

Method of increasing the oxidation stability of biodiesel

The invention relates to a method of increasing the oxidation stability of biodiesel.

5 An alternative to conventional diesel fuel which is being used to an increasing extent today is biodiesel, which comprises monoalkyl esters of vegetable oils, animal fats and also used cooking fats. Biodiesel is obtained by transesterification of oils, for example rapeseed oil, soybean oil or sunflower oil and also used cooking oils, with an alcohol in the presence of a catalyst.

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Since the importance of biodiesel as an alternative diesel fuel for passenger cars has been continually increasing in importance in recent times, the production of biodiesel has also increased to a corresponding extent in recent years. Biodiesel has a high content of unsaturated fatty acid esters which can easily be oxidized by atmospheric oxygen. The products formed
15 (including acids, resins) can lead to corrosion and blockages in injection pumps and/or fuel lines. The increasing use of the alternative biodiesel as automobile fuel has led to a need for oxidation-stabilized biodiesel. According to the prior art, preference is given to adding 2,6-di-tert-butyl-4-methylphenol (BHT) as primary antioxidant to the biodiesel in order to meet the oxidation stability requirements of the standard DIN EN 14214.

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The use of 2,6-di-tert-butyl-4-methylphenol as antioxidant is described in the European patent EP 0 189 049. Here, the use of 2,6-di-tert-butyl-4-methylphenol in amounts of from 10 to 100 ppm as exclusive stabilizer in methyl esters of palm kernel oil having from 12 to 18 carbon atoms in the fatty acid is described.

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DE 102 52 714 and WO 2004/044104, too, describe a method of increasing the oxidation stability of biodiesel by addition of di-2,6-tert-butyl-4-hydroxytoluene. A liquid stock solution containing from 15 to 60% by weight of monoalkylhydroxytoluene or dialkylhydroxytoluene dissolved in biodiesel is added to the biodiesel to be stabilized to give a concentration of 0.005
30 to 2% by weight of monoalkylhydroxytoluene or dialkylhydroxytoluene, based on the total solution in biodiesel.

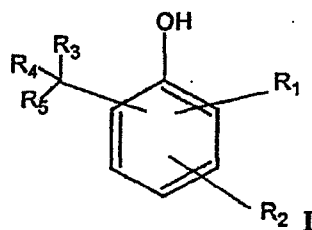
DE 102 52 715 describes a method of increasing the storage stability of biodiesel, in which a liquid stock solution containing from 15 to 60% by weight of 2,4-di-tert-butylhydroxytoluene dissolved in biodiesel is added to the biodiesel to be stabilized to give a concentration of from 0.005 to 2% by weight of 2,4-di-tert-butylhydroxytoluene, based on the total solution in
5 biodiesel.

It is an object of the present invention to provide an improved method of increasing the oxidation stability of biodiesel, or to at least provide a useful alternative. In particular, it is an object of the invention to improve the processability of the primary antioxidant in biodiesel and thus improve the economics or the use of primary antioxidants in biodiesel, or to at least provide a useful alternative.

It has surprisingly been found that the addition of a liquid primary antioxidant based on substituted alkylphenols having the structure I to biodiesel makes it possible to improve the handleability of the primary antioxidants in biodiesel. The primary antioxidant used in the
15 method of the invention has a low melting point, i.e. a melting point of less than or equal to 40°C. Owing to its low melting point, this primary antioxidant can, in the method of the invention, be mixed as liquid directly into the biodiesel without this primary antioxidant firstly having to be dissolved in a solvent, for example alcohol, or in biodiesel. Thus, the preparation of a masterbatch of this primary antioxidant in biodiesel can be dispensed with. The
20 masterbatches are generally prepared using the biodiesel for which the masterbatch is ready to be used. In the case of large distances between biodiesel and antioxidant manufacturers in particular, this leads to high costs for storage and transport in the case of primary antioxidants according to the prior art. The primary antioxidant used in the method of the invention thus leads to low production costs for the oxidation-stabilized biodiesel, since, firstly, the
25 preparation of solutions or masterbatches comprising the active ingredient primary antioxidant can be dispensed with and, secondly, the present method shows that a product mixture from the manufacturing process of substituted alkylphenols can be used without complicated separation and purification steps. A further advantage of the method of the invention is that the production of the oxidation-stabilized biodiesel can be carried out at low temperatures and within a
30 relatively short time. The method of the invention thus makes it possible to improve the economics of the production of oxidation-stabilized biodiesel. The active content of the liquid primary antioxidant used according to the present invention is 100% compared to 20% of the liquid primary antioxidants according to the prior art, since the liquid generally contains only

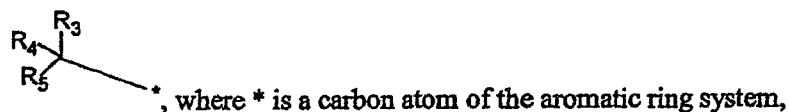
about 20% by weight of the active ingredient antioxidant. The use of a liquid primary antioxidant according to the method of the invention likewise enables transport and storage costs to be saved as a result of the high active content of primary antioxidant per liter. The use of a liquid primary antioxidant according to the method of the invention also leads to reduced crystallization of the primary antioxidant in the biodiesel or in plant components at low temperatures.

The present invention provides a method of increasing the oxidation stability of biodiesel, which comprises adding a primary antioxidant having a melting point of less than or equal to 40°C to the biodiesel to be stabilized in an amount of from 10 to 20 000 ppm (w/w), where the primary antioxidant comprises at least one compound having the structure



where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or

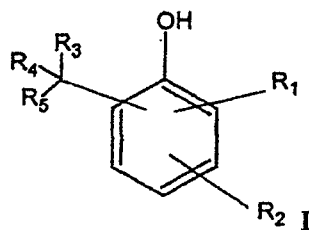


R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

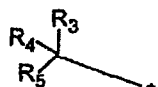
where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

The invention further provides for the use of a primary antioxidant which has a melting point of less than or equal to 40°C and comprises at least one compound having the structure



where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



5, where * is a carbon atom of the aromatic ring system,

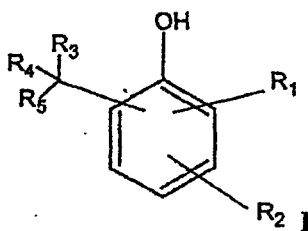
R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different, for increasing the oxidation stability of biodiesel.

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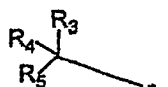
The invention likewise provides an oxidation-stabilized biodiesel comprising from 10 to 20 000 ppm (w/w) of a primary antioxidant which has a melting point of less than or equal to 40°C and comprises at least one compound having the structure



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where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



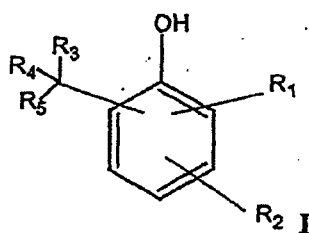
20, where * is a carbon atom of the aromatic ring system,

R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

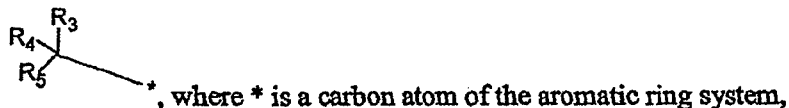
The inventive method of increasing the oxidation stability of biodiesel comprises adding a
 5 primary antioxidant having a melting point or less than or equal to 40°C to the biodiesel to be stabilized in an amount of from 10 to 20 000 ppm (w/w), where the primary antioxidant comprises at least one compound having the structure



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where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



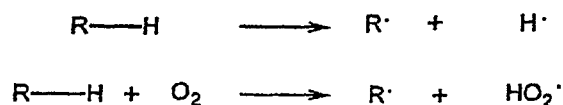
R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

15 R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

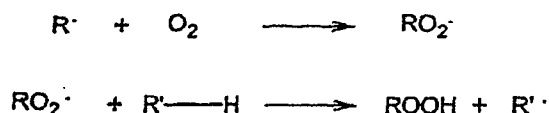
where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

For the purposes of the present invention, primary antioxidants are compounds or mixtures of
 20 compounds which inhibit or prevent undesirable degradation reactions in the biodiesel caused by oxygen. The mode of action of these primary antioxidants in the biodiesel is described in the following reaction scheme, where R and R' are each an organic radical and AOH is a primary antioxidant used in the method of the invention.

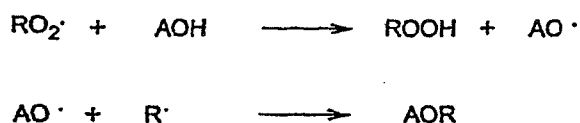
25 1. Chain initiation



2. Chain propagation

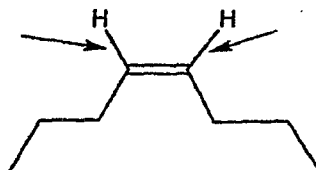


3. Chain termination



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Apart from the abovementioned reactions, it is also possible for reactions on the double bonds of the alkyl esters of fatty acids, which can likewise be initiated by oxygen, to occur. Here, the carbon-hydrogen bond which is located in the allyl position relative to the double bond is preferentially attacked by the oxygen:



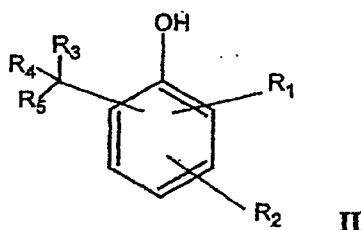
The primary antioxidant used in the method of the invention comprises neither organic solvents, for example alcohols, nor biodiesel, as is the case, for example, when a masterbatch is employed. The primary antioxidant used therefore preferably comprises exclusively alkylphenols and/or substituted alkylphenols. In particular, a mixture comprising various substituted and/or unsubstituted alkylphenols, preferably a mixture comprising from 0.1 to 99.9% by weight, preferably from 50 to 99% by weight and particularly preferably from 55 to 90% by weight, of one or more compounds having the structure I, is used as primary antioxidant in the method of the invention.

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Particular preference is given to using a mixture comprising exclusively compounds having the structure I as primary antioxidant in the method of the invention. This mixture has the advantage that it comprises exclusively compounds having the structure I which all have an oxidation-stabilizing action on biodiesel.

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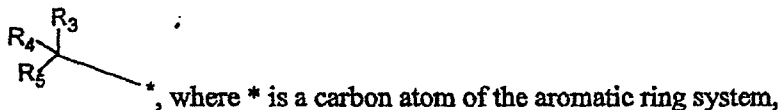
In the method of the invention, preference is given to using a primary antioxidant comprising at least one compound having the structure II



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where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 4 carbon atoms or

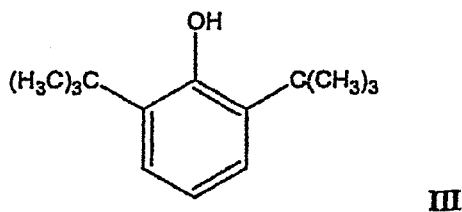


R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 4 carbon atoms,

15 R_4 = hydrogen, a linear alkyl group having from 1 to 4 carbon atoms,

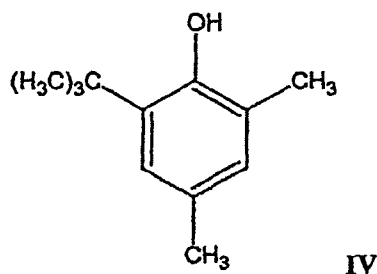
where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

Preference is given to adding a primary antioxidant comprising at least one compound having
20 the structure III



to the biodiesel in the method of the invention.

Particular preference is given to adding a primary antioxidant comprising at least one compound having the structure IV



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to the biodiesel in the method of the invention.

Furthermore, the primary antioxidant used in the method of the invention can comprise exclusively compounds selected from among

- 10 - tri-tert-butylphenols, in particular 2,4,6-tri-tert-butylphenol,
- di-tert-butylphenols, in particular 2,4-di-tert-butylphenol, 2,5-di-tert-butylphenol, 2,6-di-tert-butylphenol,
- di-tert-butylmethylphenols, in particular 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,
- 15 - tert-butylmethylphenols, in particular 2-tert-butyl-4-methylphenol, 6-tert-butyl-2-methylphenol, 4-tert-butyl-2-methylphenol, 6-tert-butyl-3-methylphenol,
- tert-butyl dimethylphenols, in particular 4-tert-butyl-2,6-dimethylphenol, 6-tert-butyl-2,4-dimethylphenol, tert-butyl-2,5-dimethylphenol,
- tert-butylphenols, in particular 2-tert-butylphenol, 4-tert-butylphenol,
- 20 - di-sec-butylphenols,
- sec-butylphenols, in particular 2-sec-butylphenol, 2-sec-butyl-4-tert-butylphenol, 4-sec-butyl-2,6-di-tert-butylphenol,
- tert-amylphenols, in particular 2-tert-amylphenol,
- di-tert-amylphenols, in particular 2,4-di-tert-amylphenol,
- 25 - 2-isopropylphenol, 4-octylphenol, 4-nonylphenol, 2,6-di-tert-butyl-4-nonylphenol, 4-dodecylphenol and/or octadecylphenol,

and mixtures of these compounds, with this primary antioxidant having a melting point of less than or equal to 40°C.

Pure substances or mixtures which are or comprise compounds having the structures I to IV and have a melting point of greater than 40°C are excluded from the present invention.

The primary antioxidant used in the method of the invention has a melting point of $\leq 40^{\circ}\text{C}$,
 5 preferably $\leq 39^{\circ}\text{C}$ and particularly preferably $\leq 38^{\circ}\text{C}$.

Secondary antioxidants which can be used in the method of the invention are alkylthiomethylphenols, preferably selected from among

- 2,4-di((octylthio)methyl)-6-tert-butylphenol,
- 10 - 2,4-di((octylthio)methyl)-6-methylphenol,
- 2,4-di((octylthio)methyl)-6-ethylphenol and
- 2,6-di((dodecylthio)methyl)-4-nonylphenol,

hydroxylated diphenyl thioethers, preferably selected from among

- 2,2'-thiobis[6-tert-butyl-4-methylphenol],
- 15 - 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] and
- 4,4'-bis[2,6-dimethyl-4-hydroxyphenyl]disulfide,

20 phosphites or phosphonites, preferably selected from among

- triphenyl phosphite,
- diphenyl alkyl phosphites,
- phenyl dialkyl phosphites,
- tris[nonylphenyl] phosphite,
- 25 - trilauryl phosphite,
- trioctadecyl phosphite,
- distearyl pentaerythrityl diphosphite,
- tris[2,4-di-tert-butylphenyl] phosphite,
- diisodecyl pentaerythrityl diphosphite,
- 30 - bis[2,4-di-tert-butylphenyl] pentaerythrityl diphosphite,
- bis[2,6-di-tert-butyl-4-methylphenyl] pentaerythrityl diphosphite,
- bis[isodecyloxy] pentaerythrityl diphosphite,

- bis[2,4-di-tert-butyl-6-methylphenyl] pentaerythrityl diphosphite,
 - bis[2,4,6-tri-tert-butylphenyl] pentaerythrityl diphosphite,
 - tristearyl sorbitol triphosphite,
 - tetrakis[2,4-di-tert-butylphenyl] 4,4'-biphenylenediphosphonite,
 - 5 - 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocine,
 - 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenzo[d,g]-1,3,2-dioxaphosphocine,
 - bis[2,4-di-tert-butyl-6-methylphenyl] methyl phosphite and
 - bis[2,4-di-tert-butyl-6-methylphenyl] ethyl phosphite,
- or peroxide-destroying compounds, preferably selected from among
- 10 - esters of β -thiodipropionic acid, preferably the lauryl, stearyl, myristyl or tridecyl ester,
 - mercaptobenzimidazole,
 - the zinc salt of 2-mercaptobenzimidazole,
 - zinc dibutyldithiocarbamate,
 - dioctadecyl disulfide and
 - 15 - pentaerythrityl tetrakis[β -dodecylmercapto]propionate,
- or mixtures of these compounds.

For the purposes of the present invention, the term biodiesel encompasses all the saturated and/or unsaturated alkyl esters of fatty acids, in particular methyl or ethyl esters of fatty acids,

20 which can be used as energy carriers. For the purposes of the present invention, energy carriers include both fuels as sources of heat, for example heating material, and fuels for powering vehicles, for example automobiles, goods vehicles, ships or aircraft. The biodiesel to which the method of the invention is applied is preferably a biodiesel which is usually marketed under the name *biodiesel* for use as automobile fuel. In particular, the biodiesel to which the method of

25 the invention is applied comprises C_{12} - C_{24} fatty acid alkyl esters, preferably C_{12} - C_{24} fatty acid methyl esters or C_{12} - C_{24} fatty acid ethyl esters, which can be present in pure form or as a mixture. In addition, the biodiesel to which the method of the invention is applied can further comprise all customary additives such as secondary antioxidants, antifoams, low-temperature flow improvers. The method of the invention is preferably applied to biodiesel produced from

30 vegetable and/or animal oils by a process of transesterification with an alcohol, preferably methanol or ethanol, particularly preferably methanol. The method of the invention is more preferably applied to biodiesel comprising transesterification products of rapeseed oil, soybean

oil, sunflower oil, palm kernel oil, coconut oil, jatropha oil, cotton seed oil, peanut oil, maize oil and/or used cooking oils. However, particular preference is given to using biodiesel which is obtained from rapeseed oil, sunflower oil or soybean oil by means of the abovementioned transesterification. The method of the invention can also be applied to mixtures of the trans-
 5 esterification products of various vegetable and/or animal oils.

In a particular embodiment of the method of the invention, mixtures of saturated and/or unsaturated fatty acid alkyl esters with liquid energy carriers, for example mineral diesel fuel or heating oil, can be used as biodiesel. Particular preference is given to using a mixture of
 10 mineral diesel fuel and from 0.1 to 99.9% by volume, in particular from 2 to 10% by volume and preferably from 3 to 5% by volume, of saturated and/or unsaturated fatty acid alkyl esters. In a subsequent step of the method of the invention, the oxidation-stabilized biodiesel can be added in an amount of from 0.1 to 99.9% by volume, in particular from 1 to 20% by volume, preferably from 2 to 10% by volume and more preferably from 3 to 5% volume, to a liquid energy carrier, in particular mineral diesel fuel or heating oil.

In the method of the invention, the primary antioxidant is preferably added directly, in particular in an amount of from 10 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). For the purposes of the present
 20 invention, direct addition means that no preparation of a solution or a masterbatch of the primary antioxidant has been carried out in a preceding step. In this step, secondary antioxidants can also be added in an amount of from 10 to 20 000 ppm (w/w), preferably from 50 to 12 000 ppm (w/w) and preferably from 100 to 8000 ppm (w/w), to the biodiesel.

25 The primary antioxidant is preferably dissolved in the biodiesel with stirring at a temperature of from 18°C to 60°C, more preferably from 20°C to 40°C.

The invention further provides for the use of a primary antioxidant which has a melting point of less than or equal to 40°C and comprises at least one compound having the structure I for
 30 increasing the oxidation stability of biodiesel.

Particular preference is given to using a mixture comprising exclusively compounds having the structure I as primary antioxidant. This mixture has the advantage that it comprises exclusively

compounds having the structure I which all have an oxidation-stabilizing action on biodiesel. Preference is given to using a primary antioxidant comprising at least one compound having the structure II. However, greater preference is given to using a primary antioxidant comprising at least one compound having the structure III. Particular preference is given to
 5 using a primary antioxidant comprising at least one compound having the structure IV.

Furthermore, it is possible to use a primary antioxidant comprising exclusively compounds selected from among

- tri-tert-butylphenols, in particular 2,4,6-tri-tert-butylphenol,
- 10 - di-tert-butylphenols, in particular 2,4-di-tert-butylphenol, 2,5-di-tert-butylphenol, 2,6-di-tert-butylphenol,
- di-tert-butylmethylphenols, in particular 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, in particular 2-tert-butyl-4-methylphenol, 6-tert-butyl-2-methylphenol, 4-tert-butyl-2-methylphenol, 6-tert-butyl-3-methylphenol,
- 15 - tert-butyl dimethylphenols, in particular 4-tert-butyl-2,6-dimethylphenol, 6-tert-butyl-2,4-dimethylphenol, tert-butyl-2,5-dimethylphenol,
- tert-butylphenols, in particular 2-tert-butylphenol, 4-tert-butylphenol,
- di-sec-butylphenols,
- 20 - sec-butylphenols, in particular 2-sec-butylphenol, 2-sec-butyl-4-tert-butylphenol, 4-sec-butyl-2,6-di-tert-butylphenol,
- tert-amylphenols, in particular 2-tert-amylphenol,
- di-tert-amylphenols, in particular 2,4-di-tert-amylphenol,
- 2-isopropylphenol, 4-octylphenol, 4-nonylphenol, 2,6-di-tert-butyl-4-nonylphenol, 4-
- 25 dodecylphenol and/or octadecylphenol,

and mixtures of these compounds, with this primary antioxidant having a melting point of less than or equal to 40°C.

Pure substances or mixtures which are or comprise compounds having the structures I to IV
 30 and have a melting point of greater than 40°C are excluded from the present invention.

The oxidation-stabilized biodiesel of the invention comprises from 10 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

a primary antioxidant which has a melting point of less than or equal to 40°C and comprises at least one compound having the structure I.

The primary antioxidant of the oxidation-stabilized biodiesel of the invention therefore preferably comprises exclusively alkylphenols and/or substituted alkylphenols. In particular, the oxidation-stabilized biodiesel of the invention comprises a mixture of various substituted and/or unsubstituted alkylphenols as primary antioxidant. The biodiesel of the present invention preferably comprises a primary antioxidant comprising from 0.1 to 99.9% by weight, more preferably from 50 to 99% by weight and particularly preferably from 55 to 99% by weight, of one or more compounds having the structure I. The biodiesel of the invention particularly preferably comprises a mixture comprising exclusively compounds having the structure I as primary antioxidant.

The biodiesel of the invention preferably comprises a primary antioxidant comprising at least one compound having the structure II. The biodiesel of the invention more preferably comprises a primary antioxidant comprising at least one compound having the structure III. The biodiesel of the invention particularly preferably comprises a primary antioxidant comprising at least one compound having the structure IV.

Furthermore, the biodiesel of the invention can comprise a primary antioxidant comprising exclusively compounds selected from among

- tri-tert-butylphenols, in particular 2,4,6-tri-tert-butylphenol,
- di-tert-butylphenols, in particular 2,4-di-tert-butylphenol, 2,5-di-tert-butylphenol, 2,6-di-tert-butylphenol,
- di-tert-butylmethylphenols, in particular 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, in particular 2-tert-butyl-4-methylphenol, 6-tert-butyl-2-methylphenol, 4-tert-butyl-2-methylphenol, 6-tert-butyl-3-methylphenol,
- tert-butyl dimethylphenols, in particular 4-tert-butyl-2,6-dimethylphenol, 6-tert-butyl-2,4-dimethylphenol, tert-butyl-2,5-dimethylphenol,
- tert-butylphenols, in particular 2-tert-butylphenol, 4-tert-butylphenol,
- di-sec-butylphenols,

- sec-butylphenols, in particular 2-sec-butylphenol, 2-sec-butyl-4-tert-butylphenol, 4-sec-butyl-2,6-di-tert-butylphenol,
 - tert-amylphenols, in particular 2-tert-amylphenol,
 - di-tert-amylphenols, in particular 2,4-di-tert-amylphenol,
 - 5 - 2-isopropylphenol, 4-octylphenol, 4-nonylphenol, 2,6-di-tert-butyl-4-nonylphenol, 4-dodecylphenol and/or octadecylphenol,
- and mixtures of these compounds.

In particular, the biodiesel of the invention comprises C_{12} - C_{24} fatty acid alkyl esters, preferably C_{12} - C_{24} fatty acid methyl esters or C_{12} - C_{24} fatty acid ethyl esters, which can be present in pure form or as a mixture. In addition, the biodiesel of the invention can further comprise all customary additives such as secondary antioxidants, antifoams. The biodiesel of the invention preferably comprises transesterification products of rapeseed oil, soybean oil, sunflower oil, palm kernel oil, coconut oil, jatropha oil and/or used cooking oils. The biodiesel of the invention particularly preferably comprises transesterification products obtained from rapeseed oil, sunflower oil or soybean oil by transesterification. The biodiesel of the invention can also comprise mixtures of transesterification products of various vegetable and/or animal oils.

In addition, the biodiesel of the invention can further comprise all customary additives such as secondary antioxidants, antifoams, low-temperature flow improvers. Secondary antioxidants which can be present in the biodiesel of the invention are alkylthiomethylphenols, preferably selected from among

- 2,4-di((octylthio)methyl)-6-tert-butylphenol,
- 2,4-di((octylthio)methyl)-6-methylphenol,
- 25 - 2,4-di((octylthio)methyl)-6-ethylphenol and
- 2,6-di((dodecylthio)methyl)-4-nonylphenol,

hydroxylated diphenyl thioethers, preferably selected from among

- 2,2'-thiobis[6-tert-butyl-4-methylphenol],
- 2,2'-thiobis[4-octylphenol],
- 30 - 4,4'-thiobis[6-tert-butyl-3-methylphenol],
- 4,4'-thiobis[6-tert-butyl-2-methylphenol],
- 4,4'-thiobis[3,6-di-sec-amylphenol] and

- 4,4'-bis[2,6-dimethyl-4-hydroxyphenyl]disulfide,
- phosphites or phosphonites, preferably selected from among
- triphenyl phosphite,
 - diphenyl alkyl phosphites,
 - 5 - phenyl dialkyl phosphites,
 - tris[nonylphenyl] phosphite,
 - trilauryl phosphite,
 - trioctadecyl phosphite,
 - distearyl pentaerythrityl diphosphite,
 - 10 - 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] pentaerythrityl diphosphite,
 - bis[isodecyloxy] pentaerythrityl diphosphite,
 - 15 - bis[2,4-di-tert-butyl-6-methylphenyl] pentaerythrityl diphosphite,
 - bis[2,4,6-tri-tert-butylphenyl] pentaerythrityl diphosphite,
 - tristearyl sorbitol triphosphite,
 - tetrakis[2,4-di-tert-butylphenyl] 4,4'-biphenylenediphosphonite,
 - 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocine,
 - 20 - 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyldibenzo[d,g]-1,3,2-dioxaphosphocine,
 - bis[2,4-di-tert-butyl-6-methylphenyl] methyl phosphite and
 - bis[2,4-di-tert-butyl-6-methylphenyl]ethyl phosphite,
- or peroxide-destroying compounds, preferably selected from among
- esters of β -thiodipropionic acid, preferably the lauryl, stearyl, myristyl or tridecyl ester,
 - 25 - mercaptobenzimidazole,
 - the zinc salt of 2-mercaptobenzimidazole,
 - zinc dibutyldithiocarbamate,
 - dioctadecyl disulfide and
 - pentaerythrityl tetrakis[β -dodecylmercapto]propionate,
 - 30 or mixtures of these compounds.

These secondary antioxidants can be present in an amount of from 10 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 the biodiesel of the invention.

- 5 The biodiesel of the invention is preferably produced using the method of the invention.

The following examples illustrate the method of the invention without restricting the invention to this embodiment.

10 **Example 1 – Production of the samples**

In a glass beaker, the primary antioxidant is dissolved in biodiesel at 20°C with stirring, and stirring is continued until a clear solution of the primary antioxidant in the biodiesel is obtained. The primary antioxidants used, the biodiesel used and the ratios are shown in Table 1.

15

Example 2 – Composition of the primary antioxidants used

Primary antioxidant 1

(procured from Degussa AG under the trade name IONOL 99):

- | | | |
|----|-------------------|----------------------------|
| | > 99.0% by weight | of 2,6-di-tert-butylphenol |
| 20 | < 0.5% by weight | of 2-tert-butylphenol |
| | < 0.5% by weight | of 2,4-di-tert-butylphenol |

Primary antioxidant 2

(procured from Degussa AG under the trade name IONOL K98):

- 25 > 98.5% by weight of 6-tert-butyl-2,4-dimethylphenol
< 1.5% by weight of 4-tert-butyl-2,6-dimethylphenol and di-tert-butylmethyl-phenols

Primary antioxidant 3

30 (procured from Degussa AG under the trade name IONOL K65):

- | | |
|------------------|-------------------------------------|
| > 55% by weight | of 6-tert-butyl-2,4-dimethylphenol |
| > 15% by weight | of 2,6-di-tert-butyl-4-methylphenol |
| 18-22% by weight | of tert-butyl-2,5-dimethylphenol |

- < 1% by weight of 4,6-di-tert-butyl-2-methylphenol
- < 3.5% by weight of di-tert-butyl-3-methylphenol
- < 3.5% by weight of 2,5-di-tert-butyl-4-methylphenol

5

Primary antioxidant 4

(procured from Degussa AG under the trade name IONOL 75):

- > 75% by weight of 2,6-di-tert-butylphenol
- < 5% by weight of 2-tert-butylphenol
- 10 < 0.5% by weight of 4-tert-butylphenol
- < 3% by weight of 2,4-di-tert-butylphenol
- < 1% by weight of 2,5-di-tert-butylphenol
- < 15.5% by weight of 2,4,6-tri-tert-butylphenol

15 Example 3 – Testing procedure

The oxidation stability of the samples produced as described in Example 1 was examined at a test temperature of 110°C in accordance with the test method DIN EN 14112.

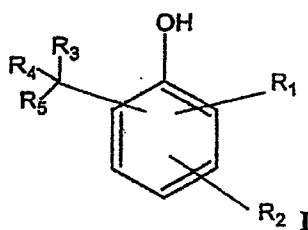
Example 4 – Results of the test method

Antioxidant	Amount of liquid antioxidant [in ppm]	Oxidation stability [in h at 110°C]
Rapeseed oil methyl ester		
-	-	5.1
1	500	6.7
2	500	6.5
3	500	6.6
4	500	6.7
Baynox	2500	7.1
Used cooking fat methyl ester		
-	-	4.0
1	2000	9.7
2	2000	9.5
3	2000	9.1
4	2000	9.4
Baynox	10 000	12.0
Soybean oil methyl ester		
-	-	3.6
1	2000	7.3
2	2000	6.6
3	2000	6.3
4	2000	7.1
Baynox	10 000	8.8
Sunflower oil methyl ester		
-	-	1.6
1	4000	8.8
2	4000	7.8
3	4000	6.9
4	4000	8.0
Baynox	20 000	9.0

* Baynox is an antioxidant from Lanxess and is a solution of the distilled, highly pure active ingredient in biodiesel. The active content has been set to 20% g/l, so that 1 l of Baynox® corresponds to 200 g of active ingredient. Analysis showed that the active ingredient in Baynox® is 2,6-di-tert-butyl-4-hydroxytoluene.

Claims:

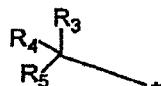
1. A method of increasing the oxidation stability of biodiesel,
which comprises
- 5 adding a primary antioxidant having a melting point of less than or equal to 40°C to the biodiesel to be stabilized in an amount of from 10 to 20 000 ppm (w/w), where the primary antioxidant comprises at least one compound having the structure



10

where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



*, where * is a carbon atom of the aromatic ring system,

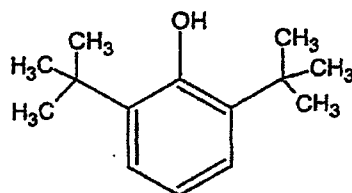
R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

15 R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

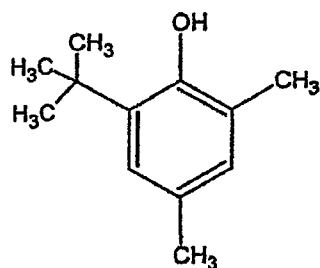
2. The method as claimed in claim 1,
- 20 wherein
a mixture comprising from 0.1 to 99.9% by weight of one or more compounds having the structure I is used as primary antioxidant.
3. The method as claimed in claim 1,
- 25 wherein
a mixture comprising exclusively compounds having the structure I is used as primary antioxidant.

4. The method as claimed in at least one of claims 1 to 3,
 wherein
 the primary antioxidant comprises at least one compound having the structure



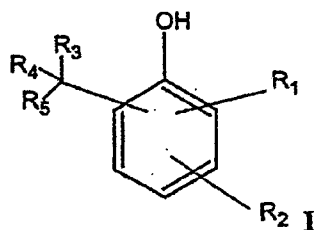
III.

5. The method as claimed in at least one of claims 1 to 3,
 wherein
 the primary antioxidant comprises at least one compound having the structure



IV.

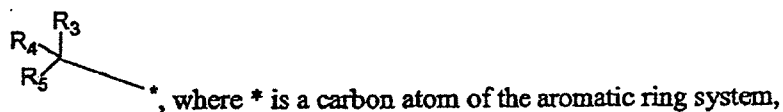
6. The use of a primary antioxidant which has a melting point of less than or equal to 40°C
 and comprises at least one compound having the structure



I

where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



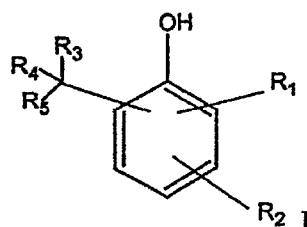
R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

- 5 where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different, for increasing the oxidation stability of biodiesel.

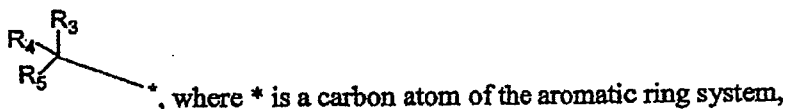
7. An oxidation-stabilized biodiesel,
comprising

- 10 from 10 to 20 000 ppm (w/w) of a primary antioxidant which has a melting point of less than or equal to 40°C and comprises at least one compound having the structure



- 15 where:

R_1, R_2 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms or



R_3, R_5 = hydrogen, a linear alkyl group having from 1 to 20 carbon atoms,

R_4 = hydrogen, a linear alkyl group having from 1 to 40 carbon atoms,

- 20 where both the substituents of the type R_1 and R_2 and those of the type R_3 and R_5 are in each case identical or different.

8. A method as claimed in any one of claims 1 to 5 substantially as herein described with reference to Examples 1 to 4.

9. An oxidation stabilised biodiesel as claimed in claim 7 substantially as herein described with reference to Examples 1 to 4.