoyloxy or

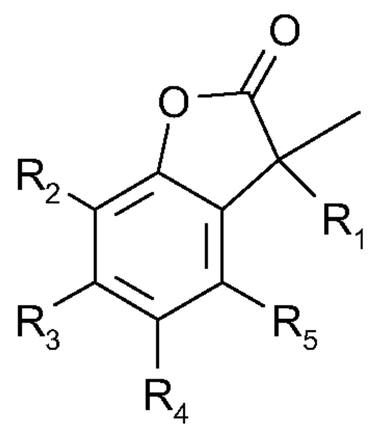
C_1-C_{12}alkyl-substituted benzoyloxy; or, in the alternative, if the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5, together with the C-atoms to which they are attached, form a benzo ring, R_4 is additionally -$(CH_2)_p$-COR_{15} or -$(CH_2)_q$OH or, if R_3, R_5 and R_6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



(III)

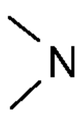
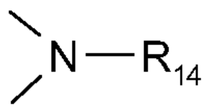
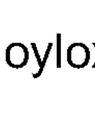
in which R_1 is defined as indicated above for n = 1,

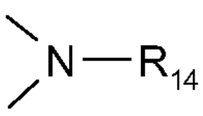
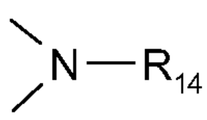
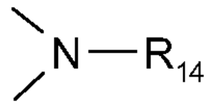
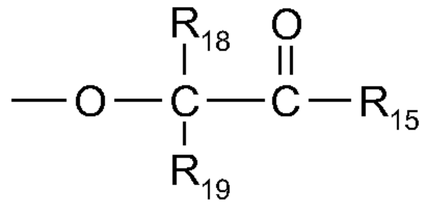
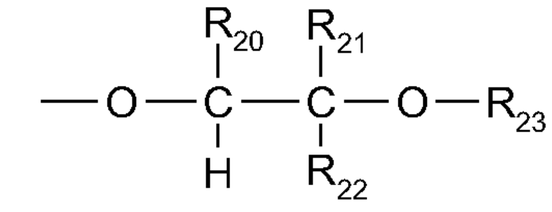
R_6 is hydrogen or a radical of the formula IV



(IV)

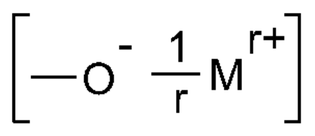
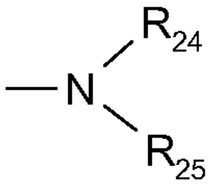
where R_4 is other than a radical of the formula III and R_1 is defined as indicated above for n = 1,

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, sulphur or  ; C_1-C_{25}alkoxy, C_2-C_{25}alkoxy interrupted by oxygen, sulphur or  ; C_1-C_{25}alkylthio, C_3-C_{25}alkenyl, C_3-C_{25}alkenyloxy, C_3-C_{25}alkynyl, C_3-C_{25}alkynyloxy, C_7-C_9phenylalkyl, C_7-C_9phenylalkoxy, unsubstituted or C_1-C_4alkyl-substituted phenyl; unsubstituted or C_1-C_4alkyl-substituted phenoxy; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkoxy; C_1-C_4alkylamino, di(C_1-C_4alkyl)amino, C_1-C_{25}alkanoyl, C_3-C_{25}alkanoyl interrupted by oxygen, sulphur or  ; C_1-C_{25}alkanoyloxy, C_3-C_{25}alkanoyloxy inter-

rupted by oxygen, sulphur or  ; C_1-C_{25}alkanoylamino, C_3-C_{25}alkenoyl, C_3-C_{25}alkenoyl interrupted by oxygen, sulphur or  ; C_3-C_{25}alkenoyloxy, C_3-C_{25}alkenoyloxy interrupted by oxygen, sulphur or  ; C_6-C_9cycloalkylcarbonyl, C_6-C_9cycloalkylcarbonyloxy, benzoyl or C_1-C_{12}alkyl-substituted benzoyl; benzoyloxy or C_1-C_{12}alkyl-substituted benzoyloxy;  or  , or in the alternative, in formula II, the radicals R_7 and R_8 or the radicals R_8 and R_{11}, together with the C-atoms to which they are attached, form a benzene ring,

R_{12} and R_{13} independently of one another are unsubstituted or C_1-C_4alkyl-substituted phenylene or naphthylene,

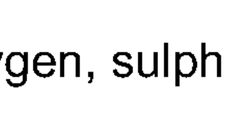
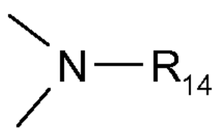
R_{14} is hydrogen or C_1-C_8alkyl,

R_{15} is hydroxyl,  , C_1-C_{18}alkoxy or  ,

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_8cycloalkylidene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl;

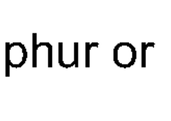
R_{18} and R_{19} independently of one another are hydrogen, C_1-C_4alkyl or phenyl,

R_{20} is hydrogen or C_1-C_4alkyl,

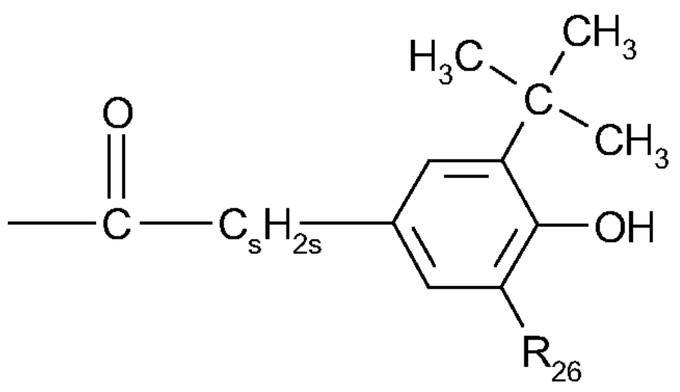
R_{21} is hydrogen, unsubstituted or C_1-C_4alkyl-substituted phenyl; C_1-C_{25}alkyl, C_2-C_{25}alkyl interrupted by oxygen, sulphur or  ; C_7-C_9phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl; C_7-C_{25}phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl and interrupted by oxygen, sulphur or  , or, in the alternative, the radicals R_{20} and R_{21}, together with the C-atoms to

which they are attached, form a C_5-C_{12}cycloalkylene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl;

R_{22} is hydrogen or C_1-C_4alkyl,

R_{23} is hydrogen, C_1-C_{25}alkanoyl, C_3-C_{25}alkenoyl, C_3-C_{25}alkanoyl interrupted by oxygen, sulphur or  ; C_2-C_{25}alkanoyl substituted by a di(C_1-C_6alkyl)phosphonate group;

C_6-C_9cycloalkylcarbonyl, thienoyl, furoyl, benzoyl or C_1-C_{12}alkyl-substituted benzoyl;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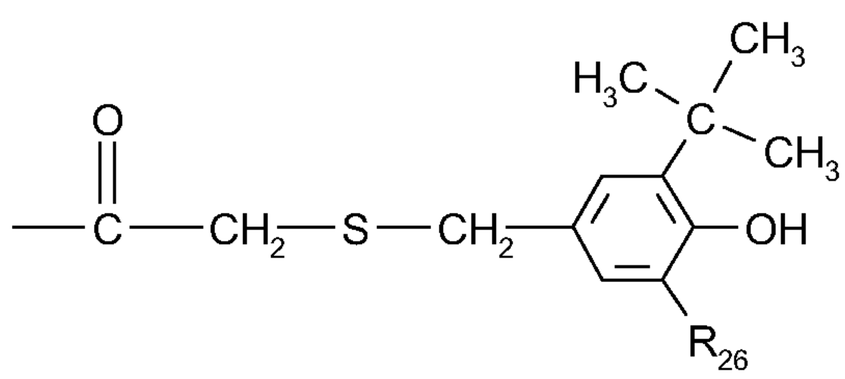
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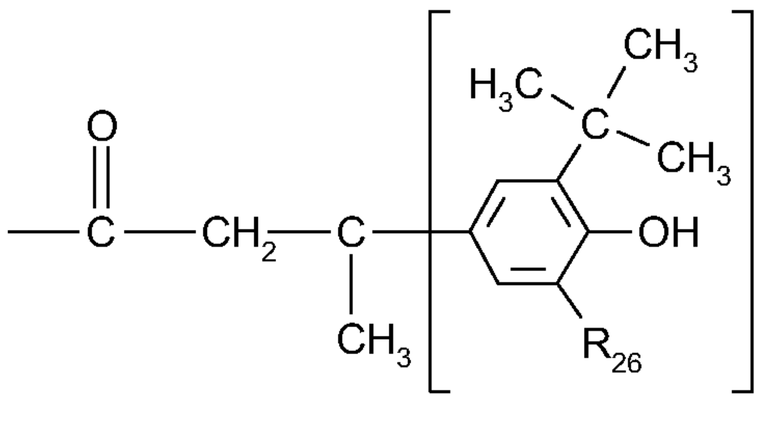
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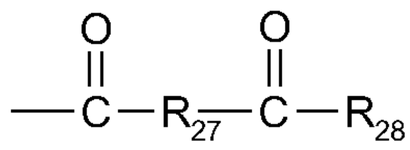
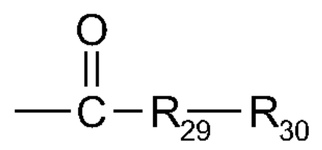
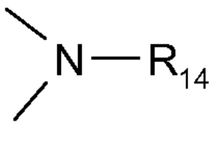
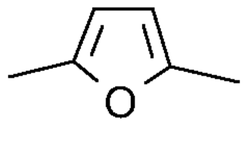
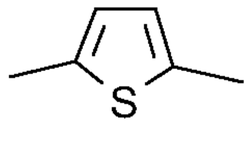

or

,

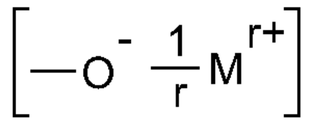
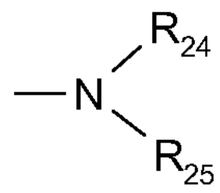
R_{24} and R_{25} independently of one another are hydrogen or C_1-C_{18}alkyl,

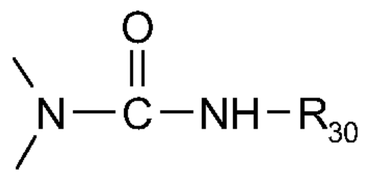
R_{26} is hydrogen or C_1-C_8alkyl,

R_{27} is a direct bond, C_1-C_{18}alkylene, C_2-C_{18}alkylene interrupted by oxygen, sulphur or  ; C_2-C_{18}alkenylene, C_2-C_{20}alkylidene, C_7-C_{20}phenylalkylidene,

C_5-C_8cycloalkylene, C_7-C_8bicycloalkylene, unsubstituted or C_1-C_4alkyl-substituted phenylene,

or  or  ,

R_{28} is hydroxyl,  , C_1-C_{18}alkoxy or  ,

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, sulphur 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.

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, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, 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 any of these carbocyclic or heterocyclic groups substituted by C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4alkylthio-, hydroxyl-, halo-, amino-, C_1-C_4alkylamino-, phenylamino- or di(C_1-C_4alkyl)amino 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-indolizinyl, 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-quinolizinyl, 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-quinazolinyl, 3-cinnolinyl, 6-cinnolinyl, 7-cinnolinyl, 3-methoxy-7-cinnolinyl, 2-pteridinyl, 6-pteridinyl, 7-pteridinyl, 6,7-dimethoxy-2-pteridinyl, 2-carbazolyl, 3-carbazolyl, 9-methyl-2-carbazolyl, 9-methyl-3-carbazolyl, β-carbolin-3-yl, 1-methyl-β-carbolin-3-yl, 1-methyl-β-carbolin-6-yl, 3-phenanthridinyl, 2-acridinyl, 3-acridinyl, 2-perimidinyl, 1-methyl-5-perimidinyl, 5-phenanthrolinyl, 6-phenanthrolinyl, 1-phenazinyl, 2-phenazinyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 2-phenothiazinyl, 3-phenothiazinyl, 10-methyl-3-phenothiazinyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 4-methyl-3-furazanyl, 2-phenoxazinyl or 10-methyl-2-phenoxazinyl.

Particular preference is given to unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4alkylthio-, hydroxyl-, phenylamino- or di(C_1-C_4alkyl)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, 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.

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

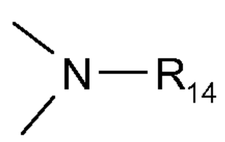
Alkanoyl having up to 25 C-atoms is a branched or unbranched radical, for example, formyl, acetyl, propionyl, butanoyl, pentanoyl, hexanoyl, heptanoyl, octanoyl, nonanoyl, decanoyl, undecanoyl, dodecanoyl, tridecanoyl, tetradecanoyl, pentadecanoyl, hexadecanoyl, heptadecanoyl, octadecanoyl, eicosanoyl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

C_2-C_{25}alkanoyl substituted by a di(C_1-C_6alkyl)phosphonate group is, for example, $(CH_3CH_2O)_2POCH_2CO$-, $(CH_3O)_2POCH_2CO$-, $(CH_3CH_2CH_2CH_2O)_2POCH_2CO$-,

$(CH_3CH_2O)_2POCH_2CH_2CO$-, $(CH_3O)_2POCH_2CH_2CO$-, $(CH_3CH_2CH_2CH_2O)_2POCH_2CH_2CO$-, $(CH_3CH_2O)_2PO(CH_2)_4CO$-, $(CH_3CH_2O)_2PO(CH_2)_8CO$- or $(CH_3CH_2O)_2PO(CH_2)_{17}CO$-.

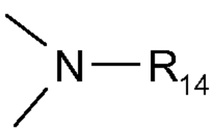
Alkanoyloxy having up to 25 C-atoms is a branched or unbranched radical, for example, formyloxy, acetoxy, propionyloxy, butanoyloxy, pentanoyloxy, hexanoyloxy, heptanoyloxy, octanoyloxy, nonanoyloxy, decanoyloxy, undecanoyloxy, dodecanoyloxy, tridecanoyloxy, tetradecanoyloxy, pentadecanoyloxy, hexadecanoyloxy, heptadecanoyloxy, octadecanoyloxy, eicosanoyloxy or docosanoyloxy. Preference is given to alkanoyloxy having 2 to 18, especially 2 to 12, for example 2 to 6 C-atoms. Particular preference is given to acetoxy.

Alkenoyl having 3 to 25 C-atoms is a branched or unbranched radical, 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 C-atoms.

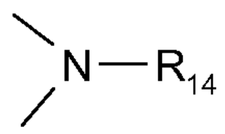
C_3-C_{25}alkenoyl interrupted by oxygen, sulphur or  is, for example,

$CH_3OCH_2CH_2CH=CHCO$- or $CH_3OCH_2CH_2OCH=CHCO$-.

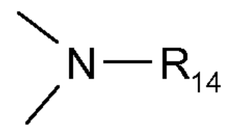
Alkenoyloxy having 3 to 25 C-atoms is a branched or unbranched radical, for example, propenoyloxy, 2-butenoyloxy, 3-butenoyloxy, isobutenoyloxy, n-2,4-pentadienoyloxy, 3-methyl-2-butenoyloxy, n-2-octenoyloxy, n-2-dodecenoyloxy, iso-dodecenoyloxy, oleoyloxy, n-2-octadecenoyloxy or n-4-octadecenoyloxy.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

C_3-C_{25}alkenoyloxy interrupted by oxygen, sulphur or  is, for example,

$CH_3OCH_2CH_2CH=CHCOO$- or $CH_3OCH_2CH_2OCH=CHCOO$-.

C_3-C_{25}alkanoyl interrupted by oxygen, sulphur 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-CH_2CO-, CH_3-(O-CH_2CH_2-)$_2$O-CH_2CO-, CH_3-(O-CH_2CH_2-)$_3$O-CH_2CO- or CH_3-(O-CH_2CH_2-)$_4$O-CH_2CO-.

C_3-C_{25}alkanoyloxy interrupted by oxygen, sulphur or  is, for example, CH_3-O-CH_2COO-, CH_3-S-CH_2COO-, CH_3-NH-CH_2COO-, CH_3-N(CH_3)-CH_2COO-, CH_3-O-CH_2CH_2-O-CH_2COO-, CH_3-(O-CH_2CH_2-)$_2$O-CH_2COO-, CH_3-(O-CH_2CH_2-)$_3$O-CH_2COO- or CH_3-(O-CH_2CH_2-)$_4$O-CH_2COO-.

C_6-C_9cycloalkylcarbonyl is, for example, cyclopentylcarbonyl, cyclohexylcarbonyl, cycloheptylcarbonyl or cyclooctylcarbonyl. Cyclohexylcarbonyl is preferred.

C_6-C_9cycloalkylcarbonyloxy is, for example, cyclopentylcarbonyloxy, cyclohexylcarbonyloxy, cycloheptylcarbonyloxy or cyclooctylcarbonyloxy. Cyclohexylcarbonyloxy is preferred.

C_1-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-di-tert-butylbenzoyl. Preferred substituents are C_1-C_8alkyl, especially C_1-C_4alkyl.

C_1-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-ethyl-benzoyloxy, 2,4,6-trimethylbenzoyloxy, 2,6-dimethyl-4-tert-butylbenzoyloxy or 3,5-di-tert-butylbenzoyloxy. Preferred substituents are C_1-C_8alkyl, especially C_1-C_4alkyl.

Alkyl having up to 25 C-atoms is a branched or unbranched radical, 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, C_1-C_{18}alkyl. A particularly preferred meaning of R_4 is C_1-C_4alkyl.

Alkenyl having 3 to 25 C-atoms is a branched or unbranched radical, 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 C-atoms.

Alkenyloxy having 3 to 25 C-atoms is a branched or unbranched radical, for example, propenyloxy, 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 C-atoms.

Alkynyl having 3 to 25 C-atoms is a branched or unbranched radical, for example, propynyl ($-CH_2-C\equiv CH$), 2-butynyl, 3-butynyl, 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 C-atoms.

Alkynyloxy having 3 to 25 C-atoms is a branched or unbranched radical, for example, propynyloxy ($-OCH_2-C\equiv CH$), 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 C-atoms.

C_2-C_{25}alkyl interrupted by oxygen, sulphur or $>N-R_{14}$ is, for example, CH_3-O-CH_2-, CH_3-S-CH_2-, CH_3-NH-CH_2-, CH_3-N(CH_3)-CH_2-, CH_3-O-CH_2CH_2-O-CH_2-, CH_3-(O-CH_2CH_2-)$_2$O-CH_2-, CH_3-(O-CH_2CH_2-)$_3$O-CH_2- or CH_3-(O-CH_2CH_2-)$_4$O-CH_2-.

C_7-C_9phenylalkyl is, for example, benzyl, α-methylbenzyl, α,α-dimethylbenzyl or 2-phenylethyl. Benzyl and α,α-dimethylbenzyl are preferred.

C_7-C_9phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl 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.

C_7-C_{25}phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl and is interrupted by oxygen, sulphur or $>N-R_{14}$ is a branched or unbranched radical, for example, phenoxymethyl, 2-methylphenoxymethyl, 3-methylphenoxymethyl, 4-methylphenoxymethyl, 2,4-dimethylphenoxymethyl, 2,3-dimethylphenoxymethyl, 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, benzyloxyethoxymethyl, N-benzyl-N-ethylmethyl or N-benzyl-N-isopropylmethyl.

C_7-C_9phenylalkoxy is, for example, benzyloxy, α-methylbenzyloxy, α,α-dimethylbenzyloxy or 2-phenylethoxy. Benzyloxy is preferred.

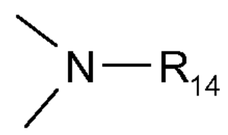
C_1-C_4alkyl-substituted phenyl, which preferably contains 1 to 3, especially 1 or 2 alkyl groups, is, for example, o-, m- or p-methylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, 3,5-dimethylphenyl, 2-methyl-6-ethylphenyl, 4-tert-butylphenyl, 2-ethylphenyl or 2,6-diethylphenyl.

C_1-C_4alkyl-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.

Unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl is, for example, cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl, dimethylcyclohexyl, trimethylcyclohexyl, tert-butylcyclohexyl, cycloheptyl or cyclooctyl. Preference is given to cyclohexyl and tert-butylcyclohexyl.

Unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkoxy is, for example, cyclopentoxy, methylcyclopentoxy, dimethylcyclopentoxy, cyclohexoxy, methylcyclohexoxy, dimethylcyclohexoxy, trimethylcyclohexoxy, tert-butylcyclohexoxy, cycloheptoxy or cyclooctoxy. Preference is given to cyclohexoxy and tert-butylcyclohexoxy.

Alkoxy having up to 25 C-atoms is a branched or unbranched radical, 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 C-atoms.

C_2-C_{25}alkoxy interrupted by oxygen, sulphur 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-)$_2$O-CH_2CH_2O-, CH_3-(O-CH_2CH_2-)$_3$O-CH_2CH_2O- or CH_3-(O-CH_2CH_2-)$_4$O-CH_2CH_2O-.

Alkylthio having up to 25 C-atoms is a branched or unbranched radical, 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 C-atoms.

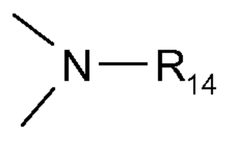
Alkylamino having up to 4 C-atoms is a branched or unbranched radical, for example, methylamino, ethylamino, propylamino, isopropylamino, n-butylamino, isobutylamino or tert-butylamino.

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

Alkanoylamino having up to 25 C-atoms is a branched or unbranched radical, for example, formylamino, acetylamino, propionylamino, butanoylamino, pentanoylamino, hexanoylamino, heptanoylamino, octanoylamino, nonanoylamino, decanoylamino, undecanoylamino, dodecanoylamino, tridecanoylamino, tetradecanoylamino, pentadecanoylamino, hexadecaneoylamino, heptadecanoylamino, octadecanoylamino, eicosanoylamino or docosanoylamino. Preference is given to alkanoylamino having 2 to 18, especially 2 to 12, for example 2 to 6 C-atoms.

C_1-C_{18}alkylene is a branched or unbranched radical, 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_8alkylene.

A C_1-C_4alkyl-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.

C_2-C_{18}alkylene interrupted by oxygen, sulphur or  is, for example, $-CH_2-O-CH_2-$, $-CH_2-S-CH_2-$, $-CH_2-NH-CH_2-$, $-CH_2-N(CH_3)-CH_2-$, $-CH_2-O-CH_2CH_2-O-CH_2-$, $-CH_2-(O-CH_2CH_2-)_2O-CH_2-$, $-CH_2-(O-CH_2CH_2-)_3O-CH_2-$, $-CH_2-(O-CH_2CH_2-)_4O-CH_2-$ or $-CH_2CH_2-S-CH_2CH_2-$.

C_2-C_{18}alkenylene is, for example, vinylene, methylvinylene, octenylethylene or dodecenylethylene. Preference is given to C_2-C_8alkenylene.

Alkylidene having 2 to 20 C-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.

Phenylalkylidene having 7 to 20 C-atoms is, for example, benzylidene, 2-phenylethylidene or 1-phenyl-2-hexylidene. Preference is given to C_7-C_9-phenylalkylidene.

C_5-C_8cycloalkylene 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.

C_7-C_8bicycloalkylene is, for example, bicycloheptylene or bicyclooctylene.

Unsubstituted or C_1-C_4alkyl-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.

A C_1-C_4alkyl-substituted C_5-C_8cycloalkylidene 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.

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^{+++}.

A particularly preferred composition of the invention contains at least one 3-arylbenzofuranone of formula I, wherein, if 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_4alkyl)amino; mono- to penta-substituted alkylphenyl containing together a total of at most 18 C-atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothiazinyl or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylthio, hydroxy or amino.

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

R_1 is -R_{12}-X-R_{13}-,

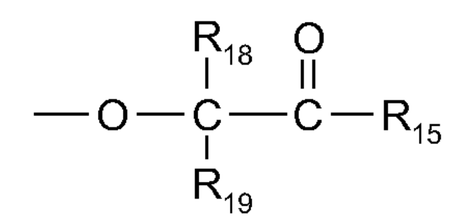
R_{12} and R_{13} are phenylene,

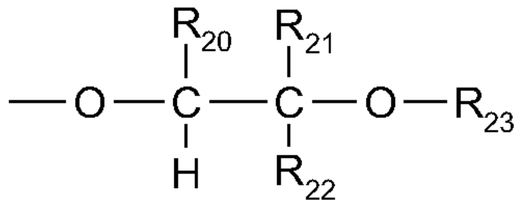
X is oxygen or -NR_{31}-, and

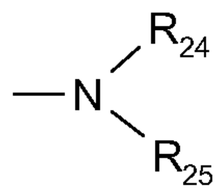
R_{31} is C_1-C_4alkyl.

Preference is also given to compounds of the formula I in which, if n is 1,

R_1 is unsubstituted or C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4alkylthio-, hydroxyl-, halo-, amino-, C_1-C_4alkylamino- or di(C_1-C_4-alkyl)amino-substituted naphthyl, phenanthryl, thienyl, dibenzofuryl, carbazolyl, fluorenyl or a radical of the formula II, wherein

R_7, R_8, R_9, R_{10} and R_{11} independently of one another are hydrogen, chlorine, bromine, hydroxyl, C_1-C_{18}alkyl, C_2-C_{18}alkyl interrupted by oxygen or sulphur; C_1-C_{18}alkoxy, C_2-C_{18}alkoxy interrupted by oxygen or sulphur; C_1-C_{18}alkylthio, C_3-C_{12}alkenyloxy, C_3-C_{12}alkynyloxy, C_7-C_9phenylalkyl, C_7-C_9phenylalkoxy, unsubstituted or C_1-C_4alkyl-substituted phenyl; phenoxy, cyclohexyl, C_5-C_8cycloalkoxy, C_1-C_4alkylamino, di(C_1-C_4-alkyl)amino, C_1-C_{12}alkanoyl, C_3-C_{12}alkanoyl interrupted by oxygen or sulphur; C_1-C_{12}alkanoyloxy, C_3-C_{12}alkanoyloxy interrupted by oxygen or sulphur; C_1-C_{12}alkanoylamino, C_3-C_{12}alkenoyl, C_3-C_{12}alkenoyloxy, cyclohexylcarbonyl, cyclohexylcarbonyloxy, benzoyl or C_1-C_4alkyl-substituted benzoyl; benzoyloxy or C_1-C_4alkyl-substituted benzoyloxy;  or

 or, in the alternative, in formula II the radicals R_7 and R_8 or the radicals R_8 and R_{11}, together with the C-atoms to which they are attached, form a benzene ring,

R_{15} is hydroxyl, C_1-C_{12}alkoxy or  ,

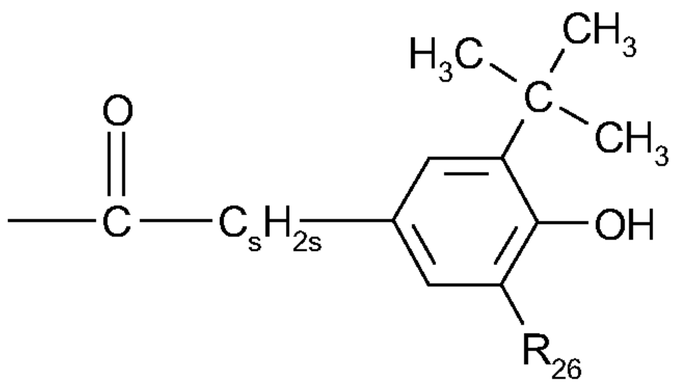
R_{18} and R_{19} independently of one another are hydrogen or C_1-C_4alkyl,

R_{20} is hydrogen,

R_{21} is hydrogen, phenyl, C_1-C_{18}alkyl, C_2-C_{18}alkyl interrupted by oxygen or sulphur; C_7-C_9phenylalkyl, C_7-C_{18}-phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl and is interrupted by oxygen or sulphur, or, in the alternative, the radicals R_{20} and R_{21}, together with the C-atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl,

R_{22} is hydrogen or C_1-C_4alkyl,

R_{23} is hydrogen, C_1-C_{18}alkanoyl, C_3-C_{18}alkenoyl, C_3-C_{12}alkanoyl interrupted by oxygen or sulphur; C_2-C_{12}alkanoyl substituted by a di(C_1-C_6-alkyl)phosphonate group; C_6-C_9cycloalkyl-carbonyl, benzoyl,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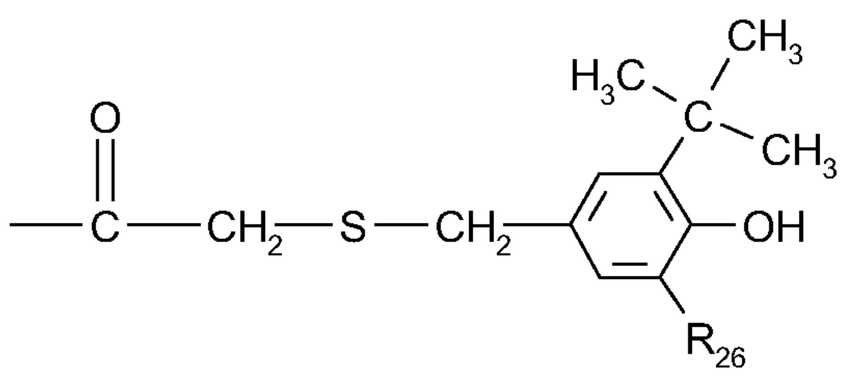
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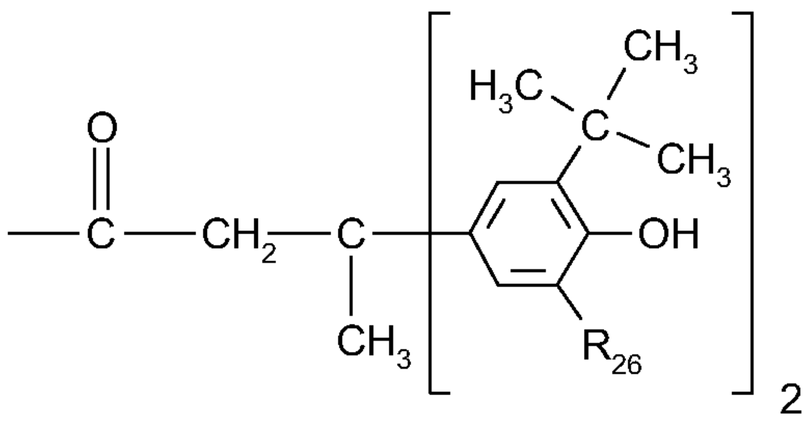
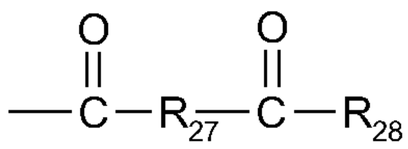
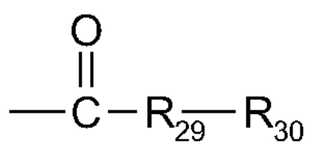
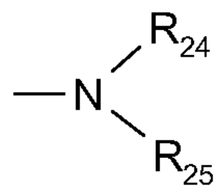

2 ,  or  ,

R_{24} and R_{25} independently of one another are hydrogen or C_1-C_{12}alkyl,

R_{26} is hydrogen or C_1-C_4alkyl,

R_{27} is C_1-C_{12}alkylene, C_2-C_8alkenylene, C_2-C_8alkylidene, C_7-C_{12}phenylalkylidene, C_5-C_8cyclo-alkylene or phenylene,

R_{28} is hydroxyl, C_1-C_{12}alkoxy or  ,

R_{29} is oxygen or -NH-,

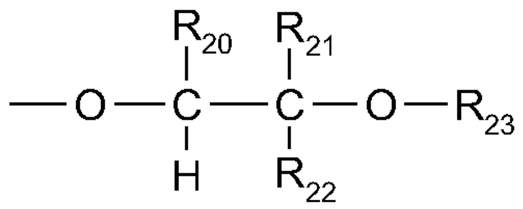
R_{30} is C_1-C_{18}alkyl or phenyl, and

s is 1 or 2.

Preference is likewise given to compounds of the formula I in which, if n is 1,

R_1 is phenanthryl, thienyl, dibenzofuryl, unsubstituted or C_1-C_4alkyl-substituted carbazolyl; or is fluorenyl; or R_1 is a radical of the formula II, wherein

R_7, R_8, R_9, R_{10} and R_{11} independently of one another are hydrogen, chlorine, hydroxyl, C_1-C_{18}alkyl, C_1-C_{18}alkoxy, C_1-C_{18}alkylthio, C_3-C_4alkenyloxy, C_3-C_4alkinyloxy,

C_2-C_{18}alkanoyloxy, phenyl, benzoyl, benzoyloxy or  ,

R_{20} is hydrogen,

R_{21} is hydrogen, phenyl or C_1-C_{18}alkyl, or, in the alternative, the radicals R_{20} and R_{21}, together with the C-atoms to which they are attached, form a cyclohexylene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl,

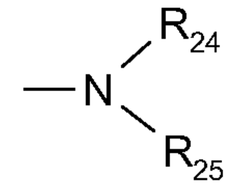
R_{22} is hydrogen or C_1-C_4alkyl, and

R_{23} is hydrogen, C_1-C_{18}alkanoyl or benzoyl.

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

R_7, R_8, R_9, R_{10} and R_{11} independently of one another are hydrogen, C_1-C_4alkylthio or phenyl.

Of particular interest is a composition containing at least one compound of the formula I in which R_2, R_3, R_4 and R_5 independently of one another are hydrogen, chlorine, C_1-C_{18}alkyl, benzyl, phenyl, C_5-C_8cycloalkyl, C_1-C_{18}alkoxy, C_1-C_{18}alkylthio, C_1-C_{18}alkanoyloxy, C_1-C_{18}alkanoylamino, C_3-C_{18}alkenoyloxy or benzoyloxy; or, in the alternative, 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 C-atoms to which they are attached, form a benzene 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,

R_{15} is hydroxyl, C_1-C_{12}alkoxy or  ,

R_{16} and R_{17} are methyl groups or, together with the C atom to which they are attached, form a C_5-C_8cycloalkylidene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl,

R_{24} and R_{25} independently of one another are hydrogen or C_1-C_{12}alkyl,

p is 1 or 2, and

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

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.

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

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

R_2 is C_1-C_4alkyl,

R_3 is hydrogen,

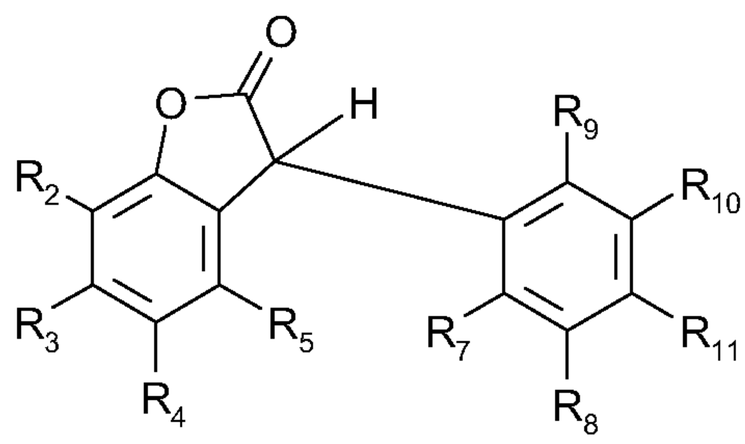
R_4 is C_1-C_4alkyl or, if R_6 is hydrogen, R_4 is additionally a radical of the formula III,

R_5 is hydrogen, and

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

The following compounds are examples of the benzofuran-2-one type which are particularly suitable in the composition of the 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.

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



(V),

in which

R_2 is hydrogen or C_1-C_6alkyl,

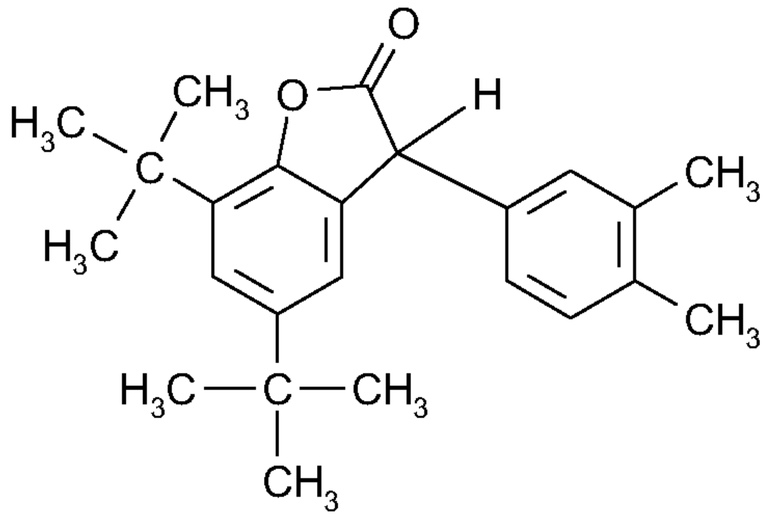
R_3 is hydrogen,

R_4 is hydrogen or C_1-C_6alkyl,

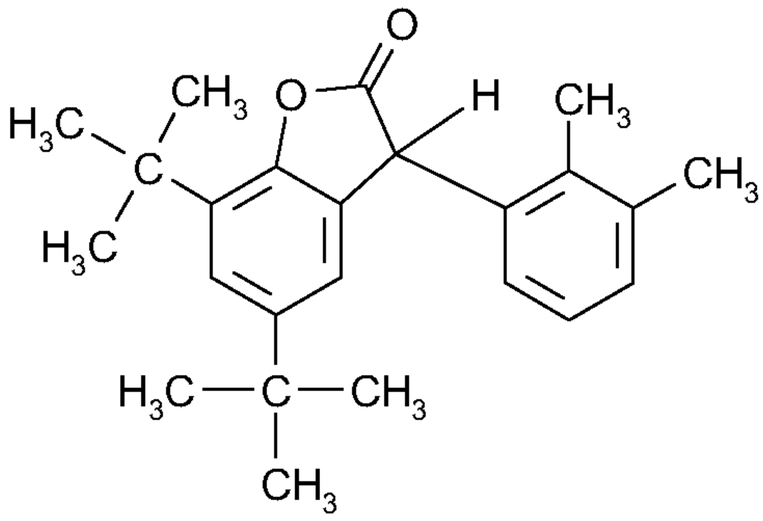
R_5 is hydrogen,

R_7, R_8, R_9, R_{10} and R_{11} independently of one another are hydrogen, C_1-C_4alkyl or C_1-C_4alkoxy, with the proviso that at least two of the radicals R_7, R_8, R_9, R_{10} or R_{11} are hydrogen.

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



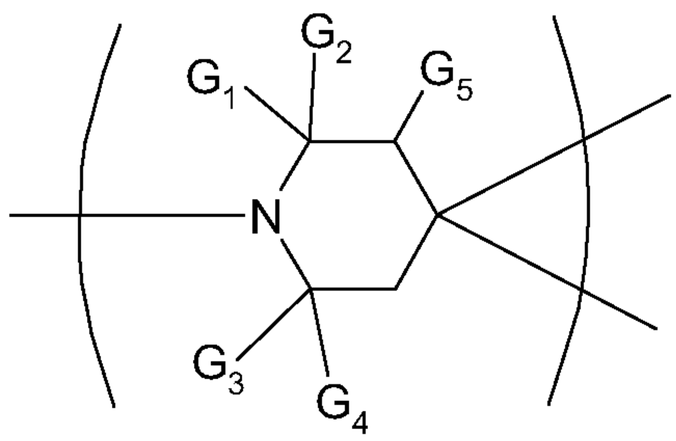
(Va)



(Vb)

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

The 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 C-atoms or G_1 and G_2 or G_3 and G_4 together are pentamethylene.

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 the published *U.S. application. Nos. 09/714,717*, filed Nov. 16, 2000 and *10/485,377*, filed August 6, 2002.

U.S. Pat. Nos. 6,271,377, 6,392,041 and *6,376,584*, cited above disclose hindered hydroxyalkoxyamine stabilizers.

Suitable hindered amines include for example:

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-hydroxybenzyl-malonate

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-butylamino}-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-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone),

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-oxo-spiro [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-C_{18}-C_{22}-α-olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine,

45) the oligomeric compound which is the condensation product of 4,4'-hexamethylenebis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(2,2,6,6-tetramethyl-

piperidin-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'-hexamethylenebis(amino-1,2,2,6,6-pentaamethylpiperidine) and 2,4-dichloro-6-[(1,2,2,6,6-pentaamethylpiperidin-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'-hexamethylenebis(amino-1-propoxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-propoxy-2,2,6,6-tetramethylpiperidin-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'-hexamethylenebis(amino-1-acyloxy-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-acyloxy-2,2,6,6-tetramethylpiperidin-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-aminopropylamino)ethane with cyanuric chloride, with (2,2,6,6-tetramethylpiperidin-4-yl)butylamine.

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.

The hindered phenolic antioxidants are for example

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

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

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

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

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α-methylcyclohexyl)-phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α-methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α-dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methyl-phenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3-tert-butyl-4-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclopentadiene, bis[2-(3'tert-butyl-2-hydroxy-5-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis-(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. Benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butyl-benzylmercaptoacetate, 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) sulphide, 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) iso-

cyanurate, 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid dioctadecyl ester and 3,5-di-tert-butyl-4-hydroxybenzyl-phosphoric acid monoethyl ester, calcium-salt.

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

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

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

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

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

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

1.14. Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, di-

ethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis-(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

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

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

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

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 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.

The 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

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 liter 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. A 6 hour induction time is necessary to meet the EN 14214 specification.

Claims

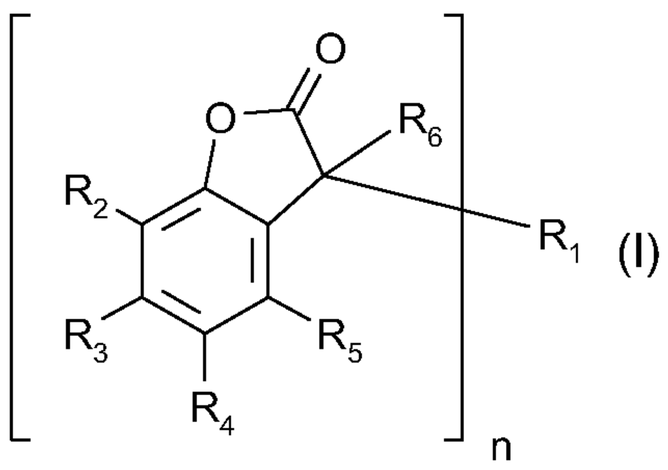
1. A biodiesel fuel composition stabilized against the deleterious effects of heat, light and oxygen, which composition comprises

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.

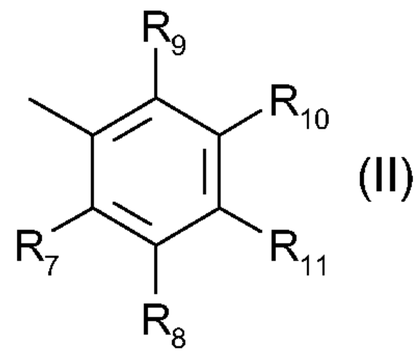
2. A composition according to claim **1** comprising one or more 3-arylbenzofuranone stabilizers of formula I



(I)

in which, if n is 1,

R_1 is 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, indolizinyl, isoindolyl, indolyl, indazolyl, purinyl, quinolizinyl, 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 any of these carbocyclic or heterocyclic groups substituted by C_1-C_4alkyl-, C_1-C_4alkoxy-, C_1-C_4alkylthio-, hydroxyl-, halo-, amino-, C_1-C_4alkylamino-, phenylamino- or di(C_1-C_4alkyl)amino; or R_1 is a radical of the formula II

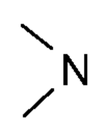


(II)

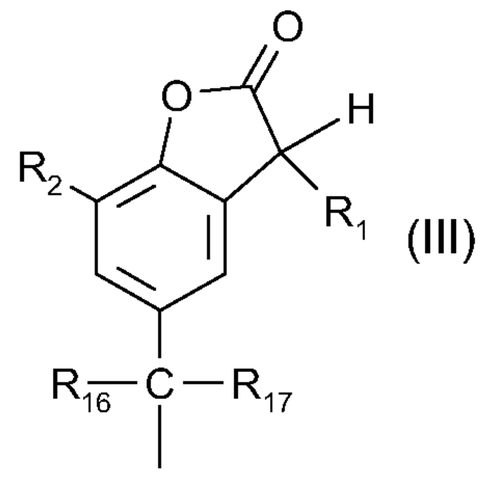
and

if n is 2,

R_1 is unsubstituted or C_1-C_4alkyl- 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_9phenylalkyl, unsubstituted or C_1-C_4alkyl-substituted phenyl; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl; C_1-C_{18}alkoxy, C_1-C_{18}alkylthio, C_1-C_4alkylamino, di(C_1-C_4alkyl)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, sulphur or  ; C_6-C_9cycloalkyl-carbonyloxy, benzoyloxy or

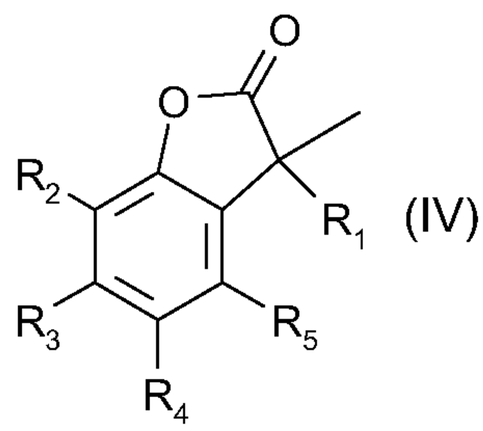
C_1-C_{12}alkyl-substituted benzoyloxy; or, in the alternative, the radicals R_2 and R_3 or the radicals R_3 and R_4 or the radicals R_4 and R_5, together with the C-atoms to which they are attached, form a benzo ring, R_4 is additionally $-(CH_2)_p-COR_{15}$ or $-(CH_2)_qOH$ or, if R_3, R_5 and R_6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



(III)

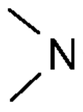
in which R_1 is defined as indicated above for n = 1,

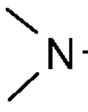
R_6 is hydrogen or a radical of the formula IV

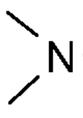
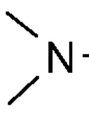
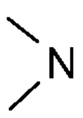
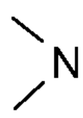
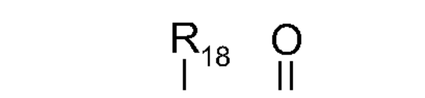
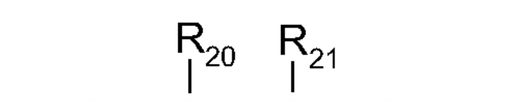


(IV)

where R_4 is other 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, sulphur or  ; C_1-C_{25}alkoxy,

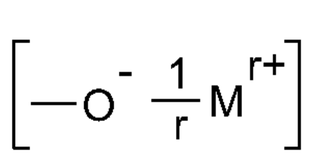
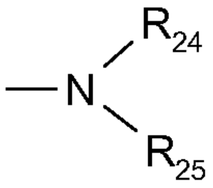
C_2-C_{25}alkoxy interrupted by oxygen, sulphur or  ; C_1-C_{25}alkylthio, C_3-C_{25}alkenyl,

C_3-C_{25}alkenyloxy, C_3-C_{25}alkynyl, C_3-C_{25}alkynyloxy, C_7-C_9phenylalkyl, C_7-C_9phenylalkoxy, unsubstituted or C_1-C_4alkyl-substituted phenyl; unsubstituted or C_1-C_4alkyl-substituted phenoxy; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkyl; unsubstituted or C_1-C_4alkyl-substituted C_5-C_8cycloalkoxy; C_1-C_4alkylamino, di(C_1-C_4alkyl)amino, C_1-C_{25}alkanoyl, C_3-C_{25}alkanoyl interrupted by oxygen, sulphur or  ; C_1-C_{25}alkanoyloxy, C_3-C_{25}alkanoyloxy interrupted by oxygen, sulphur or  ; C_1-C_{25}alkanoylamino, C_3-C_{25}alkenoyl, C_3-C_{25}alkenoyl interrupted by oxygen, sulphur or  ; C_3-C_{25}alkenoyloxy, C_3-C_{25}alkenoyloxy interrupted by oxygen, sulphur or  ; C_6-C_9cycloalkylcarbonyl, C_6-C_9cycloalkylcarbonyloxy, benzoyl or C_1-C_{12}alkyl-substituted benzoyl; benzoyloxy or C_1-C_{12}alkyl-substituted benzoyloxy;  or  , or

else, in formula II, the radicals R_7 and R_8 or the radicals R_8 and R_{11}, together with the C-atoms to which they are attached, form a benzo ring,

R_{12} and R_{13} independently of one another are unsubstituted or C_1-C_4alkyl-substituted phenylene or naphthylene,

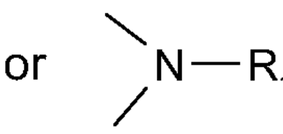
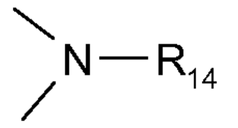
R_{14} is hydrogen or C_1-C_8alkyl,

R_{15} is hydroxyl,  , C_1-C_{18}alkoxy or  ,

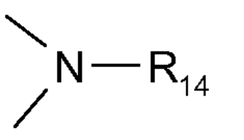
R_{16} and R_{17} independently of one another are hydrogen, CF_3, C_1-C_{12}alkyl or phenyl, or R_{16} and R_{17}, together with the C atom to which they are attached, form a C_5-C_8cycloalkylidene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl;

R_{18} and R_{19} independently of one another are hydrogen, C_1-C_4alkyl or phenyl,

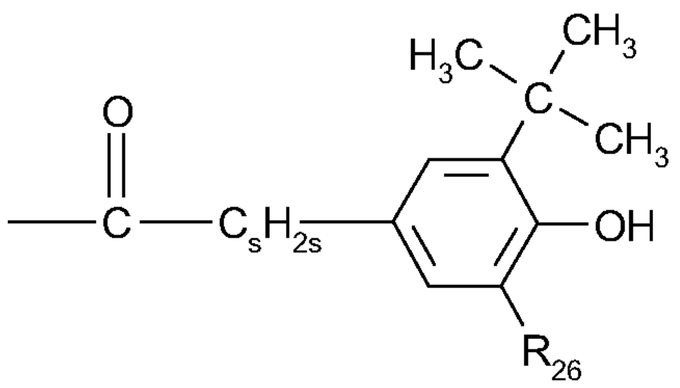
R_{20} is hydrogen or C_1-C_4alkyl,

R_{21} is hydrogen, unsubstituted or C_1-C_4alkyl-substituted phenyl; C_1-C_{25}alkyl, C_2-C_{25}alkyl interrupted by oxygen, sulphur or  ; C_7-C_9phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl; C_7-C_{25}phenylalkyl which is unsubstituted or substituted on the phenyl radical by 1-3 C_1-C_4alkyl and interrupted by oxygen, sulphur or  , or, in the alternative, the radicals R_{20} and R_{21}, together with the C-atoms to which they are attached, form a C_5-C_{12}cycloalkylene ring which is unsubstituted or substituted by 1-3 C_1-C_4alkyl;

R_{22} is hydrogen or C_1-C_4alkyl,

R_{23} is hydrogen, C_1-C_{25}alkanoyl, C_3-C_{25}alkenoyl, C_3-C_{25}alkanoyl interrupted by oxygen, sulphur or  ; C_2-C_{25}alkanoyl substituted by a di(C_1-C_6alkyl)phosphonate group;

C_6-C_9cycloalkylcarbonyl, thenoyl, furoyl, benzoyl or C_1-C_{12}alkyl-substituted benzoyl;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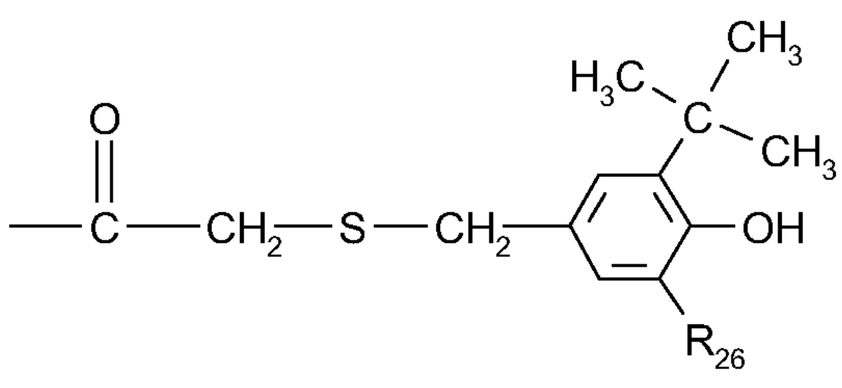
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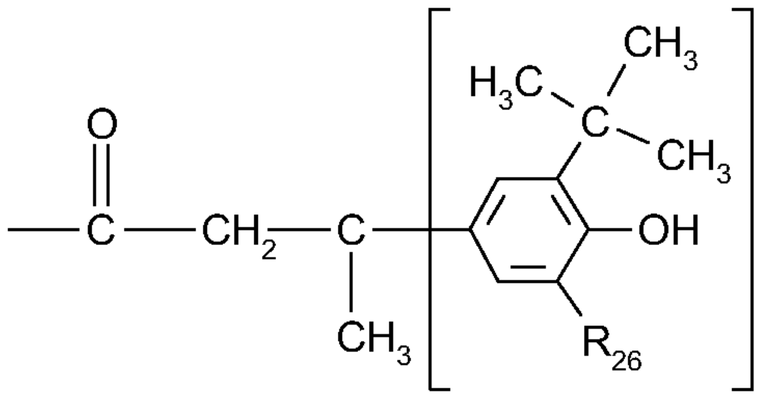
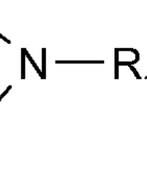

,

or

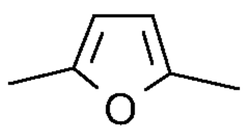
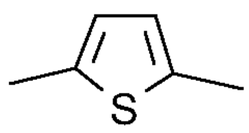
,

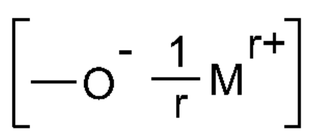
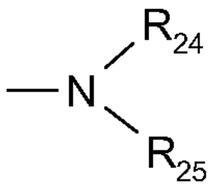
R_{24} and R_{25} independently of one another are hydrogen or C_1-C_{18}alkyl,

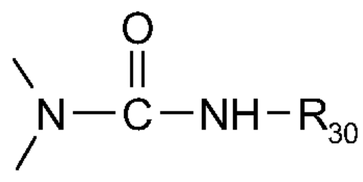
R_{26} is hydrogen or C_1-C_8alkyl,

R_{27} is a direct bond, C_1-C_{18}alkylene, C_2-C_{18}alkylene interrupted by oxygen, sulphur or  ; C_2-C_{18}alkenylene, C_2-C_{20}alkylidene, C_7-C_{20}phenylalkylidene,

C_5-C_8cycloalkylene, C_7-C_8bicycloalkylene, unsubstituted or C_1-C_4alkyl-substituted phenylene,

or  or  ,

R_{28} is hydroxyl,  , C_1-C_{18}alkoxy or  ,

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, sulphur 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.

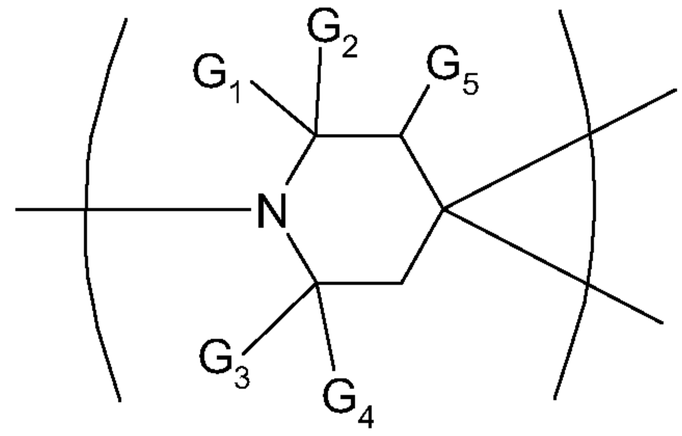
3. A composition according to claim **2** wherein the 3-arylbenzofuranones are of formula I wherein n = 1, R_1 is phenyl which is unsubstituted or substituted in para-position by C_1-C_{18}alkylthio or di(C_1-C_4alkyl)amino; mono- to penta-substituted alkyphenyl containing together a total of at most 18 C-atoms in the 1 to 5 alkyl substituents; naphthyl, biphenyl, terphenyl, phenanthryl, anthryl, fluorenyl, carbazolyl, thienyl, pyrrolyl, phenothiazinyl or 5,6,7,8-tetrahydronaphthyl, each of which is unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, C_1-C_4alkylthio, hydroxy or amino.

4. A composition according to claim **2** 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_4alkyl.

5. A composition according to claim **2** 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-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 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 G_1, G_2, G_3, G_4 and G_5 are independently alkyl of 1 to 8 C-atoms or G_1 and G_2 or G_3 and G_4 together are pentamethylene.

7. 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.

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

9. A composition according to claim **8,** 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.

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