

Process for increasing the oxidation stability of biodiesel

5 The invention relates to a process for increasing the oxidation stability of biodiesel.

Biodiesel, which consists of monoalkyl esters of vegetable oils, animal fats and also used cooking oils, is increasingly becoming an alternative to conventional
10 diesel fuel. Biodiesel is obtained by transesterifying oils, for example rapeseed oil, soybean oil or sunflower oil, but also used cooking oils, with an alcohol in the presence of a catalyst.

15 Since the significance of biodiesel has in recent times gained ever greater significance as an alternative diesel fuel in the motor vehicle sector, the production of biodiesel has also increased correspondingly in the last few years. Biodiesel has a high content of
20 unsaturated fatty acid esters which can readily be oxidized by atmospheric oxygen. The products formed (including acids, resins) can lead to corrosion and blockages in injection pumps and/or feed lines. The increasing use of the alternative biodiesel as an
25 automobile fuel leads to a need for oxidation-stabilized biodiesel. According to the prior art, the primary antioxidant added to the biodiesel is preferably 2,6-di-*tert*-butyl-4-methylphenol (BHT), in order to meet the oxidation stability required in the
30 standard DIN EN 14214.

The use of 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant is described by the European patent EP 0 189 049. Herein, the use of 2,6-di-*tert*-butyl-4-
35 methylphenol in amounts of from 10 to 100 ppm as the exclusive stabilizer in palm kernel fatty acid methyl esters of the C₁₂-C₁₈ fatty acid range is described.

DE 102 52 714 and WO 2004/044104, respectively, also describe a process for increasing the oxidation stability of biodiesel by adding di-2,6-*tert*-butyl-4-hydroxytoluene. A liquid stock solution which contains
5 from 15 to 60% by weight of mono- or dialkylhydroxytoluene dissolved in biodiesel is metered into the biodiesel to be stabilized up to a concentration of from 0.005 to 2% by weight of mono- or dialkylhydroxytoluene based on the overall solution of
10 biodiesel.

DE 102 52 715 describes a process for increasing the storage stability of biodiesel in which a liquid stock solution which contains from 15 to 60% by weight of
15 2,4-di-*tert*-butylhydroxytoluene dissolved in biodiesel is metered into the biodiesel to be stabilized up to a concentration of from 0.005 to 2% by weight of 2,4-di-*tert*-butylhydroxytoluene, based on the overall solution of biodiesel.

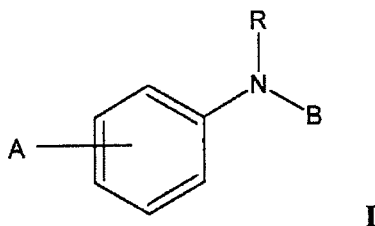
20 It was an object of the present invention to provide an improved process for increasing the oxidation stability of biodiesel; more particularly, it was an object of the present invention to provide an aging stabilizer
25 for biodiesel which has, in particular, improved effectiveness compared to additives for biodiesel according to the prior art, for example 2,6-di-*tert*-butylhydroxytoluene.

30 It has been found that, surprisingly, phenylene-diamines, and also the diphenylamines which are typically used as ozone protectants for rubber or as stabilizers for synthetic lubricants and fossil fuels, are effective for the stabilization of biodiesel. The
35 effectiveness of this compound class of the phenylenediamines is in many cases higher than that of the phenolic antioxidants used to date, while the effectiveness of the diphenylamines is comparable with

the effectiveness of the phenolic antioxidants. Owing to the distinctly higher effectiveness, significantly smaller amounts can be additized in order to achieve the same stability of the biodiesel.

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The present invention therefore provides a process for increasing the oxidation stability of biodiesel, in which at least one aging stabilizer of the structure **I**



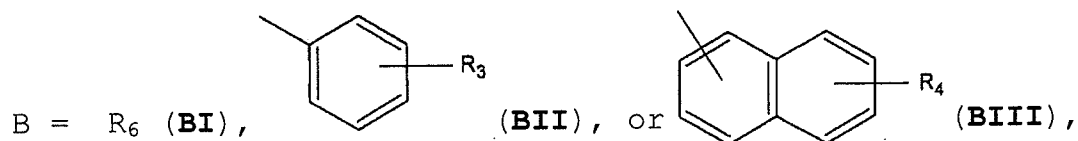
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where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group

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A = R₅ (**AI**) or -NR₁R₂ (**AII**) and



20

where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group, are the same or different, and the phenyl or naphthyl structural unit in structure **I**, **BII** and **BIII** has one, two or three substituents of the R₃, R₄ and/or R₅ type,

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is added to the biodiesel to be stabilized in an amount of from 5 to 20 000 ppm (w/w).

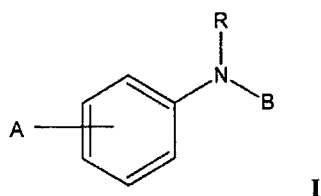
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The invention further provides for the use of compounds of the structure **I** as aging stabilizers for increasing the oxidation stability of biodiesel.

The invention likewise provides oxidation-stabilized biodiesel which comprises from 5 to 20 000 ppm (w/w) of at least one aging stabilizer of the structure **I**.

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In the process according to the invention for increasing the oxidation stability of biodiesel, at least one aging stabilizer of the structure **I**



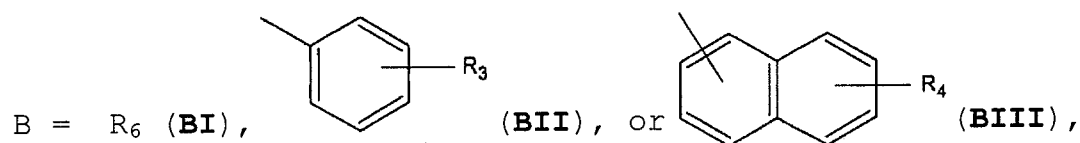
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where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group

15

A = R₅ (**AI**) or -NR₁R₂ (**AII**) and



20

where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group, are the same or different, and the phenyl or naphthyl structural unit in structure **I**, **BII** and **BIII** has one, two or three substituents of the R₃, R₄ and/or R₅ type,

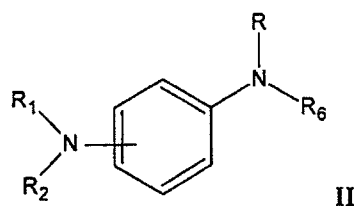
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is added to the biodiesel to be stabilized in an amount of from 5 to 20 000 ppm (w/w), preferably from 50 to 12 000 ppm (w/w) and more preferably from 100 to 8000 ppm (w/w).

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In the process according to the invention, preference is given to using at least one aging stabilizer of the structure **I** where the substituent of the A type = **AI** and that of the B type = **BII** or **BIII**, or the substituent of the A type = **AII** and that of the B type = **BI**.

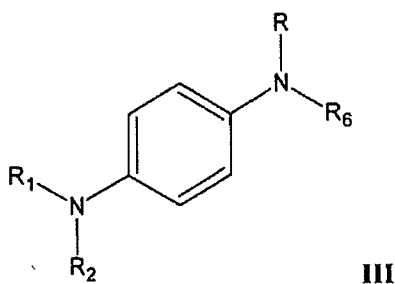
In the process according to the invention, preference is given to using at least one aging stabilizer of the structure **II**



where:

R , R_1 , R_2 and R_6 = hydrogen, alkyl, cycloalkyl and/or aryl group, where the substituents of the R , R_1 , R_2 and R_6 type are the same or different,

particular preference to using at least one aging stabilizer of the structure **III**:



where:

R , R_1 , R_2 and R_6 = hydrogen, alkyl, cycloalkyl and/or aryl group, where the substituents of the R , R_1 , R_2 and R_6 type are the same or

different.

In the process according to the invention, it is possible to use at least one aging stabilizer of the structure **III** which has, as substituents of the R, R₁, R₂ and R₆ type, alkyl, cycloalkyl and/or aryl groups having a number of carbon atoms of from 1 to 20, preferably from 1 to 10, or hydrogen.

The alkyl groups of the substituents of the R, R₁, R₂ and R₆ type may be either linear or branched. The alkyl groups of the substituents of the R, R₁, R₂ and R₆ type are preferably unsubstituted. Particular preference is given to alkyl groups selected from isopropyl, 1-methylethyl, sec-butyl, 1,3-dimethylbutyl, 1,4-dimethylpentyl, 1-ethyl-3-methylpentyl and 1-methylheptyl group, as substituents of the R, R₁, R₂ and R₆ type.

A suitable cycloalkyl group is preferably the cyclohexyl group for the substituents of the R, R₁, R₂ and R₆ type. The aryl group of the substituents of the R, R₁, R₂ and R₆ type is preferably a phenyl, tolyl or naphthyl group, these aryl groups being substituted or unsubstituted.

In particular, in the process according to the invention, at least one aging stabilizer of the structure **III** where the substituents of the R and R₁ type are each hydrogen is added; preference is given to adding an aging stabilizer of the structure **III** where the substituents of the R and R₁ type are each hydrogen and the substituents of the R₂ and R₆ type are identical.

Aging stabilizers selected from N,N'-dialkyl-p-phenylenediamines, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine

(44PD), N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine
(77PD), N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylene-
diamine (DOPD) or N,N'-bis(1-methylheptyl)-p-
phenylenediamine, N,N'-dicycloalkyl-p-phenylene-
5 diamines, for example N,N'-dicyclohexyl-p-phenylene-
diamine, and N,N'-diaryl-p-phenylenediamines, for
example N,N'-diphenyl-p-phenylenediamine, N,N'-ditolyl-
p-phenylenediamine and N,N'-di(naphth-2-yl)-p-
phenylenediamine are added with particular preference
10 to the biodiesel to be stabilized in the process
according to the invention.

It is alternatively possible in the process according
to the invention to add aging stabilizers of the
15 structure **III** where the substituents of the R and R₁
type here too are each hydrogen, but the two
substituents of the R₂ and R₆ type are different from
one another. Preference is given here to using aging
stabilizers selected from N-isopropyl-N'-phenyl-p-
20 phenylenediamine (IPPD), N-(1,3-dimethylbutyl)-N'-
phenyl-p-phenylenediamine (6PPD), N-(1-methylethyl)-N'-
phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-
phenyl-p-phenylenediamine, N-isopropyl-N'-phenyl-p-
phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylene-
25 diamine and N,N'-diaryl-p-phenylenediamine derivatives.

In a particular embodiment in the process according to
the invention, aging stabilizers of the structure **I** are
added to the biodiesel to be stabilized, where the
30 substituent of the A type = **AI** and that of the B type =
BII or **BIII**. In particular, aging stabilizers selected
from diphenylamine, alkylated diphenylamines, these
alkyl groups on the phenyl structural units
particularly having from 1 to 10 carbon atoms,
35 preferably from 4 to 9 carbon atoms, and styrenated
diphenylamines are used here.

The aging stabilizers of the structure **I** to **III** may be

used in the process according to the invention either as a single aging stabilizer or as a mixture of different compounds of structures **I** to **III**.

5 In the process according to the invention, in addition to the aging stabilizers of the structures **I** to **III**, it is also possible to use so-called primary and/or secondary antioxidants, as a pure substance or as a mixture of different primary and secondary
10 antioxidants. In the context of this invention, primary antioxidants are understood to mean compounds which are capable of stopping free-radical degradation reactions by chain termination reactions as free-radical scavengers.

15

The primary antioxidants added to the biodiesel to be stabilized in the process according to the invention may be sterically hindered phenols, preferably selected from

20 - alkylated monophenols, preferably 2-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-*iso*-butylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-
25 dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-*tert*-butyl-4-methoxymethylphenol, nonylphenols where the nonyl group may be linear or branched, for example 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-
30 6-(1'-methyl-undec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyl-heptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyl-tridec-1'-yl)phenol, tri-*tert*-butylphenols, especially 2,4,6-tri-*tert*-butylphenol, di-*tert*-butylphenols, especially 2,4-di-*tert*-butylphenol, 2,5-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, di-*tert*-butylmethylphenols, especially 2,5-di-*tert*-butyl-4-methylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 4,6-di-*tert*-

butyl-2-methylphenol, di-*tert*-butyl-3-methylphenol, *tert*-butylmethylphenols, especially 2-*tert*-butyl-4-methylphenol, 6-*tert*-butyl-2-methylphenol, 4-*tert*-butyl-2-methylphenol, 6-*tert*-butyl-3-methylphenol, *tert*-butyldimethylphenols, especially 4-*tert*-butyl-2,6-dimethylphenol, 6-*tert*-butyl-2,4-dimethylphenol, *tert*-butyl-2,5-dimethylphenol, *tert*-butylphenols, especially 2-*tert*-butylphenol, 4-*tert*-butylphenol, di-*sec*-butylphenols, *sec*-butylphenols, especially 2-*sec*-butylphenol, 2-*sec*-butyl-4-*tert*-butylphenol, 4-*sec*-butyl-2,6-di-*tert*-butylphenol, *tert*-amylphenols, especially 2-*tert*-amylphenol, di-*tert*-amylphenols, especially 2,4-di-*tert*-amylphenol, 2-isopropylphenol, 4-octylphenol, 4-nonylphenols, especially 2,6-di-*tert*-butyl-4-nonylphenol, 4-dodecylphenol, octadecylphenol;

- alkylthiomethylphenols, preferably 2,4-dioctylthiomethyl-6-*tert*-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol;
- hydroquinones and alkylated hydroquinones, preferably 2,6-di-*tert*-butyl-4-methoxyphenol, *tert*-butylhydroquinone (TBHQ), especially 2,5-di-*tert*-butyl-hydroquinone, 2,6-di-*tert*-butyl-hydroquinone, 2,5-di-*tert*-amyl-hydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, butylated hydroxyanisole (BHA), especially 2,5-di-*tert*-butyl-4-hydroxyanisole, 3,5-di-*tert*-butyl-4-hydroxyphenyl stearate, bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) adipate;
- tocopherols, preferably α -, β -, γ - or δ -tocopherols (vitamin E);
- hydroxylated thiodiphenyl ethers, preferably 2,2'-thiobis[4-octylphenol], 2,2'-thiobis[6-*tert*-butyl-4-methylphenol], 4,4'-bis[2,6-dimethyl-4-hydroxyphenyl] disulfide, 4,4'-thiobis[2-*tert*-butyl-5-methylphenol], 4,4'-thiobis[3,6-di-*sec*-amylphenol], 4,4'-thiobis[6-*tert*-butyl-2-methyl-

phenol], 4,4'-thiobis[6-*tert*-butyl-3-methylphenol];
- alkylated bisphenols, preferably 2,2'-ethylidene-
bis[4,6-di-*tert*-butylphenol], 2,2'-ethylidenebis-
[6-*tert*-butyl-4-isobutylphenol], 2,2'-iso-
5 butylidenebis[4,6-dimethylphenol], 2,2'-methylene-
bis[4,6-di-*tert*-butylphenol], 2,2'-methylenebis-
[4-methyl-6-(α -methylcyclohexyl)phenol],
2,2'-methylenebis[4-methyl-6-cyclohexylphenol],
2,2'-methylenebis[4-methyl-6-nonylphenol],
10 2,2'-methylenebis[6-(α,α' -dimethylbenzyl)-4-nonyl-
phenol], 2,2'-methylenebis[6-(α -methylbenzyl)-
4-nonylphenol], 2,2'-methylenebis[6-cyclohexyl-
4-methylphenol], 2,2'-methylenebis[6-*tert*-butyl-
4-ethylphenol], 2,2'-methylenebis[6-*tert*-butyl-
15 4-methylphenol], 4,4'-butylidenebis[2-*tert*-butyl-
5-methylphenol], 4,4'-methylenebis[2,6-di-*tert*-
butylphenol], 4,4'-methylenebis[6-*tert*-butyl-
2-methylphenol], 4,4'-isopropylidenediphenol,
1,1-bis(5-*tert*-butyl-4-hydroxy-2-methylphenyl)-
20 butane, 2,6-bis(3-*tert*-butyl-5-methyl-2-hydroxy-
benzyl)-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-dodecyl-
mercaptobutane, ethylene glycol bis[3,3-bis-
25 (3'-*tert*-butyl-4'-hydroxyphenyl)butyrate],
bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl)dicyclo-
pentadiene, bis[2-(3'-*tert*-butyl-2'-hydroxy-
5'-methylbenzyl)-6-*tert*-butyl-4-methylphenyl]
terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxy-
30 phenyl)butane, 2,2-bis(3,5-di-*tert*-butyl-4-hydroxy-
phenyl)propane, 2,2-bis(5-*tert*-butyl-4-hydroxy-
2-methylphenyl)4-n-dodecylmercaptobutane,
1,1,5,5-tetrakis(5-*tert*-butyl-4-hydroxy-2-methyl-
phenyl)pentane;
35 - O-, N- and S-benzyl compounds, preferably
3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxydibenzyl
ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl
mercaptoacetate, tridecyl-4-hydroxy-3,5-di-*tert*-

- butylbenzyl mercaptoacetate, tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine, bis(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) sulfide,
5 *iso*-octyl-3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptoacetate;
- hydroxybenzylated malonates, preferably dioctadecyl 2,2-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-*tert*-butyl-4-hydroxy-5-methyl-
10 benzyl)malonate, didodecyl mercaptoethyl-2,2-bis-(3,5-di-*tert*-butyl-4-hydroxybenzyl)malonate, di[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis-(3,5-di-*tert*-butyl-4-hydroxybenzyl)malonate;
 - hydroxybenzylaromatics, preferably 1,3,5-tris-
15 (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;
 - triazine compounds, preferably 1,3,5-tris-
20 (3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(4-*tert*-butyl-3-hydroxy-2,6-dimethyl-
25 benzyl) isocyanurate, 2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 2,4,6-tris-(3,5-di-*tert*-butyl-hydroxyphenoxy)-1,2,3-triazine, 2,4-bisooctylmercapto-6-(3,5-di-*tert*-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-
30 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;
 - acylaminophenols, preferably 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-*tert*-butyl-
35 4-hydroxyphenyl) carbamate;
 - esters of β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionic acid, β -(5-*tert*-butyl-4-hydroxy-3-methylphenyl)propionic acid, β -(3,5-dicyclohexyl-

- 4-hydroxyphenyl)propionic acid and/or 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid, where the alcohol component may in each case be methanol, ethanol, n-octanol, iso-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)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane;
- amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)-propionic acid, for example N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine;
 - 20 - ascorbic acid (vitamin C);
 - pentaerythrityl tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (IRGANOX 1010), N,N'-hexane-1,6-diyl-bis[3-(3,5-di-tert-butyl-4-hydroxyphenylpropionamide)] (IRGANOX 1098), ethylene-bis(oxyethylene)-bis[3-(5-tert-butyl-4-hydroxy-m-tolyl)propionate] (IRGANOX 245)
- and mixtures of these compounds.

In the context of this invention, secondary antioxidants are understood to mean compounds which are capable of degrading hydroperoxide groups directly with reduction, without free radicals being formed again.

The secondary antioxidants used in the process according to the invention may be alkylthiomethylphenols, preferably selected from:

- 2,4-di-((octylthio)methyl)-6-tert-butylphenol,
- 2,4-di-((octylthio)methyl)-6-methylphenol,

- 2,4-di-((octylthio)methyl)-6-ethylphenol or
 - 2,6-di-((dodecylthio)methyl)-4-nonylphenol,
- hydroxylated thiodiphenyl ethers, preferably selected from
- 5 - 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] or
 - 10 - 4,4'-bis[2,6-dimethyl-4-hydroxyphenyl] disulfide,
- phosphites or phosphonites, preferably selected from
- triphenyl phosphite,
 - diphenyl alkyl phosphites,
 - phenyl dialkyl phosphites,
 - 15 - tris[nonylphenyl] phosphite,
 - trilauryl phosphite,
 - trioctadecyl phosphite,
 - distearyl pentaerythrityl diphosphite,
 - tris[2,4-di-tert-butylphenyl] phosphite,
 - 20 - diisodecyl pentaerythrityl diphosphite,
 - bis[2,4-di-tert-butylphenyl] pentaerythrityl diphosphite,
 - bis[2,6-di-tert-butyl-4-methylphenyl] pentaerythrityl diphosphite
 - 25 - bis[isodecyloxy] pentaerythrityl diphosphite
 - bis[2,4-di-tert-butyl-6-methylphenyl] pentaerythrityl diphosphite
 - bis[2,4,6-tri-tert-butylphenyl] pentaerythrityl diphosphite,
 - 30 - tristearyl sorbitol triphosphite,
 - tetrakis[2,4-di-tert-butylphenyl]-4,4'-biphenylene diphosphonite,
 - 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocine,
 - 35 - 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocine,
 - bis[2,4-di-tert-butyl-6-methylphenyl]methyl phosphite or

- bis[2,4-di-tert-butyl-6-methylphenyl]ethyl phosphite,
 - or peroxide-destroying compounds, preferably selected from
 - 5 - esters of β -thiodipropionic acid, preferably lauryl, stearyl, myristyl or tridecyl ester,
 - mercaptobenzimidazole,
 - zinc salt of 2-mercaptobenzimidazole,
 - zinc dibutyldithiocarbamate
 - 10 - dioctadecyl disulfide or
 - pentaerythrityl tetrakis[β -dodecylmercapto]-propionate,
 - or mixtures of these compounds.
- 15 In the context of this invention, biodiesel is understood to mean all saturated and/or unsaturated fatty acid alkyl esters usable as energy sources, especially fatty acid methyl esters or fatty acid ethyl esters. Examples of energy sources in the context of
- 20 this invention include both fuels as heating material and fuels for, for example, automobiles, trucks, ships or aircraft. In the process according to the invention, preference is given to using a biodiesel which is typically supplied under the name *Biodiesel* in Germany
- 25 for use as an automobile fuel. The biodiesel used in the process according to the invention comprises in particular C₁₂-C₂₄ fatty acid alkyl esters, preferably C₁₂-C₂₄ fatty acid methyl esters or C₁₂-C₂₄ fatty acid ethyl esters, which may be present in pure form or else
- 30 as a mixture. The biodiesel used in the process according to the invention may additionally contain all customary additives, for example primary and/or secondary antioxidants, antifoams, cold flow improvers. In the process according to the invention, preference
- 35 is given to using biodiesel which is produced from vegetable and/or animal oils by a transesterification process with an alcohol, preferably methanol or ethanol, more preferably methanol. In the process

according to the invention, preference is given to using biodiesel consisting of transesterification products of rapeseed oil, soybean oil, sunflower oil, palm oil, palm kernel oil, coconut oil, jatropha oil, cottonseed oil, peanut oil, cornseed oil and/or used cooking oils. However, particular preference is given to using biodiesel which is obtained by the transesterification mentioned from rapeseed oil, palm oil, sunflower oil or soybean oil. In the process according to the invention, it is also possible to use mixtures of the transesterification products of different vegetable and/or animal oils.

In a particular embodiment of the process according to the invention, the biodiesel used may be mixtures (also known as blends) of saturated and/or unsaturated fatty acid alkyl esters, in which case the fatty acid alkyl esters may also be present as a mixture of different fatty acid alkyl esters, with liquid energy sources, for example mineral diesel fuel, heating oil. Particular preference is given to using a mixture of mineral diesel fuel and from 0.1 to 99.9% by volume, in particular from 1 to 50% by volume and preferably from 2 to 25% by volume of saturated and/or unsaturated fatty acid alkyl esters. In a downstream process step of the process according to the invention, the oxidation-stabilized biodiesel may be added to a liquid energy source, especially mineral diesel fuel or heating oil, in an amount of from 0.1 to 99.9% by volume, in particular from 1 to 50% by volume and preferably from 2 to 25% by volume.

The aging stabilizer may be added to the biodiesel as a solid or as a liquid in the process according to the invention in an amount of from 5 to 20 000 ppm (w/w), preferably from 50 to 12 000 ppm (w/w) and more preferably from 100 to 8000 ppm (w/w). In this process step, it is also possible to add primary and/or

secondary antioxidants to the biodiesel in an amount of from 5 to 20 000 ppm (w/w) preferably from 50 to 12 000 ppm (w/w) and more preferably from 100 to 8000 ppm (w/w).

5

The aging stabilizers which are present in solid form at room temperature are preferably dissolved in the biodiesel in the process according to the invention with stirring at a temperature of from 18°C to 80°C, preferably from 20°C to 35°C. Aging stabilizers which are present in liquid form at room temperature may be mixed homogeneously by stirring with the biodiesel to be stabilized without a temperature increase.

15 In a particular embodiment of the process according to the invention, the aging stabilizer is dissolved in biodiesel to produce a masterbatch before the addition to the biodiesel energy source. For this purpose, preferably from 2 to 99% by weight, preferentially from 20 15 to 70% by weight, more preferably from 20 to 60% by weight of the aging stabilizer is first dissolved in biodiesel. This masterbatch can then be added to the biodiesel energy source, preferably with stirring at a temperature of from 18°C to 80°C, preferentially at 25 from 20°C to 35°C.

In a further embodiment of the process according to the invention, the aging stabilizer, when it is in solid form at room temperature, before the addition to the biodiesel, is dissolved in an organic solvent, preferably in an alcohol or in an aromatic. For this purpose, preferably from 10 to 60% by weight, preferentially from 15 to 50% by weight, more preferably from 20 to 40% by weight of the aging stabilizer is first dissolved in an alcohol, especially 35 ethanol, n- or isopropanol, n- or isobutanol, or in an aromatic, especially toluene, xylene. The solution of the aging stabilizer can then be added to the biodiesel

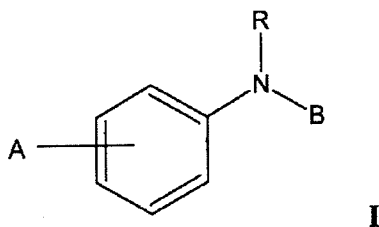
energy source, preferably with stirring at a temperature of from 18°C to 80°C, preferentially at from 20°C to 35°C.

5 However, the aging stabilizer can be added directly in the process according to the invention when the aging stabilizer is in liquid form, especially in an amount of from 5 to 20 000 ppm (w/w), preferably from 50 to 12 000 ppm (w/w) and preferentially from 100 to 8000 ppm (w/w), direct addition being understood to mean that there is no preparation of a solution or of a masterbatch of the aging stabilizer in a preceding process step. In this process step, primary and secondary antioxidants may also additionally be added 15 to the biodiesel in an amount of from 5 to 20 000 ppm (w/w), preferably of from 50 to 12 000 ppm (w/w) and preferentially of from 100 to 8000 ppm (w/w).

The aging stabilizer is preferably dissolved in the biodiesel with stirring at a temperature of from 18°C to 80°C, preferentially at from 20°C to 40°C.

The invention further provides for the use of compounds of the structure **I**

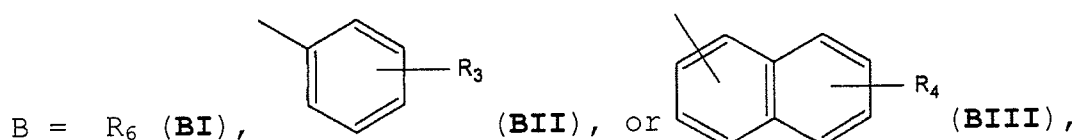
25



where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or 30 aryl group

A = R₅ (**AI**) or -NR₁R₂ (**AII**) and

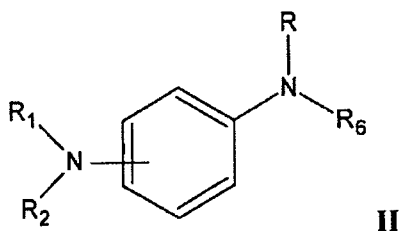


where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group, are the same or
5 different, and the phenyl or naphthyl structural unit in structure **I**, **BII** and **BIII** has one, two or three substituents of the R₃, R₄ and/or R₅ type,

as aging stabilizers for increasing the oxidation
10 stability of biodiesel.

In the process according to the invention, preference is given to using at least one aging stabilizer of the structure **I** where the substituent of the A type = **AI**
15 and that of the B type = **BII** or **BIII**, or the substituent of the A type = **AII** and that of the B type = **BI**.

In the inventive use, preference is given to using at
20 least one aging stabilizer consisting of phenylene-diamines of the structure **II**



where:

25 R, R₁, R₂ and R₆ = hydrogen, alkyl, cycloalkyl and/or aryl group, where the substituents of the R, R₁, R₂ and R₆ type are the same or different,

30 particular preference to using at least one aging

In particular, in the use according to the invention, at least one aging stabilizer of the structure **III** where the substituents of the R and R₁ type are each hydrogen is added to the biodiesel to be stabilized; preference is given to adding an aging stabilizer of the structure **III** where the substituents of the R and R₁ type are each hydrogen and the substituents of the R₂ and R₆ type are identical.

10

Aging stabilizers selected from N,N'-dialkyl-p-phenylenediamines, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine (44PD), N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine (77PD), N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine (DOPD) or N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicycloalkyl-p-phenylenediamines, for example N,N'-dicyclohexyl-p-phenylenediamine, and N,N'-diaryl-p-phenylenediamines, for example N,N'-diphenyl-p-phenylenediamine, N,N'-ditolyl-p-phenylenediamine and N,N'-di(naphth-2-yl)-p-phenylenediamine are added with particular preference to the biodiesel to be stabilized in the use according to the invention.

25

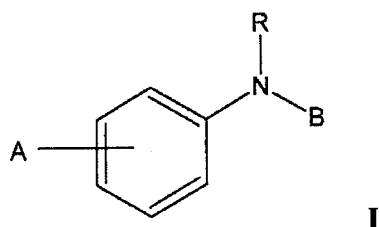
It is alternatively possible in the use according to the invention to add aging stabilizers of the structure **III** where the substituents of the R and R₁ type here too are each hydrogen, but the two substituents of the R₂ and R₆ type are different from one another. Preference is given here to using aging stabilizers selected from N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), N-(1-methylethyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine and N,N'-diaryl-p-phenylenediamine derivatives.

35

In a particular embodiment in the use according to the invention, aging stabilizers of the structure **I** are added to the biodiesel to be stabilized, where the substituent of the A type = **AI** and that of the B type = **BII** or **BIII**. In particular, aging stabilizers selected from diphenylamine, alkylated diphenylamines, particularly these alkyl groups on the phenyl structural units have from 1 to 10 carbon atoms, preferably from 4 to 9 carbon atoms, and styrenated diphenylamines are used here.

The aging stabilizers of the structure **I** to **III** may be used in the use according to the invention either as a single aging stabilizer or as a mixture of different compounds of structures **I** to **III**.

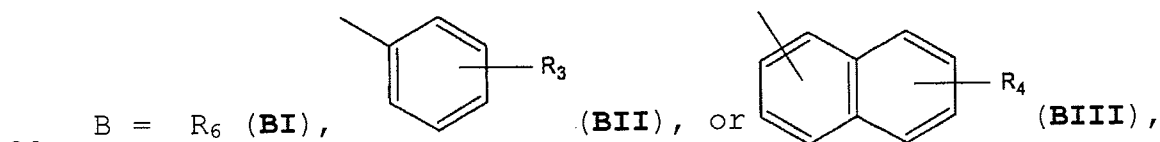
The invention likewise provides oxidation-stabilized biodiesel which comprises from 5 to 20 000 ppm (w/w), preferably from 50 to 12 000 ppm (w/w) and more preferably from 100 to 8000 ppm (w/w) of at least one aging stabilizer of the structure **I**



where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group

A = R₅ (**AI**) or -NR₁R₂ (**AII**) and

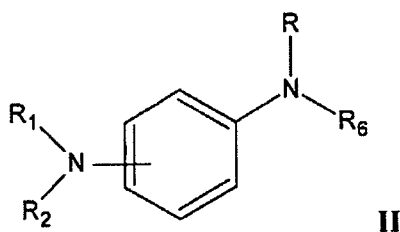


where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl,

alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group, are the same or different, and the phenyl or naphthyl structural unit in structure **I**, **BII** and **BIII** has one, two or three substituents of the R_3 , R_4 and/or R_5 type.

The inventive biodiesel preferably comprises at least one aging stabilizer of the structure **I** where the substituent of the A type = **AI** and that of the B type = **BII** or **BIII**, or the substituent of the A type = **AII** and that of the B type = **BI**.

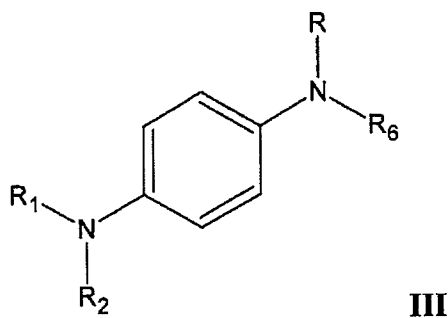
The inventive biodiesel preferably comprises at least one aging stabilizer of the structure **II**



where:

R , R_1 , R_2 and R_6 = hydrogen, alkyl, cycloalkyl and/or aryl group, where the substituents of the R , R_1 , R_2 and R_6 type are the same or different;

this biodiesel more preferably comprises at least one aging stabilizer of the structure **III**



where:

R , R_1 , R_2 and R_6 = hydrogen, alkyl, cycloalkyl

and/or aryl group, where the substituents of the R, R₁, R₂ and R₆ type are the same or different.

5 The inventive biodiesel may comprise at least one aging stabilizer of the structure **III** which has, as substituents of the R, R₁, R₂ and R₆ type, alkyl, cycloalkyl and/or aryl groups having a number of carbon atoms of from 1 to 20 and preferably of from 1 to 10, or hydrogen.

10 The alkyl groups of the substituents of the R, R₁, R₂ and R₆ type may be either linear or branched. The alkyl groups of the substituents of the R, R₁, R₂ and R₆ type are preferably unsubstituted. Particular preference is
15 given to alkyl groups selected from isopropyl, 1-methylethyl, sec-butyl, 1,3-dimethylbutyl, 1,4-dimethylpentyl, 1-ethyl-3-methylpentyl and 1-methylheptyl group, as substituents of the R, R₁, R₂ and R₆ type.

20 A suitable cycloalkyl group is preferably the cyclohexyl group for the substituents of the R, R₁, R₂ and R₆ type. The aryl group of the substituents of the R, R₁, R₂ and R₆ type is preferably a phenyl, tolyl or naphthyl
25 group, these aryl groups being substituted or unsubstituted.

In particular, the inventive biodiesel comprises at least one aging stabilizer of the structure **III** where
30 the substituents of the R and R₁ type are each hydrogen; this biodiesel preferably comprises at least an aging stabilizer of the structure **III** where the substituents of the R and R₁ type are each hydrogen and the substituents of the R₂ and R₆ type are identical.

35 Aging stabilizers selected from N,N'-dialkyl-p-phenylenediamines, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine

(44PD), N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine
(77PD), N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylene-
diamine (DOPD) or N,N'-bis(1-methylheptyl)-p-
phenylenediamine, N,N'-dicycloalkyl-p-phenylene-
5 diamines, for example N,N'-dicyclohexyl-p-phenylene-
diamine, and N,N'-diaryl-p-phenylenediamines, for
example N,N'-diphenyl-p-phenylenediamine, N,N'-ditolyl-
p-phenylenediamine and N,N'-di(naphth-2-yl)-p-
phenylenediamine are more preferably comprised in the
10 inventive biodiesel.

It is alternatively possible for the inventive
biodiesel to comprise aging stabilizers of the
structure **III** where the substituents of the R and R₁
15 type here too are each hydrogen, but the two
substituents of the R₂ and R₆ type are different from
one another. The inventive biodiesel preferably
comprises aging stabilizers selected from N-isopropyl-
N'-phenyl-p-phenylenediamine (IPPD), N-(1,3-
20 dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), N-
(1-methylethyl)-N'-phenyl-p-phenylenediamine, N-(1-
methylheptyl)-N'-phenyl-p-phenylenediamine, N-
isopropyl-N'-phenyl-p-phenylenediamine, N-cyclohexyl-
N'-phenyl-p-phenylenediamine and N,N'-diaryl-p-
25 phenylenediamine derivatives.

In a particular embodiment, the inventive biodiesel
comprises aging stabilizers of the structure **I** where
the substituent of the A type = **AI** and that of the B
30 type = **BII** or **BIII**. In particular, the inventive
biodiesel comprises aging stabilizers selected from
diphenylamine; alkylated diphenylamines, in particular,
these alkyl groups on the phenyl structural units have
from 1 to 10 carbon atoms, preferably from 4 to 9
35 carbon atoms, and styrenated diphenylamines.

The inventive biodiesel may comprise either the
compounds of the structures **I** to **III** as a pure

substance or as a mixture of different compounds of the structures **I** to **III** as aging stabilizers.

The inventive biodiesel comprises in particular C₁₂-C₂₄
5 fatty acid alkyl esters, preferably C₁₂-C₂₄ fatty acid
methyl esters or C₁₂-C₂₄ fatty acid ethyl esters, which
may be present in pure form or as a mixture. In
addition, the inventive biodiesel may comprise all
10 customary additives, for example primary and/or
secondary antioxidants, antifoams, cold flow improvers.
The inventive biodiesel preferably comprises
transesterification products of rapeseed oil, soybean
oil, sunflower oil, palm kernel oil, coconut oil,
15 jatropha oil, cottonseed oil, peanut oil, cornseed oil
and/or used cooking oils. The inventive biodiesel more
preferably comprises transesterification products which
are obtained by the transesterification of rapeseed
oil, palm oil, sunflower oil or soybean oil. The
inventive biodiesel may also comprise mixtures of the
20 transesterification products of different vegetable
and/or animal oils.

As primary antioxidants, the inventive biodiesel may
contain sterically hindered phenols, preferably
25 selected from

- alkylated monophenols, preferably 2-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-*iso*-butylphenol, 2,6-dicyclopentyl-
30 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 where the nonyl
group may be linear or branched, for example
35 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-
6-(1'-methyl-undec-1'-yl)phenol, 2,4-dimethyl-
6-(1'-methyl-heptadec-1'-yl)phenol, 2,4-dimethyl-
6-(1'-methyl-tridec-1'-yl)phenol, tri-*tert*-

butylphenols, especially 2,4,6-tri-*tert*-butylphenol, di-*tert*-butylphenols, especially 2,4-di-*tert*-butylphenol, 2,5-di-*tert*-butylphenol, 2,6-di-*tert*-butylphenol, di-*tert*-butylmethylphenols, especially 2,5-di-*tert*-butyl-4-methylphenol, 2,6-di-*tert*-butyl-4-methylphenol, 4,6-di-*tert*-butyl-2-methylphenol, di-*tert*-butyl-3-methylphenol, *tert*-butylmethylphenols, especially 2-*tert*-butyl-4-methylphenol, 6-*tert*-butyl-2-methylphenol, 4-*tert*-butyl-2-methylphenol, 6-*tert*-butyl-3-methylphenol, *tert*-butyldimethylphenols, especially 4-*tert*-butyl-2,6-dimethylphenol, 6-*tert*-butyl-2,4-dimethylphenol, *tert*-butyl-2,5-dimethylphenol, *tert*-butylphenols, especially 2-*tert*-butylphenol, 4-*tert*-butylphenol, di-*sec*-butylphenols, *sec*-butylphenols, especially 2-*sec*-butylphenol, 2-*sec*-butyl-4-*tert*-butylphenol, 4-*sec*-butyl-2,6-di-*tert*-butylphenol, *tert*-amylphenols, especially 2-*tert*-amylphenol, di-*tert*-amylphenols, especially 2,4-di-*tert*-amylphenol, 2-isopropylphenol, 4-octylphenol, 4-nonylphenols, especially 2,6-di-*tert*-butyl-4-nonylphenol, 4-dodecylphenol, octadecylphenol;

- alkylthiomethylphenols, preferably 2,4-dioctylthiomethyl-6-*tert*-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-didodecylthiomethyl-4-nonylphenol;
- hydroquinones and alkylated hydroquinones, preferably 2,6-di-*tert*-butyl-4-methoxyphenol, *tert*-butylhydroquinone (TBHQ), especially 2,5-di-*tert*-butyl-hydroquinone, 2,6-di-*tert*-butyl-hydroquinone, 2,5-di-*tert*-amyl-hydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, butylated hydroxyanisole (BHA), especially 2,5-di-*tert*-butyl-4-hydroxyanisole, 3,5-di-*tert*-butyl-4-hydroxyphenyl stearate, bis(3,5-di-*tert*-butyl-4-hydroxyphenyl) adipate;
- tocopherols, preferably α -, β -, γ - or δ -tocopherols (vitamin E);

- hydroxylated thiodiphenyl ethers, preferably
2,2'-thiobis[4-octylphenol], 2,2'-thiobis[6-tert-
butyl-4-methylphenol], 4,4'-bis[2,6-dimethyl-
4-hydroxyphenyl] disulfide, 4,4'-thiobis[2-tert-
5 butyl-5-methylphenol], 4,4'-thiobis[3,6-di-sec-
amylphenol], 4,4'-thiobis[6-tert-butyl-2-methyl-
phenol], 4,4'-thiobis[6-tert-butyl-3-methylphenol];
- alkylated bisphenols, preferably 2,2'-ethylidene-
bis[4,6-di-tert-butylphenol], 2,2'-ethylidenebis-
10 [6-tert-butyl-4-isobutylphenol], 2,2'-iso-
butylidenebis[4,6-dimethylphenol], 2,2'-methylene-
bis[4,6-di-tert-butylphenol], 2,2'-methylenebis-
[4-methyl-6-(α -methylcyclohexyl)phenol],
2,2'-methylenebis[4-methyl-6-cyclohexylphenol],
15 2,2'-methylenebis[4-methyl-6-nonylphenol],
2,2'-methylenebis[6-(α,α' -dimethylbenzyl)-4-nonyl-
phenol], 2,2'-methylenebis[6-(α -methylbenzyl)-
4-nonylphenol], 2,2'-methylenebis[6-cyclohexyl-
4-methylphenol], 2,2'-methylenebis[6-tert-butyl-
20 4-ethylphenol], 2,2'-methylenebis[6-tert-butyl-
4-methylphenol], 4,4'-butylidenebis[2-tert-butyl-
5-methylphenol], 4,4'-methylenebis[2,6-di-tert-
butylphenol], 4,4'-methylenebis[6-tert-butyl-
2-methylphenol], 4,4'-isopropylidenediphenol,
25 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-
butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxy-
benzyl)-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-dodecyl-
30 mercaptobutane, ethylene glycol bis[3,3-bis-
(3'-tert-butyl-4'-hydroxyphenyl)butyrate],
bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclo-
pentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-
5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]
35 terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxy-
phenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxy-
phenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-
2-methylphenyl)4-n-dodecylmercaptobutane,

- 1,1,5,5-tetrakis(5-*tert*-butyl-4-hydroxy-2-methyl-phenyl)pentane;
- 5 - O-, N- and S-benzyl compounds, preferably 3,5,3',5'-tetra-*tert*-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzyl mercaptoacetate, tridecyl-4-hydroxy-3,5-di-*tert*-butylbenzyl mercaptoacetate, tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)amine, bis(4-*tert*-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate,
- 10 bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) sulfide, *iso*-octyl-3,5-di-*tert*-butyl-4-hydroxybenzyl mercaptoacetate;
- 15 - hydroxybenzylated malonates, preferably dioctadecyl 2,2-bis(3,5-di-*tert*-butyl-2-hydroxybenzyl)malonate, dioctadecyl 2-(3-*tert*-butyl-4-hydroxy-5-methylbenzyl)malonate, didodecyl mercaptoethyl-2,2-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)malonate, di[4-(1,1,3,3-tetramethylbutyl)phenyl] 2,2-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)malonate;
- 20 - hydroxybenzylaromatics, preferably 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;
- 25 - triazine compounds, preferably 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine,
- 30 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, 2,4,6-tris(3,5-di-*tert*-butyl-hydroxyphenoxy)-1,2,3-triazine, 2,4-bis(octylmercapto-6-(3,5-di-*tert*-butyl-
- 35 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;

- acylaminophenols, preferably 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-*tert*-butyl-4-hydroxyphenyl) carbamate;
 - esters of β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-
5 propionic acid, β -(5-*tert*-butyl-4-hydroxy-3-methyl-phenyl)propionic acid, β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid and/or 3,5-di-*tert*-butyl-4-hydroxyphenyl acetic acid, where the alcohol component may in each case be methanol,
10 ethanol, n-octanol, *iso*-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,
15 N,N'-bis(hydroxyethyl)oxalamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane;
 - amides of β -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-
20 propionic acid, for example N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)trimethylenediamine, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)-
25 hydrazine;
 - ascorbic acid (vitamin C);
 - pentaerythrityl tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate] (IRGANOX 1010),
N,N'-hexane-1,6-diylbis[3-(3,5-di-*tert*-butyl-4-hydroxyphenylpropionamide)] (IRGANOX 1098),
30 ethylenebis(oxyethylene) bis[3-(5-*tert*-butyl-4-hydroxy-*m*-tolyl)propionate (IRGANOX 245)
and mixtures of these compounds.
- 35 As secondary antioxidants, the inventive biodiesel may comprise alkylthiomethylphenols, preferably selected from:
- 2,4-di-((octylthio)methyl)-6-*tert*-butylphenol,

- 2,4-di-((octylthio)methyl)-6-methylphenol,
 - 2,4-di-((octylthio)methyl)-6-ethylphenol or
 - 2,6-di-((dodecylthio)methyl)-4-nonylphenol,
- hydroxylated thiodiphenyl ethers, preferably selected
- 5 from
- 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],
- 10 - 4,4'-thiobis[3,6-di-sec-amylphenol] or
- 4,4'-bis[2,6-dimethyl-4-hydroxyphenyl] disulfide,
- phosphites or phosphonites, preferably selected from
- triphenyl phosphite,
 - diphenyl alkyl phosphites,
- 15 - phenyl dialkyl phosphites,
- tris[nonylphenyl] phosphite,
 - trilauryl phosphite,
 - trioctadecyl phosphite,
 - distearyl pentaerythrityl diphosphite,
- 20 - tris[2,4-di-tert-butylphenyl] phosphite,
- diisodecyl pentaerythrityl diphosphite,
 - bis[2,4-di-tert-butylphenyl] pentaerythrityl
- diphosphite,
- bis[2,6-di-tert-butyl-4-methylphenyl]
- 25 pentaerythrityl diphosphite
- bis[isodecyloxy] pentaerythrityl diphosphite
 - bis[2,4-di-tert-butyl-6-methylphenyl]
- pentaerythrityl diphosphite
- bis[2,4,6-tri-tert-butylphenyl] pentaerythrityl
- 30 diphosphite,
- tristearyl sorbityl triphosphite,
 - tetrakis[2,4-di-tert-butylphenyl]-4,4'-biphenylene
- diphosphonite,
- 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-
- 35 dibenz[d,g]-1,3,2-dioxaphosphocine,
- 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-
- dibenz[d,g]-1,3,2-dioxaphosphocine,
- bis[2,4-di-tert-butyl-6-methylphenyl]methyl

phosphite or
- bis[2,4-di-tert-butyl-6-methylphenyl]ethyl
phosphite,
or peroxide-destroying compounds, preferably selected
5 from
- esters of β -thiodipropionic acid, preferably
lauryl, stearyl, myristyl or tridecyl ester,
- mercaptobenzimidazole,
- zinc salt of 2-mercaptobenzimidazole,
10 - zinc dibutyldithiocarbamate
- dioctadecyl disulfide or
- pentaerythrityl tetrakis[β -dodecylmercapto]-
propionate,
or mixtures of these compounds.

15 In a particular embodiment of the inventive biodiesel,
it may comprise mixtures (also known as blends) of
saturated and/or unsaturated fatty acid alkyl esters,
which may also be present as a mixture of different
20 fatty acid alkyl esters, with liquid energy sources,
for example mineral diesel fuel, heating oil. The
inventive biodiesel more preferably comprises a mixture
of mineral diesel fuel and from 0.1 to 99.9% by volume,
especially from 1 to 50% by volume and preferably from
25 2 to 25% by volume of saturated and/or unsaturated
fatty acid alkyl esters.

The inventive biodiesel comprises the aging stabilizer
in an amount of from 5 to 20 000 ppm (w/w), preferably
30 of from 50 to 12 000 ppm (w/w) and more preferably of
from 100 to 8000 ppm (w/w). In addition, the inventive
biodiesel may also comprise primary and/or secondary
antioxidants in an amount of from 5 to 20 000 ppm
(w/w), preferably from 50 to 12 000 ppm (w/w) and more
35 preferably from 100 to 8000 ppm (w/w).

The inventive biodiesel is preferably produced by the
process according to the invention.

The examples which follow are intended to illustrate the process according to the invention in detail, without any intention that the invention be restricted to this embodiment.

Example 1 - Preparation of the samples

In a beaker, the aging stabilizer is dissolved in biodiesel at 20°C with stirring, the stirring being continued until a solution is obtained. The aging stabilizers used and the biodiesel used, and also the quantitative ratios, can be taken from Table 1.

Example 2 - Performance of the test method

The samples prepared in Example 1 were examined for their oxidation stability at a test temperature of 110°C in accordance with the test method DIN EN 14112.

Example 3 - Results of the test method

Table 1:

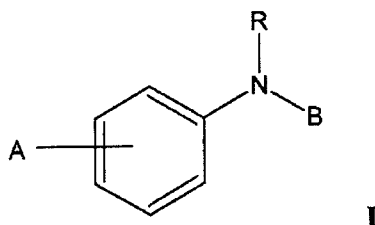
Aging stabilizer	Amount of aging stabilizer [in ppm]	Oxidation stability [in h at 110°C]
Biodiesel from used cooking oils and fats		
-	-	2.1
2,6-Di- <i>tert</i> -butyl- <i>p</i> -cresol (BHT)	1500	7.4
N-(1,3-Dimethyl-butyl)-N'-phenyl- <i>p</i> -phenylenediamine (6PPD)	1500	31.6
N-(1-Methylethyl)-N'-phenyl- <i>p</i> -phenylenediamine (IPPD)	1500	25.2
Mixture of different N,N'-diaryl- <i>p</i> -phenylenediamines (DAPD) ¹	1500	30.7

¹ The aging stabilizer had the following composition:

50-60% by weight of N-(1,4-dimethylphenyl)-N'-phenyl-*p*-phenylenediamine
 30-40% by weight of N-(1,3-dimethylbutyl)-N'-phenyl-*p*-phenylenediamine
 0-3% by weight of N-phenyl-*p*-phenylenediamine
 0-1% by weight of diphenylamines
 0-1% by weight of N-(1-methylethyl)-N'-phenyl-*p*-phenylenediamine

Claims:

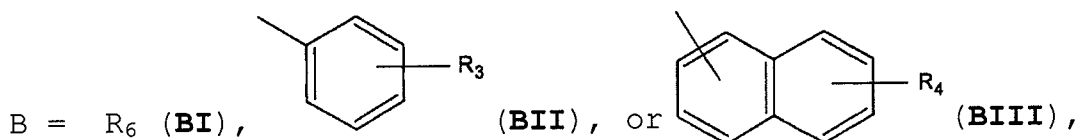
1. A process for increasing the oxidation stability of biodiesel,
characterized in that
at least one aging stabilizer of the structure



where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group

A = R₅ (**AI**) or -NR₁R₂ (**AII**) and



where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl, alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl, cycloalkyl, hydroxyl or aryl group, are the same or different, and the phenyl or naphthyl structural unit in structure **I**, **BII** and **BIII** has one, two or three substituents of the R₃, R₄ and/or R₅ type,

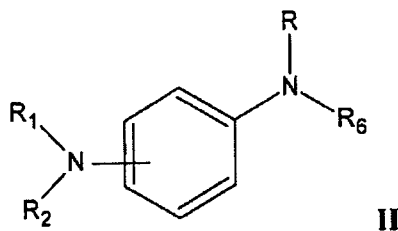
is added to the biodiesel to be stabilized in an amount of from 5 to 20 000 ppm (w/w).

2. A process according to claim 1, characterized in that the substituent of the A type = **AI** and that of the B type = **BII** or **BIII**, or the substituent of the A type = **AII** and that of the B type = **BI**.

3. A process according to claim 2,
characterized in that
the substituent of the A type = **AI** and that of the
B type = **BII** or **BIII**.

5

4. A process according to claim 2,
characterized in that
at least one aging stabilizer of the structure



10

where:

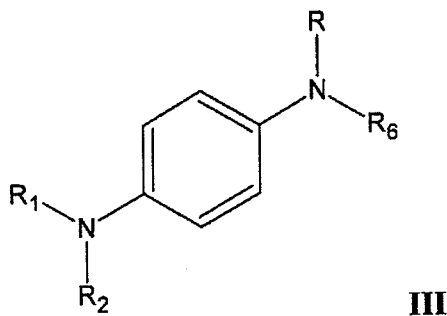
R, R₁, R₂ and R₆ = hydrogen, alkyl, cycloalkyl
and/or aryl group, where the substituents of
the R, R₁, R₂ and R₆ type are the same or
different

15

is used.

5. A process according to claim 4,
characterized in that
at least one aging stabilizer of the structure

20



where:

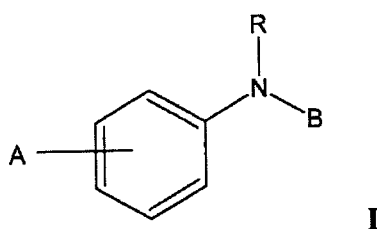
R, R₁, R₂ and R₆ = hydrogen, alkyl, cycloalkyl
and/or aryl group, where the substituents of
the R, R₁, R₂ and R₆ type are the same or

25

different
is used.

6. A process according to any one of claims 1 to 5,
characterized in that
the aging stabilizer used is a mixture of
different compounds of structures **I** to **III**.

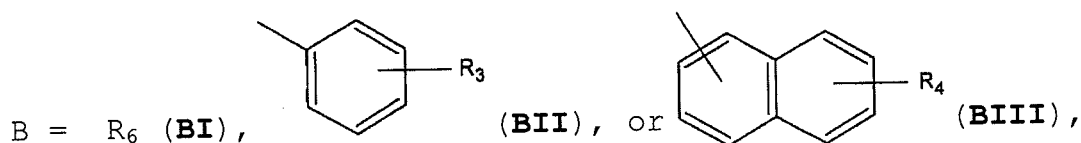
7. The use of compounds of the structure



where:

R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy,
alkylaryl, arylalkyl, cycloalkyl, hydroxyl or
aryl group

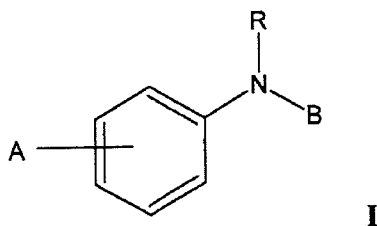
A = R₅ (**AI**) or -NR₁R₂ (**AII**) and



where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl,
alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl,
cycloalkyl, hydroxyl or aryl group, are the same
or different, and the phenyl or naphthyl
structural unit in structure **I**, **BII** and **BIII** has
one, two or three substituents of the R₃, R₄
and/or R₅ type,

as aging stabilizers for increasing the oxidation
stability of biodiesel.

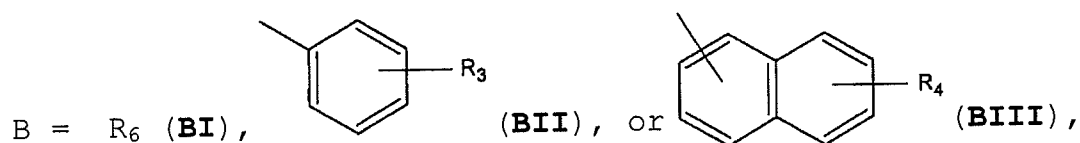
8. An oxidation-stabilized biodiesel,
characterized in that
the biodiesel comprises from 5 to 20 000 ppm (w/w)
of at least one aging stabilizer of the structure:



where:

5 R = hydrogen, alkyl, alkenyl, alkynyl, alkoxy,
 alkylaryl, arylalkyl, cycloalkyl, hydroxyl or
 aryl group

A = R₅ (**AI**) or -NR₁R₂ (**AII**) and



10 where R₁, R₂, R₃, R₄, R₅ and R₆ = hydrogen, alkyl,
 alkenyl, alkynyl, alkoxy, alkylaryl, arylalkyl,
 cycloalkyl, hydroxyl or aryl group, are the same
 or different, and the phenyl or naphthyl
 structural unit in structure **I**, **BII** and **BIII** has
15 one, two or three substituents of the R₃, R₄
 and/or R₅ type.