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(54) Title: USE OF ADDITIVES WITH DETERGENT ACTION FOR FURTHER INCREASING THE CETANE NUMBER OF FUEL OILS

(57) Abstract: The present invention relates to the use of additives with detergent action selected from: (i) compounds with moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups; (ii) nitrogen compounds quaternized in an acid-free manner, obtainable by addition of a compound comprising an oxygen- or nitrogen-containing group reactive with an anhydride and additionally aquaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization; (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines for further increasing the cetane number of fuel oils which comprise cetane number improvers; furthermore, it relates to a fuel additive concentrate consisting of additives (i) to (iii), cetane number improvers, organic diluents or solvents and possibly customary co-additives.



Use of additives with detergent action for further increasing the cetane number of fuel oils

Description

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The present invention relates to the use of at least one additive with detergent action which is selected from the following groups:

- 10 (i) compounds with moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups;
- 15 (ii) nitrogen compounds quaternized in an acid-free manner, obtainable by addition of a compound comprising at least one oxygen- or nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization;
- (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines

20 for further increasing the cetane number of fuel oils which comprise at least one cetane number improver.

25 Furthermore, the present invention relates to a fuel additive concentrate consisting of one or more of the above additives with detergent action of groups (i) to (iii), one or more cetane number improvers, solvents and customary co-additives.

30 Fuel oils generally comprise cetane number improvers, which are also referred to as ignition accelerators or combustion improvers. For this purpose, typically organic nitrates are used, which have been known for some time as cetane number improvers in fuel oils or middle distillates such as diesel fuels, and have also been used therein.

Higher cetane numbers lead to more rapid engine starts, especially in cold weather, to lower engine noise, to more complete combustion, to less evolution of smoke and, under some circumstances, to lower injector carbonization.

35 Typical organic nitrates which are suitable as cetane number improvers in fuel oils, especially in diesel fuels, are nitrates of short- and medium-chain, linear and branched alkanols and nitrates of cycloalkanols, such as n-hexyl nitrate, 2-ethyl-hexyl nitrate, n-heptyl nitrate, n-octyl nitrate, isooctyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, n-dodecyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate and isopropylcyclohexyl nitrate. Specific branched decyl nitrates of the formula
40 $R^1R^2CH-CH_2-O-NO_2$ in which R^1 denotes an n-propyl or isopropyl radical and R^2 a linear or branched alkyl radical having 5 carbon atoms are also recommended in WO 2008/092809 as combustion improvers or cetane number improvers. However, the most commercially important cetane number improver is 2-ethylhexyl nitrate.

However, the prior art methods of further increasing cetane numbers in fuel oils are still in need of improvement in terms of action. It was thus an object of the present invention to further increase the cetane number of fuel oils, especially of diesel fuels and of mixtures of biofuel oils and middle distillates of fossil, vegetable or animal origin, by a suitable measure without increasing the amount of cetane number improvers already present in the fuel oils.

Accordingly the use of additives with detergent action selected from groups (i) to (iii) as defined above has been found.

The further increase in cetane number according to the present invention can, for example, be determined in fuel oils which already comprise one or more cetane number improvers in a stipulated concentration in the fuel oil. Stipulated concentration means that no additional amount of cetane number improver is added for increasing the cetane number, the said further increase is solely effected by the addition of one or more additives with detergent action selected from groups (i) to (iii).

Another aspect of further increasing the cetane number in fuel oils according to the present invention comprises increasing the amount of cetane number improvers in the fuel oils from zero or from a given low amount and simultaneously adding additives with detergent action of groups (i) to (iii). Then the increase in cetane number caused by the addition of cetane number improvers in the absence of additives with detergent action of groups (i) to (iii) is lower than the increase in cetane number caused by adding the same amount of cetane number improvers in the presence of additives with detergent action of groups (i) to (iii).

The further increase in cetane number according to the present invention can be achieved by adding additional additives with detergent action of groups (i) to (iii) to fuel oils already containing cetane number improvers and optionally additives with detergent action different from those of groups (i) to (iii) which, for example, have been provided to the fuel oils in form of a diesel detergent package, or can be achieved by providing a fuel oil detergent package, especially a diesel detergent package, to the fuel oils which contains additives with detergent action of groups (i) to (iii) and a higher amount of cetane number improvers compared to a corresponding fuel oil detergent package, especially a diesel detergent package, as used or recommended before with a lower amount of cetane number improvers.

International Patent Application File No. PCT/EP2011/072449 discloses the use of mixtures of

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(A) aliphatic saturated or unsaturated monocarboxylic acids having 12 to 24 carbon atoms or the dimerization or trimerization products thereof, which may be present in the form of free carboxylic acids and/or in the form of ammonium salts, amides,

esters and/or nitriles, and

(B) polycyclic hydrocarbon compounds which are obtainable from distillation residues of natural oils, which have been extracted from tree resins

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for increasing the cetane number of fuel oils which comprise at least one additive with detergent action and at least one cetane number improver, the mixtures of components (A) and (B) being used in a concentration of 10 to 500 ppm by weight, based on the total amount of the fuel oil.

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Mixtures of said monocarboxylic acids or the dimerization or trimerization products thereof (A) and said polycyclic carbon compounds (B), which are obtainable from distillation residues of natural oils which have been extracted from tree resins, are described in WO 2007/082825 for improvement of the storage stability of fuel additive concentrates which comprise at least one detergent and at least one cetane number improver. The said monocarboxylic acids or fatty acids and their dimerization or trimerization products of component (A) may be present as free carboxylic acids and/or as ammonium salts. Particularly suitable mixtures of components (A) and (B) are those of tall oil fatty acid and dimerized tall oil fatty acid.

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In a preferred embodiment, subject matter of the present invention is the above-defined use of the at least one additive with detergent action selected from the groups (i) to (iii), in which the fuel oils are free of mixtures of

25 (A) aliphatic saturated or unsaturated monocarboxylic acids having 12 to 24 carbon atoms or the dimerization or trimerization products thereof, which may be present in the form of free carboxylic acids and/or in the form of ammonium salts, amides, esters and/or nitriles, and

30 (B) polycyclic hydrocarbon compounds which are obtainable from distillation residues of natural oils, which have been extracted from tree resins.

The above embodiment preferably applies when the mixtures of components (A) and (B) is being used in a concentration of 10 to 500 ppm by weight, based on the total amount of the fuel oil.

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For the avoidance of doubt, the above embodiment provides for the absence of both components (A) and (B), i.e. component (A) and component (B) are not allowed to be present at the same time in the fuel oils.

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Additives with detergent action of groups (i) to (iii) are, in the context of the present invention, compounds whose effect in an internal combustion engine, especially a diesel engine, consists predominantly or at least essentially of eliminating and/or

preventing deposits. The detergents are normally amphiphilic substances which have at least one hydrophobic hydrocarbyl radical having a number-average molecular weight (M_n) of 85 to 20 000, especially of 300 to 5000, and in particular of 500 to 2500, and at least one polar moiety.

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Additives of group (i) comprising moieties deriving from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups are preferably corresponding derivatives of polyisobutenylsuccinic anhydride, which are obtainable by reaction of conventional or high-reactivity polyisobutene with $M_n = 300$ to 5000, in particular with
10 $M_n = 500$ to 2500, with maleic anhydride by a thermal route or via the chlorinated polyisobutene. Of particular interest in this context are derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. The moieties with hydroxyl and/or amino and/or amido and/or
15 imido groups are for example carboxylic acid groups, acid amides, acid amides of di- or polyamines, which, as well as the amide function, also have free amine groups, succinic acid derivatives with an acid and an amide function, carboxymides with monoamines, carboxymides with di- or polyamines, which, as well as the imide
20 function, also have free amine groups, and diimides, which are formed by the reaction of di- or polyamines with two succinic acid derivatives. Such fuel additives are described especially in US-A 4 849 572.

Nitrogen compounds quaternized in an acid-free manner of group (ii), which are obtainable by addition of a compound which comprises at least one oxygen- or
25 nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization, especially with an epoxide in the absence of free acid, are described in WO 2012/004300. Suitable compounds having at least one oxygen- or nitrogen-
30 containing group reactive with anhydride and additionally at least one quaternizable amino group are especially polyamines having at least one primary or secondary amino group and at least one tertiary amino group. Useful polycarboxylic anhydrides are especially dicarboxylic acids such as succinic acid, having a relatively long-chain
hydrocarbyl substituent, preferably having a number-average molecular weight M_n for the hydrocarbyl substituent of 200 to 10 000, in particular of 350 to 5000. A typical
35 quaternized nitrogen compound is, for example, the reaction product, obtained at 40°C, of polyisobutenylsuccinic anhydride, in which the polyisobutenyl radical typically has an M_n of 1000, with 3-(dimethylamino)propylamine, which constitutes a polyisobutenyl-
succinic monoamide and which is subsequently quaternized with styrene oxide in the absence of free acid at 70°C.

40 In a preferred embodiment, the at least one additive with detergent action of group (ii) is the reaction product, obtained at a reaction temperature of from 25 to 60°C, preferably of from 35 to 50°C, of a polyisobutenylsuccinic anhydride, in which the polyisobutenyl radical has an M_n of from 500 to 2,500, preferably of from 700 to 2,300,

with one or more N,N-di-(C₁- to C₄-alkyl)amino-C₂- to C₄-alkyleneamines, which constitutes a polyisobutenylsuccinic monoamide, and which is subsequently quaternized with an epoxide selected from the group of ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide and styrene oxide, propylene oxide being most preferred, in the absence of free acid at a temperature of from 50 to 100°C, preferably of from 60 to 80°C.

Suitable N,N-di-(C₁- to C₄-alkyl)amino-C₂- to C₄-alkyleneamines are for example 2-(N,N-dimethylamino)ethylamine, 2-(N,N-diethylamino)ethylamine, 2-(N,N-di-n-propylamino)ethylamine, 2-(N,N-diisopropylamino)ethylamine, 2-(N,N-di-n-butylamino)ethylamine, 2-(N,N-diisobutylamino)ethylamine, 2-(N,N-di-sec-butylamino)ethylamine, 2-(N,N-di-tert-butylamino)ethylamine, 3-(N,N-dimethylamino)propylamine, 3-(N,N-diethylamino)propylamine, 3-(N,N-di-n-propylamino)propylamine, 3-(N,N-diisopropylamino)propylamine, 3-(N,N-di-n-butylamino)propylamine, 3-(N,N-diisobutylamino)propylamine, 3-(N,N-di-sec-butylamino)propylamine, 3-(N,N-di-tert-butylamino)propylamine, 2-(N,N-dimethylamino)propylamine, 2-(N,N-diethylamino)propylamine, 2-(N,N-di-n-propylamino)propylamine, 2-(N,N-diisopropylamino)propylamine, 2-(N,N-di-n-butylamino)propylamine, 2-(N,N-diisobutylamino)propylamine, 2-(N,N-di-sec-butylamino)propylamine, 2-(N,N-di-tert-butylamino)propylamine, 4-(N,N-dimethylamino)butylamine, 4-(N,N-diethylamino)butylamine, 4-(N,N-di-n-propylamino)butylamine, 4-(N,N-diisopropylamino)butylamine, 4-(N,N-di-n-butylamino)butylamine, 4-(N,N-diisobutylamino)butylamine, 4-(N,N-di-sec-butylamino)butylamine and 4-(N,N-di-tert-butylamino)butylamine.

Polytetrahydrobenzoxazines and bistetrahydrobenzoxazines of group (iii) are described in EP Patent Application File No. 10 194 307.4. Such polytetrahydrobenzoxazines and bistetrahydrobenzoxazines are obtainable by successively reacting, in a first reaction step, a C₁- to C₂₀-alkylenediamine having two primary amino functions, e.g. 1,2-ethylenediamine, with a C₁- to C₁₂-aldehyde, e.g. formaldehyde, and a C₁- to C₈-alkanol at a temperature of 20 to 80°C with elimination and removal of water, where both the aldehyde and the alcohol can each be used in more than twice the molar amount, especially in each case in 4 times the molar amount, relative to the diamine, in a second reaction step reacting the condensation product thus obtained with a phenol which bears at least one long-chain substituent having 6 to 3000 carbon atoms, e.g. a tert-octyl, n-nonyl, n-dodecyl or polyisobutyl radical having an M_n of 1000, in a stoichiometric ratio relative to the originally used alkylenediamine of 1.2:1 to 3:1 at a temperature of 30 to 120°C and optionally in a third reaction step heating the bistetrahydrobenzoxazine thus obtained to a temperature of 125 to 280°C for at least 10 minutes.

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The at least one additive with detergent action used for the present invention is more preferably a compound from group (ii).

Cetane number improvers used are typically organic nitrates. Such organic nitrates are especially nitrate esters of unsubstituted or substituted aliphatic or cycloaliphatic alcohols, usually having up to about 10, in particular having 2 to 10 carbon atoms. The alkyl group in these nitrate esters may be linear or branched, and saturated or
5 unsaturated. Typical examples of such nitrate esters are methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate,
10 cyclohexyl nitrate, methylcyclohexyl nitrate and isopropylcyclohexyl nitrate and also branched decyl nitrates of the formula $R^1R^2CH-CH_2-O-NO_2$ in which R^1 is an n-propyl or isopropyl radical and R^2 is a linear or branched alkyl radical having 5 carbon atoms, as described in WO 2008/092809. Additionally suitable are, for example, nitrate esters of alkoxy-substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-
15 ethoxy)ethyl nitrate, 1-methoxypropyl nitrate or 4-ethoxybutyl nitrate. Additionally suitable are also diol nitrates such as 1,6-hexamethylene dinitrate. Among the cetane number improver classes mentioned, preference is given to primary amyl nitrates, primary hexyl nitrates, octyl nitrates and mixtures thereof.

20 In one preferred embodiment, 2-ethylhexyl nitrate is present in the fuel oils as the sole cetane number improver or in a mixture with other cetane number improvers.

The additives with detergent action of groups (i) to (iii) can in principle be used to increase the cetane numbers in any fuel oils which comprise cetane number improvers.
25 However, they are especially suitable for use in middle distillate fuels, especially in diesel fuels. However, use in heating oil or kerosene is also possible. Diesel fuels or middle distillate fuels are typically mineral oil raffinates which generally have a boiling range from 100 to 400°C. These are usually distillates having a 95% point up to 360°C or even higher. However, these may also be what is called "ultra low sulfur diesel" or
30 "city diesel", characterized by a 95% point of, for example, not more than 345°C and a sulfur content of not more than 0.005% by weight, or by a 95% point of, for example, 285°C and a sulfur content of not more than 0.001% by weight. In addition to the diesel fuels obtainable by refining, the main constituents of which are relatively long-chain paraffins, those obtainable by coal gasification or gas liquefaction ["gas to liquid" (GTL)
35 fuels] are suitable. Also suitable are mixtures of the aforementioned diesel fuels with renewable fuels (biofuel oils) such as biodiesel or bioethanol. Of particular interest at present are diesel fuels with low sulfur content, i.e. with a sulfur content of less than 0.05% by weight, preferably of less than 0.02% by weight, particularly of less than 0.005% by weight and especially of less than 0.001% by weight of sulfur. Diesel fuels
40 may also comprise water, for example in an amount of up to 20% by weight, for example in the form of diesel-water microemulsions or in the form of what is called "white diesel".

In a preferred embodiment, said additives with detergent action of groups (i) to (iii) are used together with cetane number improvers according to the present invention in fuel oils which consist

- 5 (a) to an extent of 0.1 to 100% by weight, preferably to an extent of 0.1 to less than 100% by weight, especially to an extent of 10 to 95% by weight and in particular to an extent of 30 to 90% by weight, of at least one biofuel oil based on fatty acid esters, and
- 10 (b) to an extent of 0 to 99.9% by weight, preferably to an extent of more than 0 to 99.9% by weight, especially to an extent of 5 to 90% by weight, and in particular to an extent of 10 to 70% by weight, of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

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Said additives with detergent action of groups (i) to (iii) can therefore be used together with cetane number improvers in fuel oils which consist to an extent of 100% by weight of at least one biofuel oil (a), based on fatty acid esters.

- 20 The said additives with detergent action of groups (i) to (iii) can of course also be used together with cetane number improvers according to the present invention in fuel oils of component (b) which consist to an extent of 100% by weight of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters. Fuel oils of fossil origin are most important as
- 25 fuel component (b).

- The fuel oil component (a) is usually also referred to as "biodiesel". This preferably comprises essentially alkyl esters of fatty acids which derive from vegetable and/or animal oils and/or fats. Alkyl esters typically refer to lower alkyl esters, especially C₁- to
- 30 C₄-alkyl esters, which are obtainable by transesterifying the glycerides which occur in vegetable and/or animal oils and/or fats, especially triglycerides, by means of lower alcohols, for example, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol or especially methanol ("FAME").

- 35 Examples of vegetable oils which can be converted to corresponding alkyl esters and can thus serve as the basis of biodiesel are castor oil, olive oil, peanut oil, palm kernel oil, coconut oil, mustard oil, cottonseed oil, and especially sunflower oil, palm oil, soybean oil and rapeseed oil. Further examples include oils which can be obtained from wheat, jute, sesame and shea tree nut; it is additionally also possible to use
- 40 arachis oil, jatropha oil and linseed oil. The extraction of these oils and the conversion thereof to the alkyl esters are known from the prior art or can be inferred therefrom.

It is also possible to convert already used vegetable oils, for example used deep fat fryer oil, optionally after appropriate cleaning, to alkyl esters, and thus for them to serve as the basis of biodiesel.

- 5 Vegetable fats can in principle likewise be used as a source for biodiesel, but play a minor role.

10 Examples of animal oils and fats which can be converted to corresponding alkyl esters and can thus serve as the basis of biodiesel are fish oil, bovine tallow, porcine tallow and similar fats and oils obtained as wastes in the slaughter or utilization of farm animals or wild animals.

15 The parent saturated or unsaturated fatty acids of said vegetable and/or animal oils and/or fats, which usually have 12 to 22 carbon atoms and may bear an additional functional group such as hydroxyl groups, and which occur in the alkyl esters, are especially lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, elaidic acid, erucic acid and/or ricinoleic acid.

20 Typical lower alkyl esters based on vegetable and/or animal oils and/or fats, which find use as biodiesel or biodiesel components, are, for example, sunflower methyl ester, palm oil methyl ester ("PME"), soybean oil methyl ester ("SME") and especially rapeseed oil methyl ester ("RME").

25 However, it is also possible to use the monoglycerides, diglycerides and especially triglycerides themselves, for example castor oil, or mixtures of such glycerides, as biodiesel or components for biodiesel.

30 In the context of the present invention, the fuel oil component (b) shall be understood to mean the abovementioned middle distillate fuels, especially diesel fuels, especially those which boil in the range from 120 to 450°C.

35 In a further preferred embodiment, said additives with detergent action of groups (i) to (iii) are used together with cetane number improvers according to the present invention in fuel oils which have at least one of the following properties:

- (α) a sulfur content of less than 50 mg/kg (corresponding to 0.005% by weight), especially less than 10 mg/kg (corresponding to 0.001% by weight);
- (β) a maximum content of 8% by weight of polycyclic aromatic hydrocarbons;
- 40 (γ) a 95% distillation point (vol/vol) at not more than 360°C.

Polycyclic aromatic hydrocarbons in (β) shall be understood to mean polyaromatic hydrocarbons according to standard EN 12916. They are determined according to this standard.

- 5 The cetane number improver or a mixture of a plurality of cetane number improvers is present in the fuel oils normally in an amount of 10 to 10 000 ppm by weight, especially 20 to 5000 ppm by weight, even more preferably of 50 to 2500 ppm by weight and especially of 100 to 1000 ppm by weight, for example of 150 to 500 ppm by weight.
- 10 The additive with detergent action of groups (i) to (iii) or a mixture of a plurality of such additives with detergent action is present in the fuel oils typically in an amount of 10 to 2000 ppm by weight, especially 20 to 1000 ppm by weight, even more preferably of 50 to 500 ppm by weight and especially of 30 to 250 ppm by weight, for example of 50 to 150 ppm by weight.
- 15 Said fuel oils such as diesel fuels or middle distillate fuels, or such as said mixtures of biofuel oils and middle distillates of fossil, vegetable or animal origin, may comprise, in addition to the additives with detergent action of groups (i) to (iii) and to the cetane number improvers, diluents and solvents and, as co-additives, further customary
- 20 additive components, especially cold flow improvers, corrosion inhibitors, demulsifiers, dehazers, antifoams, antioxidants and stabilizers, metal deactivators, antistats, lubricity improvers and dyes and markers.
- Cold flow improvers suitable as further co-additives are, for example, copolymers of
- 25 ethylene with at least one further unsaturated monomer, in particular ethylene-vinyl acetate copolymers.
- Corrosion inhibitors suitable as further co-additives are, for example, succinic esters, in particular with polyols, fatty acid derivatives, for example oleic esters, oligomerized
- 30 fatty acids and substituted ethanolamines.
- Demulsifiers suitable as further co-additives are, for example, the alkali metal and alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal and alkaline earth metal salts of fatty acid, and also alcohol alkoxylates,
- 35 e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylates or tert-pentylphenol ethoxylates, fatty acid, alkylphenols, condensation products of ethylene oxide and propylene oxide, e.g. ethylene oxide-propylene oxide block copolymers, polyethyleneimines and polysiloxanes.
- 40 Dehazers suitable as further co-additives are, for example, alkoxyated phenol-formaldehyde condensates.

Antifoams suitable as further co-additives are, for example, polyether-modified polysiloxanes.

5 Antioxidants suitable as further co-additives are, for example, substituted phenols, e.g. 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-3-methylphenol, and also phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine.

10 Metal deactivators suitable as further co-additives are, for example, salicylic acid derivatives, e.g. N,N'-disalicylidene-1,2-propanediamine.

A lubricity improver suitable as a further co-additive is, for example, glyceryl monooleate.

15 Suitable solvents, especially for diesel performance packages, are, for example, nonpolar organic solvents, especially aromatic and aliphatic hydrocarbons, for example toluene, xylenes, "white spirit" and the technical solvent mixtures of the designations Shellsol® (manufacturer: Royal Dutch/Shell Group), Exxol® (manufacturer: ExxonMobil) and Solvent Naphtha. Also useful here, especially in a blend with the nonpolar organic solvents mentioned, are polar organic solvents, in particular alcohols
20 such as 2-ethylhexanol, decanol and isotridecanol.

When the coadditives and/or solvents mentioned are used additionally, they are used in the amounts customary therefor.

25 Subject matter of the present invention is also a fuel additive concentrate suitable for use in fuel oils – also called "fuel additive package" or especially "diesel detergent package" – consisting of:

30 (C1) 5 to 45%, preferably 10 to 30% by weight of at least one additive with detergent action which is selected from the following group:

- (i) compounds with moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups;
- 35 (ii) nitrogen compounds quaternized in an acid-free manner, obtainable by by addition of a compound comprising at least one oxygen- or nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization;
- 40 (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines;

(C2) 20 to 90%, preferably 50 to 80% by weight of at least one cetane number

improver;

5 (C3) 5 to 35%, preferably 10 to 20% by weight of at least one organic diluent or solvent selected from the group of aromatic and aliphatic hydrocarbons and alcohols;

(C4) 0 to 10%, preferably 0.1 to 5% by weight of one or more customary co-additives selected from the following group:

10 (iv) corrosion inhibitors except for mixtures of (A) aliphatic saturated or unsaturated monocarboxylic acids having 12 to 24 carbon atoms or the dimerization or trimerization products thereof, which may be present in the form of free carboxylic acids and/or in the form of ammonium salts, amides, esters and/or nitriles, and (B) polycyclic hydrocarbon com-
15 pounds which are obtainable from distillation residues of natural oils, which have been extracted from tree resins;

(v) demulifiers;

20 (vi) dehazers;

(vii) antifoams;

25 (viii) antioxidants and stabilizers;

(ix) metal deactivators;

(x) antistats;

30 (xi) lubricity improvers;

(xii) dyes and markers;

the sum of all components (C1) to (C4) being 100% by weight.

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Examples for components (C2), (C3) and (C4) (iv) to (xii) are given above.

The following examples shall illustrate the present invention without restricting it.

Examples

In a diesel fuel which is typical for the European market, conforms to standard EN 590 B7 and comprised a proportion of 6.1% by weight of biodiesel (FAME), the cetane numbers were determined to EN ISO 5165 with the following additions:

Sample No.	Dosage [ppm by weight]	Cetane number to EN ISO 5165 (Δ = difference to base value)
10	1 none (base fuel)	54.8
	2 175 2-ethylhexyl nitrate	55.4 (Δ = 0.6)
15	3 56 DCA *	
	175 2-ethylhexyl nitrate	
	24 2-ethylhexanol	
	8 Solvent Naphtha heavy	
	9 customary antifoam + dehazer	55.9 (Δ = 1.1)
20	4 200 2-ethylhexyl nitrate	55.5 (Δ = 0.7)
	5 56 DCA *	
	200 2-ethylhexyl nitrate	
	24 2-ethylhexanol	
25	8 Solvent Naphtha heavy	
	9 customary antifoam + dehazer	56.1 (Δ = 1.3)

* DCA = reaction product, obtained at 40°C, of polyisobutenylsuccinic anhydride, in which the polyisobutenyl radical typically has an M_n of 1000, with 3-(N,N-dimethyl-amino)propylamine, which constitutes a polyisobutenyl-succinic monoamide and which is subsequently quaternized with propylene oxide in the absence of free acid at 70°C (prepared in analogy to Preparation Example No. 1 of WO 2012/004300)

Claims

1. The use of at least one additive with detergent action which is selected from the following groups:
- 5
- (i) compounds with moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups;
- (ii) nitrogen compounds quaternized in an acid-free manner, obtainable by addition of a compound comprising at least one oxygen- or nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization;
- 10
- (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines
- 15
- for further increasing the cetane number of fuel oils which comprise at least one cetane number improver.
- 20
2. The use according to Claim 1, in which the fuel oils are free of mixtures of
- (A) aliphatic saturated or unsaturated monocarboxylic acids having 12 to 24 carbon atoms or the dimerization or trimerization products thereof, which may be present in the form of free carboxylic acids and/or in the form of ammonium salts, amides, esters and/or nitriles, and
- 25
- (B) polycyclic hydrocarbon compounds which are obtainable from distillation residues of natural oils, which have been extracted from tree resins.
- 30
3. The use according to Claim 1 or 2 of at least one additive with detergent action which is selected from group (ii).
4. The use according to Claim 3, in which the at least one additive with detergent action of group (ii) is the reaction product, obtained at a reaction temperature of from 25 to 60°C, of a polyisobutenylsuccinic anhydride, in which the polyisobutenyl radical has an M_n of from 500 to 2,500, with one or more N,N-di-(C₁- to C₄-alkyl)-amino-C₂- to C₄-alkyleneamines, which constitutes a polyisobutenylsuccinic monoamide, and which is subsequently quaternized with an epoxide selected from the group of ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide and styrene oxide, in the absence of free acid at a temperature of
- 35
- 40
- from 50 to 100°C.

5. The use according to Claims 1 to 4, in which the fuel oils comprise 2-ethylhexyl nitrate as the at least one cetane number improver.
6. The use according to Claims 1 to 5, in which the fuel oils consist
- 5
- (a) to an extent of 0.1 to 100% by weight of at least one biofuel oil based on fatty acid esters, and
- (b) to an extent of 0 to 99.9% by weight of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.
- 10
7. The use according to Claims 1 to 6, in which the fuel oils which have at least one of the following properties:
- 15
- (α) a sulfur content of less than 50 mg/kg;
- (β) a maximum content of 8% by weight of polycyclic aromatic hydrocarbons;
- (γ) a 95% distillation point (vol/vol) at not more than 360°C.
- 20
8. A fuel additive concentrate consisting of:
- (C1) 5 to 45% by weight of at least one additive with detergent action which is selected from the following group:
- 25
- (i) compounds with moieties derived from succinic anhydride and having hydroxyl and/or amino and/or amido and/or imido groups;
- (ii) nitrogen compounds quaternized in an acid-free manner, obtainable by addition of a compound comprising at least one oxygen- or nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group onto a polycarboxylic anhydride compound and subsequent quaternization;
- 30
- (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines;
- 35
- (C2) 20 to 90% by weight of at least one cetane number improver;
- (C3) 5 to 35% by weight of at least one organic diluent or solvent selected from the group of aromatic and aliphatic hydrocarbons and alcohols;
- 40

(C4) 0 to 10% by weight of one or more customary co-additives selected from the following group:

- 5
- (iv) corrosion inhibitors except for mixtures of (A) aliphatic saturated or unsaturated monocarboxylic acids having 12 to 24 carbon atoms or the dimerization or trimerization products thereof, which may be present in the form of free carboxylic acids and/or in the form of ammonium salts, amides, esters and/or nitriles, and (B) polycyclic hydrocarbon compounds which are obtainable from distillation
- 10 residues of natural oils, which have been extracted from tree resins;
- (v) demulifiers;
- (vi) dehazers;
- 15
- (vii) antifoams;
- (viii) antioxidants and stabilizers;
- 20
- (ix) metal deactivators;
- (x) antistats;
- (xi) lubricity improvers;
- 25
- (xii) dyes and markers;

the sum of all components (C1) to (C4) being 100% by weight.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/058378

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10L1/14 C10L10/12 C10L1/233 C10L1/23 C10L1/238
 C10L1/2383 C10L1/2387
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 93/08244 A1 (EXXON CHEMICAL PATENTS INC [US]) 29 April 1993 (1993-04-29) page 1, paragraph 1; claims 1-14,19-21,25,26; examples 1-3; tables 1,2 page 1, paragraph 4 - page 2, paragraph 2 page 4, paragraph 5 - page 5, paragraph 2 page 7, paragraph 2 page 9, paragraph 2 - paragraph 4 page 23, paragraph 2 ----- -/--	1-7

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 5 September 2013	Date of mailing of the international search report 19/09/2013
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer de La Morinerie, B
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/058378

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A	WO 2012/004300 A1 (BASF SE [DE]; GRABARSE WOLFGANG [DE]; BOEHNKE HARALD [DE]; TOCK CHRIST) 12 January 2012 (2012-01-12) cited in the application page 1, line 4 - line 16; claims 1-8,13,15,18,19,21-23 page 33, line 7 - page 34, line 2 page 50, line 5 - line 8 page 51, line 14 - page 52, line 23 -----	1-8
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International application No
PCT/EP2013/058378

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 2007/012580 A1 (BASF AG [DE]; LANGE ARNO [DE]; MACH HELMUT [DE]; RATH HANS PETER [DE];) 1 February 2007 (2007-02-01) page 9, line 12 - line 13; claims 1,8,10; examples 9,11,12 page 12, line 5 - line 9 page 13, line 5 - line 10 page 13, line 40 - page 14, line 5 page 16, line 13 - line 31 -----</p>	1,8
A	<p>WO 2008/092809 A1 (BASF SE [DE]; KORMANN CLAUDIUS [DE]; REBHOLZ UWE [DE]; NORDMANN GERO []) 7 August 2008 (2008-08-07) cited in the application page 1, line 6 - line 11; claims 10,11 page 1, line 37 - page 2, line 21 page 6, line 18 - line 37 page 7, line 18 - line 41 page 10, line 31 - page 11, line 5 page 11, line 20 - line 38 page 14, line 7 - page 15, line 8 -----</p>	1-8
A	<p>EP 0 947 577 A1 (ROHM & HAAS [US]) 6 October 1999 (1999-10-06) paragraphs [0001] - [0011], [0021], [0022], [0032], [0051]; claims 1,3,13; examples 1,3,5; tables 1,3,5,7 -----</p>	1,2,5-7

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