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(54) NEW MIXTURES FOR IMPROVING OR BOOSTING THE SEPARATION OF WATER FROM FUELS

(57) The present invention relates to the use of mixtures of certain carboxylic acids (A) with at least one additive with detergent action, preferably at least one quaternary nitrogen compound (B) and optionally further fuel additives for improving or boosting the separation of water from fuel oils and gasoline fuels.

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Description

[0001] The present invention relates to the use of mixtures of certain carboxylic acids (A) with at least one additive with detergent action, preferably at least one quaternary nitrogen compound (B) and optionally further fuel additives for improving or boosting the separation of water from fuel oils and gasoline fuels.

[0002] Fuel oils such as middle distillates, e.g. diesel fuels, heating oils or jet fuels, as well as gasoline fuels often contain small amounts of water, typically in the region of from several parts per millions up to several per cent by weight, due to condensation of water into the cold fuel oils or gasoline fuels and into the storage tanks and pipelines during transport and storage. This amount of water partly separates as a layer at the bottom of the storage tank and partly is emulsified in the fuel oil or gasoline fuel. The presence of water is undesired as it can cause severe problems on transport and on use in combustion engines and heating devices.

[0003] U.S. Patent No. 4 129 508 discloses reaction products of hydrocarbyl-substituted succinic acids or their anhydrides with polyalkylene glycols or their monoethers, organic alkaline metal salts and alkoxylated amines. Such reaction products act as demulsifiers in fuels like diesel fuel.

[0004] Canadian Patent Application 2 027 269 discloses reaction products of alkenyl or alkyl succinic acids or their anhydrides, exhibiting at most 32 carbon atoms in the alkenyl or alkyl substituent, respectively, with alkylether diamines. Such reaction products act as dehazers in hydrocarbon fuels.

[0005] WO 15/003961 discloses the use of hydrocarbyl-substituted dicarboxylic acids to improve and complete the phase separation of water from fuel oils and gasoline fuels comprising additives with detergent action. The hydrocarbyl substituent comprises 10 to 3000 carbon atoms, explicit examples are made with polyisobutenylsuccinic anhydride, the polyisobutenyl residue having an Mn of 1000.

[0006] However, even if the hydrocarbyl-substituted dicarboxylic acids described therein improve the water separation a need exists for further improvement of the water and phase separation.

[0007] "Dehazing" as referred to in several of the cited documents above and as generally understood in the art shall mean clearing up water-containing hydrocarbons or fuels, respectively, by generating clear hydrocarbon-water-emulsions ("emulsification") and shall not include separating water in separate phase ("demulsification"), thus enabling to remove the water by phase separation.

[0008] There is a need to separate also larger amounts of water from fuel oils and gasoline fuels using suitable additive which are capable of completely or practically completely remove the water from the fuel oils and gasoline fuels. Such additives should interact with other performance additives present in the fuel oils or gasoline fuels in an advantageous way. Especially, the tendency of modern additives with detergent action to support the undesired formation and stabilization of fuel oil-water-emulsions or gasoline fuel-water-emulsions should be counteracted.

[0009] Accordingly, the above defined use of mixtures of at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids (A) with at least one additive with detergent action selected from the group consisting of quaternary nitrogen compounds (B) and polyisobutenylsuccinimides (G) for improving or boosting the separation of water from fuel oils and gasoline fuels has been found.

[0010] Saturated or unsaturated fatty acids and dimer fatty acids are often used in fuel additive packages as corrosion inhibitors. It has been found that carboxylic acids (A) are effective as boosters for dehazing in amounts lower than the amounts usually necessary for an anti-corrosion effect. Therefore, according to the invention the carboxylic acids (A) are present in the fuels in amounts of at most 5 ppm by weight, preferably up to 4, more preferably up to 3, even more preferably up to 2.5, and especially up to 2 ppm by weight.

[0011] According to the present invention, water present in the fuel oils or gasoline fuels is separated as a layer at the bottom of a separation device and, thereafter, can be easily removed. The water content in fuel oils or gasoline fuels which can be removed in this way is normally from about 200 ppm by weight to about 10% by weight, especially from about 1000 ppm by weight to about 5% by weight. Emulsifying water in the fuel oil or gasoline fuel by interaction with the mixture of at least one carboxylic acid (A) with at least one quaternary nitrogen compound (B) occurs only to a negligible minor amount.

[0012] According to the present invention improvement of the separation of water from gasoline fuels is preferred over that from diesel fuels.

Compound (A)

[0013] Compound (A) at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids, preferably 12 to 28, more preferably 14 to 26, even more preferably 16 to 24, and especially 18 to 20 carbon atoms.

[0014] The monocarboxylic acids may be saturated or unsaturated. Unsaturated carboxylic acids may bear one, two or more double bonds, preferably one or two, even more preferably one double bond.

[0015] In one embodiment the monocarboxylic acid is a naturally occurring fatty acid or a mixture thereof with an even number of carbon atoms.

[0016] Compound (A) is preferably applied in the form of a mixture of at least 2 carboxylic acids, preferably 2 to 6 individual carboxylic acids, more preferably 2 to 5 individual carboxylic acids.

[0017] In a preferred embodiment compound (A) may be a mixture of carboxylic acids of natural origin, e.g. fatty acids which derive from vegetable and/or animal oils and/or fats

[0018] Such fatty acids occur in vegetable and/or animal oils and/or fats, especially in the form of triglycerides from which the fatty acids are obtainable e.g. by saponification.

[0019] Examples of vegetable oils 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 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.

[0020] It is also possible to convert already used vegetable oils, for example used deep fat fryer oil, optionally after appropriate cleaning.

[0021] Examples of animal oils and fats 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.

[0022] The parent saturated or unsaturated fatty acids of said vegetable and/or animal oils and/or fats, usually has 12 to 22 carbon atoms and may bear an additional functional group such as hydroxyl groups.

[0023] Preferred are lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, elaidic acid, erucic acid and/or ricinoleic acid.

[0024] Preferred mixtures of fatty acids are based on vegetable and/or animal oils and/or fats are, for example, based on sunflower oil, palm oil, soybean oil, and especially rapeseed oil.

[0025] It is also possible to use monocarboxylic acids which are not naturally occurring fatty acids.

[0026] Preferred examples are 2-propylheptanoic acid, isononanoic acid, isotridecanoic acid, and iso-heptadecanoic acid.

[0027] As used herein, isononanoic acid refers to one or more branched-chain aliphatic carboxylic acids with 9 carbon atoms. Embodiments of isononanoic acid may include 7-methyloctanoic acid (e.g., CAS Nos. 693-19-6 and 26896-18-4), 6,6-dimethylheptanoic acid (e.g., CAS No. 15898-92-7), 3,5,5-trimethylhexanoic acid (e.g., CAS No. 3302-10-1), 3,4,5-trimethylhexanoic acid, 2,5,5-trimethylhexanoic acid, 2,2,4,4-tetramethylpentanoic acid (e.g., CAS No. 3302-12-3) and combinations thereof. In a preferred embodiment, isononanoic acid has as its main component greater than 90% of one of 7-methyloctanoic acid, 6,6-dimethylheptanoic acid, 3,5,5-trimethylhexanoic acid, 3,4,5-trimethylhexanoic acid, 2,5,5-trimethylhexanoic acid, and 2,2,4,4-tetramethylpentanoic acid. The balance of the isononanoic acid may include other nine carbon carboxylic acid isomers and minor amounts of one or more contaminants. In a preferred embodiment, the isononanoic acid has as its main component greater than 90% of 3,5,5-trimethylhexanoic acid and even more preferably, the main component is greater than 95% 3,5,5-trimethylhexanoic acid.

[0028] Dimer fatty acids are dimers of the above-mentioned unsaturated monocarboxylic acid. Such dimers usually comprise 20 to 60 carbon atoms, preferably 24 to 44, more preferably 28 to 40, and especially 32 to 38 carbon atoms.

[0029] The dimer may comprise trimers or higher oligomers of unsaturated monocarboxylic acid in minor amounts.

[0030] Dimerisation respectively oligomerisation usually takes place via Diels-Alder reaction so that the dimers typically comprise at least one substituted cyclohexene substructure. It is also possible that oligomerisation takes place via Alder ene-reaction or radical oligomerisation.

[0031] The at least one carboxylic acid (A) is applied in the form of the free acid, i.e. COOH groups are present. To a minor extent, some of the carboxylic functions may be present in salt form, e.g. as alkali or alkaline metal salts salts or as ammonium or substituted ammonium salts, depending on the pH value of the liquid phase. Preferably at least 50 % of all carboxylic acid groups are available in the form of the free acid as COOH-groups, more preferably at least 66 %, very preferably at least 75 %, even more preferably at least 85 %, and especially at least 95%.

[0032] According to the present invention, the mixtures of carboxylic acid (A) with at least one additive with detergent action selected from the group consisting of

- quaternary nitrogen compounds (B) and
- polyisobutenylsuccinimides (G), preferably at least one quaternary nitrogen compound (B) improve and complete the phase separation of water from the fuel oils and gasoline fuels which occurs with larger amounts of water present in the fuel oils or gasoline fuels already without any performance additive but in an incomplete way. Furthermore, mixtures of (A) and (B) and/or (G) boost the phase separation of water from fuel oils and gasoline fuels if other surface active additives, especially certain commercially available dehazers, are already present in the fuel oils and gasoline fuels. Astonishingly, the interaction between (A), (B) respectively (G) and certain commercially available dehazers which are by nature emulsifying additives also leads to an improved demulsifying and water phase separating action.

[0033] The at least one quaternary nitrogen component (B) refer, in the context of the present invention, to nitrogen compounds quaternized in the presence of an acid or in an acid-free manner, preferably 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.

[0034] In most cases the quaternary nitrogen component (B) is an ammonium compound, however in the context of the present document morpholinium, piperidinium, piperazinium, pyrrolidinium, imidazolinium or pyridinium cations are also encompassed by the phrase "quaternary nitrogen component".

[0035] The quaternary ammonium compounds (B) are preferably of the formula

$$^{+}NR^{1}R^{2}R^{3}R^{4}\ A^{-}$$

in which

A^- stands for an anion, preferably a carboxylate R^5COO^- or a carbonate $R^5O\text{-}COO^-$, and

R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with from 1 to 100 carbon atoms, substituted or unsubstituted, preferably unsubstituted, linear or branched alkyl, alkenyl or hydroxyalkyl residue with 1 to 100, more preferably 1 to 75, even more preferably 1 to 30, most preferably 1 to 25 and especially 1 to 20 carbon atoms,

R^5 additionally may be substituted or unsubstituted cycloalkyl or aryl residues bearing 5 to 20, preferably 5 to 12 carbon atoms.

[0036] It is also possible that the anion may be multiply charged negatively, e.g. if anions of dibasic acids are used, in this case the stoichiometric ratio of the ammonium ions to the anions corresponds to the ratio of positive and negative charges.

[0037] The same is true for salts in which the cation bears more than one ammonium ion, e.g. of the substituents connect two or more ammonium ions.

[0038] In the organic residues the carbon atoms may be interrupted by one or more oxygen and/or sulphur atoms and/or one or more substituted or unsubstituted imino groups, and may be substituted by C_6-C_{12}-aryl, C_5-C_{12}-cycloalkyl or a five- or six-membered, oxygen-, nitrogen- and/or sulphur-containing heterocycle or two of them together form an unsaturated, saturated or aromatic ring which may be interrupted by one or more oxygen and/or sulphur atoms and/or one or more substituted or unsubstituted imino groups, where the radicals mentioned may each be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles.

[0039] Two of the residues R^1 to R^4 may together form an unsaturated, saturated or aromatic ring, preferably a five-, six- or seven-membered ring (including the nitrogen atom of the ammonium ion).

[0040] In this case the ammonium cation may be a morpholinium, piperidinium, piperazinium, pyrrolidinium, imidazolinium or pyridinium cation.

[0041] In these definitions

C_1-C_{20}-alkyl which may be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, decyl, dodecyl, tetradecyl, heptadecyl, octadecyl, eicosyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, benzhydryl, p-tolylmethyl,1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxy-benzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonylethyl, 2-ethoxycarbonylethyl, 2-butoxy-carbonylpropyl, 1,2-di-(methoxycarbonyl)ethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, 2-ethoxyethyl, butylthiomethyl, 2-dodecylthioethyl, 2-phenylthioethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-methyl-aminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylamino-hexyl, 2-hydroxy-2,2-dimethylethyl, 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxyethyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-ethoxyethyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl or 6-ethoxyhexyl, and

C_2-C_{20}-alkyl interrupted by one or more oxygen and/or sulphur atoms and/or one or more substituted or unsubstituted imino groups is, for example, 5-hydroxy-3-oxa-pentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4-oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-oxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxa-undecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl.

[0042] If two radicals form a ring, they can together be 1,3-propylene, 1,4-butylene, 1,5-pentylene, 2-oxa-1,3-propylene, 1-oxa-1,3-propylene, 2-oxa-1,3-propylene, 1-oxa-1,3-propenylene, 1-aza-1,3-propenylene, 1-C_1-C_4-alkyl-1-aza-1,3-propenylene, 1,4-buta-1,3-dienylene, 1-aza-1,4-buta-1,3-dienylene or 2-aza-1,4-buta-1,3-dienylene.

[0043] The number of oxygen and/or sulphur atoms and/or imino groups is not subject to any restrictions. In general, there will be no more than 5 in the radical, preferably no more than 4 and very particularly preferably no more than 3.

[0044] Furthermore, there is generally at least one carbon atom, preferably at least two carbon atoms, between any two heteroatoms.

[0045] Substituted and unsubstituted imino groups can be, for example, imino, methylimino, isopropylimino, n-butylimino or tert-butylimino.

[0046] Furthermore,

functional groups can be carboxy, carboxamide, hydroxy, di(C_1-C_4-alkyl)amino, C_1-C_4-alkyloxycarbonyl, cyano or C_1-C_4-alkyloxy,

C_6-C_{12}-aryl which may be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, phenyl, tolyl, xylyl, α-naphthyl, β-naphthyl, 4-diphenylyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylnaphthyl, isopropylnaphthyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethyl-phenyl, 2,6-dimethoxyphenyl, 2,6-dichlorophenyl, 4-bromophenyl, 2- or 4-nitrophenyl, 2,4- or 2,6-dinitrophenyl, 4-dimethylaminophenyl, 4-acetylphenyl, methoxyethylphenyl or ethoxymethylphenyl,

C_5-C_{12}-cycloalkyl which may be substituted by functional groups, aryl, alkyl, aryloxy, alkyloxy, halogen, heteroatoms and/or heterocycles is, for example, cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, butylcyclohexyl, methoxycyclohexyl, dimethoxycyclohexyl, diethoxycyclohexyl, butylthiocyclohexyl, chlorocyclohexyl, dichlorocyclohexyl, dichlorocyclopentyl or a saturated or unsaturated bicyclic system such as norbornyl or norbornenyl,

a five- or six-membered, oxygen-, nitrogen- and/or sulphur-containing heterocycle is, for example, furyl, thienyl, pyrryl, pyridyl, indolyl, benzoxazolyl, dioxolyl, dioxyl, benzimidazolyl, benzothiazolyl, dimethylpyridyl, methylquinolyl, dimethylpyrryl, methoxyfuryl, dimethoxypyridyl, difluoropyridyl, methylthienyl, isopropylthienyl or tert-butylthienyl and

C_1 to C_4-alkyl is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

[0047] The residues R^1 to R^5 are preferably C_2-C_{18}-alkyl or C_6-C_{12}-aryl, more preferably C_4-C_{16}-alkyl or C_6-C_{12}-aryl, and even more preferably C_4-C_{16}-alkyl or C_6-aryl.

[0048] The residues R^1 to R^5 may be saturated or unsaturated, preferably saturated.

[0049] Preferred residues R^1 to R^5 do not bear any heteroatoms other than carbon of hydrogen.

[0050] Preferred examples of R^1 to R^4 are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, 2-propylheptyl, decyl, dodecyl, tetradecyl, heptadecyl, octadecyl, eicosyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, benzhydryl, p-tolylmethyl or 1-(p-butylphenyl)ethyl.

[0051] In a preferred embodiment at least one of the residues R^1 to R^4 is selected from the group consisting of 2-hydroxyethyl, hydroxyprop-1-yl, hydroxyprop-2-yl, 2-hydroxybutyl or 2-hydroxy-2-phenylethyl.

[0052] In one embodiment R^5 is a polyolefin-homo- or copolymer, preferably a polypropylene, polybutene or polyisobutene residue, with a number-average molecular weight (M_n) of 85 to 20000, for example 113 to 10 000, or 200 to 10000 or 350 to 5000, for example 350 to 3000, 500 to 2500, 700 to 2500, or 800 to 1500. Preferred are polypropenyl, polybutenyl and polyisobutenyl radicals, for example with a number-average molecular weight M_n of 3500 to 5000, 350 to 3000, 500 to 2500, 700 to 2500 and 800 to 1500 g/mol.

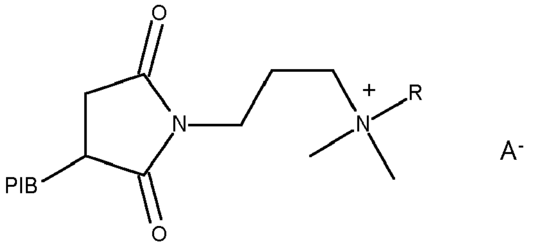
[0053] Preferred examples of anions A^- are the anions of acetic acid, propionic acid, butyric acid, 2-ethylhexanoic acid, trimethylhexanoic acid, 2-propylheptanoic acid, isononanoic acid, versatic acids, decanoic acid, undecanoic acid, dodecanoic acid, saturated or unsaturated fatty acids with 12 to 24 carbon atoms, or mixtures thereof, salicylic acid, oxalic acid mono-C_1-C_4-alkyl ester, phthalic acid mono-C_1-C_4-alkyl ester, C_{12}-C_{100}-alkyl- and -alkenyl succinic acid, especially dodecenyl succinic acid, hexadecenyl succinic acid, eicosenyl succinic acid, and polyisobutenyl succinic acid. Further examples are methyl carbonate, ethyl carbonate, n-butyl carbonate, 2-hydroxyethyl carbonate, and 2-hydroxypropyl carbonate.

[0054] In one preferred embodiment the nitrogen compounds quaternized in the presence of an acid or in an acid-free manner are obtainable by addition of a compound which comprises 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, especially with an epoxide, e.g. styrene or propylene oxide, in the absence of free acid, as described in WO 2012/004300, or with a carboxylic ester, e.g. dimethyl oxalate or methyl salicylate. Suitable compounds having at least one oxygen- or nitrogen-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, especially N,N-dimethyl-1,3-propane diamine, N,N-dimethyl-1,2-ethane diamine or N,N, N'-trimethyl-1,2-ethane diamine. 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. Such a 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 polyisobutenylsuccinic monoamide and which is subsequently quaternized with dimethyl oxalate or methyl salicylate or with styrene oxide or propylene oxide in the absence of free acid.

[0055] Further quaternized nitrogen compounds suitable as compounds (B) are described in

WO 2006/135881 A1, page 5, line 13 to page 12, line 14;
WO 10/132259 A1, page 3, line 28 to page 10, line 25;
WO 2008/060888 A2, page 6, line 15 to page 14, line 29;
WO 2011/095819 A1, page 4, line 5 to page 9, line 29;
GB 2496514 A, paragraph [00012] to paragraph [00041];
WO 2013/117616 A1, page 3, line 34 to page 11, line 2;
WO 14/202425 A2, page 3, line 14 to page 5, line 9;
WO 14/195464 A1, page 15, line 31 to page 45, line 26 and page 75, lines 1 to 4;
WO 15/040147 A1, page 4, line 34 to page 5, line 18 and page 19, line 11 to page 50, line 10;
WO 14/064151 A1, page 5, line 14 to page 6, line 17 and page 16, line 10 to page 18, line 12;
WO 2013/064689 A1, page 18, line 16 to page 29, line 8; and
WO 2013/087701 A1, page 13, line 25 to page 19, line 30,
WO 13/000997 A1, page 17, line 4 to page 25, line 3,
WO 12/004300, page 5, lines 20 to 30, page 8, line 1 to page 10, line 10, and page 19, line 29 to page 28, line 3, each of which is incorporated herein by reference.

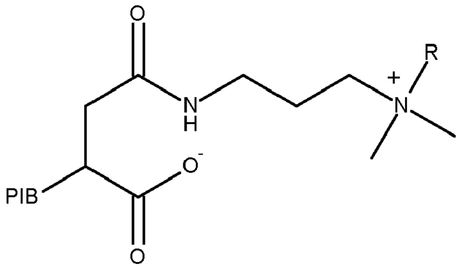
[0056] In one embodiment the quaternized ammonium compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for an C_1- to C_4-alkyl or hydroxy-Ci- to C_4-alkyl, preferably methyl or 2-hydroxypropyl, and
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate R^5O-COO^- as defined above, more preferably acetate, salicylate or methyloxalate.

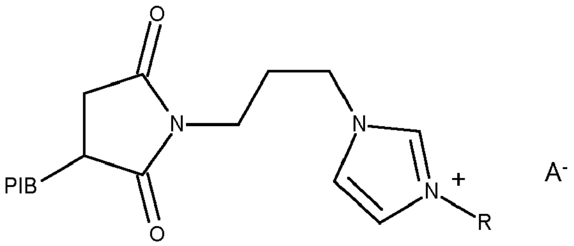
[0057] In another preferred embodiment the quaternized ammonium compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for a hydroxy-Ci- to C_4-alkyl, preferably 2-hydroxypropyl.

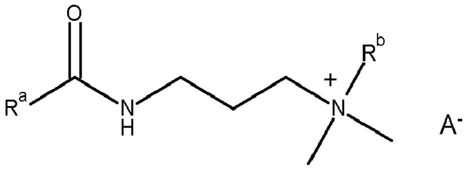
[0058] In another embodiment the quaternized compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for an C_1- to C_4-alkyl or hydroxy-Ci- to C_4-alkyl, preferably methyl, and
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate R^5O-COO^- as defined above, more preferably salicylate or methyloxalate.

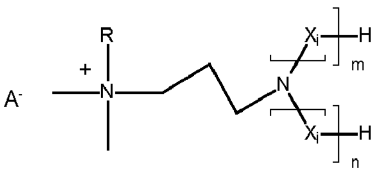
[0059] In another embodiment the quaternized ammonium compound (B) is of formula



wherein in this formula

R^a stands for C_1-C_{20}-alkyl, preferably C_9- to C_{17}-alkyl, more preferably for undecyl, tridecyl, pentadecyl or heptadecyl,
R^b stands for a hydroxy-C_1- to C_4-alkyl, preferably 2-hydroxypropyl or 2-hydroxybutyl, and
A^- stands for an anion, preferably carboxylate R^5COO^-, as defined above, more preferably R^5COO^- being a carboxylate of a fatty acid, especially A^- being acetate, 2-ethylhexanoate, oleate or polyisobutenyl succinate.

[0060] In one embodiment the quaternized ammonium compound (B) is of formula



wherein in this formula

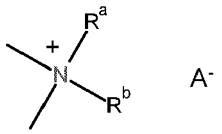
X_i for i = 1 to n and 1 to m are independently of another selected from the group consisting of - CH_2-CH_2-O-, -CH_2-CH(CH_3)-O-, -CH(CH_3)-CH_2-O-, -CH_2-C(CH_3)$_2$-O-, -C(CH_3)$_2$-CH_2-O-, -CH_2-CH(C_2H_5)-O-, -CH(C_2H_5)-CH_2-O- and -CH(CH_3)-CH(CH_3)-O-, preferably selected from the group consisting of -CH_2-CH(CH_3)-O-, -CH(CH_3)-CH_2-O-, -CH_2-C(CH_3)$_2$-O-, -C(CH_3)$_2$-CH_2-O-, -CH_2-CH(C_2H_5)-O-, -CH(C_2H_5)-CH_2-O- and -CH(CH_3)-CH(CH_3)-O-, more preferably selected from the group consisting of -CH_2-CH(CH_3)-O-, -CH(CH_3)-CH_2-O-, -CH_2-C(CH_3)$_2$-O-, -C(CH_3)$_2$-CH_2-O-, - CH_2-CH(C_2H_5)-O- and -CH(C_2H_5)-CH_2-O-, most preferably selected from the group consisting of -CH_2-CH(C_2H_5)-O-, -CH(C_2H_5)-CH_2-O-, -CH_2-CH(CH_3)-O- and -CH(CH_3)-CH_2-O-, and especially selected from the group consisting of -CH_2-CH(CH_3)-O- and -CH(CH_3)-CH_2-O-,

m and n independently of another are positive integers, with the proviso that the sum (m + n) is from 2 to 50, preferably from 5 to 40, more preferably from 10 to 30, and especially from 15 to 25,

R stands for an C_1- to C_4-alkyl, preferably methyl, and

A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate R^5O-COO^- as defined above, more preferably salicylate or methyloxalate.

[0061] In another preferred embodiment the quaternized ammonium compound (B) is of formula

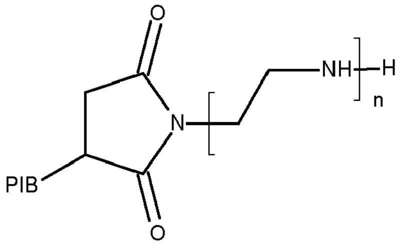


wherein in this formula

R^a and R^b independently of another stand for C_1-C_{20}-alkyl or hydroxy-Ci- to C_4-alkyl, preferably R^a stands for C_1-C_{20}-alkyl, preferably ethyl, n-butyl, n-octyl, n-dodecyl, tetradecyl or hexadecyl, and R^b stands for hydroxy-Ci- to C_4-alkyl, preferably 2-hydroxypropyl,

A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate R^5O-COO^- as defined above, more preferably C_{12}-C_{100}-alkyl- and -alkenyl succinic acid, especially dodecenyl succinic acid, hexadecenyl succinic acid, eicosenyl succinic acid, and polyisobutenyl succinic acid.

[0062] Polyisobutenylsuccinimides (G) are of formula



wherein in this formula
PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol, and n stands for a positive integer of from 2 to 6, preferably 2 to 5, and more preferably 3 or 4.

[0063] Among the additives with detergent action quaternary nitrogen compounds (B) are preferred over the polyisobutenylsuccinimides (G).

[0064] Furthermore, the at least one carboxylic acid (A) and the at least one additive of detergent action, preferably the quaternized component (B) exhibit superior performance - even in the sense of synergism - in improving and/or boosting the separation of water from fuel oils and gasoline fuels when applied together with at least one dehazer exhibiting emulsifying action on its own when used alone as additive component (C) selected from

(C1) alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins;

(C2) alkoxylated phenol formaldehyde resins.

[0065] Dehazer components (C1) and (C2) are normally commercially available products, e.g. the dehazer products available from Baker Petrolite under the brand name of Tolad® such as Tolad® 2898, 9360K, 9348, 9352K, 9327 or 286K.

[0066] In a further preferred embodiment of the present invention, the fuel oils additionally comprise as additive component (D) at least one cetane number improver. 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 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, cyclohexyl nitrate, methylcyclohexyl nitrate and isopropylcyclohexyl nitrate and also branched decyl nitrates of the formula $R^aR^bCH\text{-}CH_2\text{-}O\text{-}NO_2$ in which R^a is an n-propyl or isopropyl radical and R^b 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-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. Most preferably, 2-ethylhexyl nitrate is present in the fuel oils as the sole cetane number improver or in a mixture with other cetane number improvers.

[0067] In the context of the present invention, fuel oils mean preferably middle distillate fuels, especially diesel fuels. However, heating oils, jet fuels and kerosene shall also be encompassed. 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 "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 in a synthetic way by coal gasification or gas liquefaction ["gas to liquid" (GTL) fuels] are suitable, too. 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.

[0068] In a preferred embodiment, the at least one carboxylic acid (A) is used together with the aforementioned components (B) respectively (G), if desired (C) and, if desired (D), in fuel oils which consist

(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

(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 synthetic origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

[0069] The at least one carboxylic acid (A) can also be used together with the aforementioned components (B) respectively (G), if desired (C) and, if desired (D), in fuel oils which consist exclusively of middle distillates of fossil origin and/or of synthetic origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

[0070] 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 C_1- to C_4-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, iso-propanol, n-butanol, isobutanol, sec-butanol, tert-butanol or especially methanol ("FAME").

[0071] 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 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.

[0072] 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.

[0073] Vegetable fats can in principle likewise be used as a source for biodiesel, but play a minor role.

[0074] 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.

[0075] 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.

[0076] 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").

[0077] 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.

[0078] 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.

[0079] In a further preferred embodiment, the at least one carboxylic acid (A) is used together with the aforementioned components (B) respectively (G), (C) and, if desired (D), 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;

(γ) a 95% distillation point (vol/vol) at not more than 360°C.

[0080] Polycyclic aromatic hydrocarbons in (β) shall be understood to mean polyaromatic hydrocarbons according to standard EN 12916. They are determined according to this standard.

[0081] The fuel oils comprise said at least one carboxylic acid (A) in the context of the present invention generally in an amount of at most 5 ppm by weight, preferably up to 4, more preferably up to 3, even more preferably up to 2.5, and especially up to 2 ppm by weight.

[0082] The additive with detergent action (B) respectively (G) or a mixture of a plurality of such additives with detergent action is present in the fuel oils typically in an amount of from 1 to 500 ppm by weight, preferably of from 2 to 250 ppm by weight, more preferably of from 3 to 100 ppm by weight, most preferably of from 4 to 75 ppm by weight, for example of from 5 to 50 ppm by weight.

[0083] One or more dehazers as additive component (C), if any, are present in the fuel oils generally in an amount of from 0.5 to 100 ppm by weight, preferably of from 1 to 50 ppm by weight, more preferably of from 1.5 to 40 ppm by weight, most preferably of from 2 to 30 ppm by weight, for example of from 3 to 20 ppm by weight.

[0084] The cetane number improver (D) or a mixture of a plurality of cetane number improvers is present in the fuel oils normally in an amount of form 10 to 10.000 ppm by weight, preferably of from 20 to 5000 ppm by weight, more preferably of from 50 to 2500 ppm by weight, most preferably of from 100 to 1000 ppm by weight, for example of from 150 to 750 ppm by weight.

[0085] Subject matter of the present invention is also a fuel additive concentrate suitable for use in fuel oils, especially in diesel fuel, comprising

(A) 0.01 to 40% by weight, preferably 0.05 to 20% by weight, more preferably 0.1 to 10% by weight, of at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids;

(B)/(G) 5 to 40% by weight, preferably 10 to 35% by weight, more preferably 15 to 30% by weight, of at least one compound (B) or (G);

(C) 0 to 5% by weight, preferably 0.01 to 5 by weight, more preferably 0.02 to 3.5% by weight, most preferably 0.05 to 2% by weight, of at least one dehazer selected from

(C1) alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins
(C2) alkoxylated phenol formaldehyde resins;

(D) 0 to 75% by weight, preferably 5 to 75% by weight, more preferably 10 to 70% by weight, of at least one cetane number improver;

(E) 0 to 50% by weight, preferably 5 to 50% by weight, more preferably 10 to 40% by weight, of at least one solvent or diluent.

[0086] In each case, the sum of components (A), (B), (C), (D) and (E) results in 100%.

[0087] Said fuel oils such as diesel fuels, or said mixtures of biofuel oils and middle distillates of fossil, synthetic, vegetable or animal origin, may comprise, in addition to the at least one carboxylic acid (A) and components (B) and, if any (C) and/or (D), as coadditives further customary additive components in amounts customary therefor, especially cold flow improvers, corrosion inhibitors, further demulsifiers, antifoams, antioxidants and stabilizers, metal deactivators, antistats, lubricity improvers, dyes (markers) and/or diluents and solvents. Said fuel additive concentrates may also comprise certain of the above coadditives in amounts customary therefor, e.g. corrosion improvers, further demulsifiers, antifoams, antioxidants and stabilizers, metal deactivators, antistats and lubricity improvers.

[0088] Cold flow improvers suitable as further coadditives are, for example, copolymers of ethylene with at least one further unsaturated monomer, in particular ethylene-vinyl acetate copolymers.

[0089] Corrosion inhibitors suitable as further coadditives are, for example, succinic esters, in particular with polyols, fatty acid derivatives, for example oleic esters, oligomerized fatty acids and substituted ethanolamines.

[0090] Further demulsifiers suitable as further coadditives 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 acids, and also alcohol alkoxylates, e.g. alcohol ethoxylates, phenol alkoxylates, e.g. tert-butylphenol ethoxylates or tert-pentylphenol ethoxylates, fatty acids themselves, alkylphenols, condensation products of ethylene oxide and propylene oxide, e.g. ethylene oxide-propylene oxide block copolymers, polyethyleneimines and polysiloxanes.

[0091] Antifoams suitable as further coadditives are, for example, polyether-modified poly-siloxanes.

[0092] Antioxidants suitable as further coadditives are, for example, substituted phenols, e.g. 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-3-methylphenol, and also phenylene-diamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine.

[0093] Metal deactivators suitable as further coadditives are, for example, salicylic acid derivatives, e.g. N,N'-disalicylidene-1,2-propanediamine.

[0094] A lubricity improver suitable as a further coadditive is, for example, glyceryl mono-oleate.

[0095] Suitable solvents and diluents as component (E), 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® (manufactured by Royal Dutch/Shell Group), Exxol® (manufactured by ExxonMobil) and Solvent Naphtha. Also useful here, especially in a blend with the nonpolar organic solvents mentioned, are polar organic solvents, in particular alcohols such as 2-ethylhexanol, decanol and isotridecanol.

[0096] In a further preferred embodiment of the present invention, the gasoline fuels additionally may comprise as additive component (F) at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral oils. The carrier oil of component (F) may be a synthetic oil or a mineral oil; for the instant invention, a refined petroleum oil is also understood to be a mineral oil.

[0097] The carrier oil of component (F) is typically employed in amounts ranging from about 50 to about 2,000 ppm by weight of the gasoline fuel, preferably from 100 to 800 ppm of the gasoline fuel. Preferably, the ratio of carrier oil (F) to additive component (B) respectively (G) will range from 0.35 : 1 to 10 : 1, typically from 0.4 : 1 to 2 : 1.

[0098] Examples for suitable mineral carrier oils are in particular those of viscosity class Solvent Neutral (SN) 500 to 2000, as well as aromatic and paraffinic hydrocarbons and alkoxyalkanols. Another useful mineral carrier oil is a fraction known as "hydrocrack oil" which is obtained from refined mineral oil (boiling point of approximately 360 to 500°C; obtainable from natural mineral oil which is isomerized, freed of paraffin components and catalytically hydrogenated under high pressure).

[0099] Examples for synthetic carrier oils which can be used for the instant invention are olefin polymers with a number average molecular weight of from 400 to 1,800 g/mol, based on poly-alphaolefins or poly-internal-olefins, especially those based on polybutene or on polyisobutene (hydrogenated or non-hydrogenated). Further examples for suitable synthetic carrier oils are polyesters, polyalkoxylates, polyethers, alkylphenol-initiated polyethers, and carboxylic acids of long-chain alkanols.

[0100] Examples for suitable polyethers which can be used for the instant invention are compounds containing polyoxy-C_2-C_4-alkylene groups, especially polyoxy-C_3-C_4-alkylene groups, which can be obtained by reacting C_1-C_{30}-alkanols, C_2-C_{60}-alkandiols, C_1-C_{30}-alkylcyclohexanols or C_1-C_{30}-alkylphenols with 1 to 30 mol ethylene oxide and/or propylene oxide and/or butylene oxides per hydroxyl group, especially with 1 to 30 mol propylene oxide and/or butylene oxides per hydroxyl group. This type of compounds is described, for example, in EP-A 310 875, EP-A 356 725, EP-A 700 985 and US-A 4,877,416.

[0101] Typical examples for suitable polyethers are tridecanol propoxylates, tridecanol butoxylates, isotridecanol butoxylates, 2-propylheptanol propoxylates, 2-propylheptanol butoxylates, heptadecanol propoxylates, isoheptadecanol propoxylates, heptadecanol butoxylates, isoheptadecanol butoxylates, isononylphenol butoxylates, polyisobutenol butoxylates and polyisobutenol propoxylates. In a preferred embodiment, carrier oil component (F) comprises at least one polyether obtained from C_1- to C_{30}-alkanols, especially C_6- to C_{18}-alkanols, or C_2- to C_{60}-alkandiols, especially C_8- to C_{24}-alkandiols, and from 1 to 30 mol, especially 5 to 30 mol, in sum, of propylene oxide and/or butylene oxides. Other synthetic carrier oils and/or mineral carrier oils may be present in component (F) in minor amounts.

[0102] In the context of the present invention, gasoline fuels mean liquid hydrocarbon distillate fuels boiling in the gasoline range. It is in principle suitable for use in all types of gasoline, including "light" and "severe" gasoline species. The gasoline fuels may also contain amounts of other fuels such as, for example, ethanol.

[0103] Typically, gasoline fuels, which may be used according to the present invention exhibit, in addition, one or more of the following features:
The aromatics content of the gasoline fuel is preferably not more than 50 volume % and more preferably not more than 35 volume %. Preferred ranges for the aromatics content are from 1 to 45 volume % and particularly from 5 to 35 volume %.

[0104] The sulfur content of the gasoline fuel is preferably not more than 100 ppm by weight and more preferably not more than 10 ppm by weight. Preferred ranges for the sulfur content are from 0.5 to 150 ppm by weight and particularly from 1 to 10 ppm by weight.

[0105] The gasoline fuel has an olefin content of not more than 21 volume %, preferably not more than 18 volume %, and more preferably not more than 10 volume %. Preferred ranges for the olefin content are from 0.1 to 21 volume % and particularly from 2 to 18 volume %.

[0106] The gasoline fuel has a benzene content of not more than 1.0 volume % and preferably not more than 0.9 volume %. Preferred ranges for the benzene content are from 0 to 1.0 volume % and preferably from 0.05 to 0.9 volume %.

[0107] The gasoline fuel has an oxygen content of not more than 45 weight %, preferably from 0 to 45 weight %, and most preferably from 0.1 to 3.7 weight % (first type) or most preferably from 3.7 to 45 weight % (second type). The gasoline fuel of the second type mentioned above is a mixture of lower alcohols such as methanol or especially ethanol, which derive preferably from natural source like plants, with mineral oil based gasoline, i.e. usual gasoline produced from crude oil. An example for such gasoline is "E 85", a mixture of 85 volume % of ethanol with 15 volume % of mineral oil based gasoline. In a preferred embodiment the gasoline may comprise up to 15 vol% ethanol, more preferably up to 10 vol%.

[0108] The content of alcohols, especially lower alcohols, and ethers in a gasoline fuel of the first type mentioned in the above paragraph is normally relatively low. Typical maximum contents are for methanol 3 volume %, for ethanol 5 volume %, for isopropanol 10 volume %, for tert-butanol 7 volume %, for iso-butanol 10 volume %, and for ethers containing 5 or more carbon atoms in the molecule 15 volume %.

[0109] For example, a gasoline fuel which has an aromatics content of not more than 38 volume % and at the same time an olefin content of not more than 21 volume %, a sulfur content of not more than 50 ppm by weight, a benzene content of not more than 1.0 volume % and an oxygen content of from 0.1 to 2.7 weight % may be applied.

[0110] The summer vapor pressure of the gasoline fuel is usually not more than 70 kPa and preferably not more than 60 kPa (at 37°C).

[0111] The research octane number ("RON") of the gasoline fuel is usually from 90 to 100. A usual range for the corresponding motor octane number ("MON") is from 80 to 90.

[0112] The above characteristics are determined by conventional methods (DIN EN 228).

[0113] The gasoline fuels comprise said at least one carboxylic acid (A) in the context of the present invention generally in an amount of from 0.1 to 5 ppm by weight, preferably of from 0.5 to 4 ppm by weight, more preferably of from 1 to 3 ppm by weight, most preferably of from 1 to 2.5 ppm by weight, for example of from 1 to 2 ppm by weight.

[0114] The additive with detergent action (B) or a mixture of a plurality of such additives with detergent action is present in the gasoline fuels typically in an amount of from 1 to 500 ppm by weight, preferably of from 2 to 250 ppm by weight, more preferably of from 3 to 100 ppm by weight, most preferably of from 4 to 50 ppm by weight, for example of from 5 to 30 ppm by weight.

[0115] In case of an additive with detergent action (G) or a mixture of a plurality of such additives with detergent action, the additive is typically present in the gasoline fuels in an amount of from 1 to 500 ppm by weight, preferably of from 1 to 300 ppm by weight, more preferably of from 1 to 250 ppm by weight, and most preferably of from 2 to 150 ppm by weight.

[0116] One or more dehazers as additive component (C), if any, are present in the gasoline fuels generally in an amount of from 0.5 to 100 ppm by weight, preferably of from 1 to 50 ppm by weight, more preferably of from 1.5 to 40 ppm by weight, most preferably of from 2 to 30 ppm by weight, for example of from 3 to 20 ppm by weight.

[0117] The one or more carrier oils (F), if any, are present in the gasoline fuels normally in an amount of form 10 to 3.000 ppm by weight, preferably of from 20 to 1000 ppm by weight, more preferably of from 50 to 700 ppm by weight, most preferably of from 70 to 500 ppm by weight, for example of from 150 to 300 ppm by weight.

[0118] Subject matter of the present invention is also a fuel additive concentrate suitable for use in gasoline fuels comprising

(A) 0.01 to 40% by weight, preferably 0.05 to 20% by weight, more preferably 0.1 to 10% by weight, of at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids;

(B)/(G) 5 to 40% by weight, preferably 10 to 35% by weight, more preferably 15 to 30% by weight, of at least one compound (B) respectively (G);

(C) 0 to 5% by weight, preferably 0.01 to 5 by weight, more preferably 0.02 to 3.5% by weight, most preferably 0.05 to 2% by weight, of at least one dehazer selected from

(C1) alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins

(C2) alkoxylated phenol formaldehyde resins;

(E) 0 to 80% by weight, preferably 5 to 50% by weight, more preferably 10 to 40% by weight, of at least one solvent or diluent;

(F) 2 to 50% by weight, preferably 10 to 50% by weight, more preferably 25 to 45% by weight, of at least one carrier oil which is substantially free of nitrogen, selected from synthetic carrier oils and mineral carrier oils.

[0119] In each case, the sum of components (A), (B) respectively (G), (C), (D), (E) and (F) results in 100%.

[0120] The amounts given throughout the text refer to the pure components excluding e.g. solvent, unless stated otherwise.

[0121] Said gasoline fuels may comprise, in addition to the at least one carboxylic acid (A) and components (B) respectively (G) and, if any (C) and/or (F), as coadditives further customary additive components in amounts customary therefor, especially corrosion inhibitors, further demulsifiers, antioxidants and stabilizers, metal deactivators, antistats, friction modifyers, dyes (markers) and/or diluents and solvents such as component (E) as defined above. Said gasoline fuel additive concentrates may also comprise certain of the said coadditives in amounts customary therefor, e.g. corrosion improvers, further demulsifiers, antifoams, antioxidants and stabilizers, metal deactivators, antistats and friction modifyers.

[0122] Another object of the present invention is a process for improving or boosting the separation of water from fuel oils and gasoline fuels by applying mixtures of

at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids (A)
with
at least one additive with detergent action selected from the group consisting of

- quaternary nitrogen compounds (B) and
- polyisobutenylsuccinimides (G)

to water containing fuel oils and gasoline fuels and
allowing the organic and aqueous phase to separate.

[0123] The phase separation usually occurs within several seconds to several hours, preferably from 1 minute to 1 hour, more preferably from 2 to 30 minutes, most preferably from 3 to 20 minutes.

[0124] The aqueous layer settles at the bottom of the container, preferably of the storage tank and may be easily removed by floor drain via a valve shut-off.

[0125] The examples which follow are intended to illustrate the present invention without restricting it.

Examples

[0126] As fuel a gasoline E0 fuel (reference fuel according to CEC RF-12-09 by Haltermann, Hamburg, Germany) in accordance with EN 228 was used, characterised as follows:

Feature	Unit		Method
RON		96.3	EN ISO 5164
MON		86.5	EN ISO 5163
Density at 15°C	kg/m3	743.0	EN ISO 12185
DVPE	kPa	63.5	EN 13016-1
Distillation IBP	°C	32.9	EN ISO 3405
Dist. 70 °C	%(V)	25.1	EN ISO 3405
Dist. 100 °C	%(V)	48.7	EN ISO 3405
Dist. 150 °C	%(V)	94.3	EN ISO 3405
Distillation FBP	°C	177.3	EN ISO 3405
Dist. Residue	%(V)	1.0	EN ISO 3405
Olefins	%(V)	8.5	EN ISO 22854
Aromatics	%(V)	34.2	EN ISO 22854
Saturates	%(V)	56.9	EN ISO 22854
Benzene	%(V)	0.88	EN ISO 22854
Methanol	%(V)	< 0.10	EN ISO 22854
Ethanol	%(V)	0.40	EN ISO 22854
iso-Propanol	%(V)	< 0.10	EN ISO 22854
Iso-Butanol	%(V)	< 0.10	EN ISO 22854
TBA	%(V)	< 0.10	EN ISO 22854
MTBE	%(V)	< 0.10	EN ISO 22854
Oxygenates	%(V)	0.40	EN ISO 22854
Oxygen Content	% w	0.2	EN ISO 22854
Sulfur	mg/kg	7.6	EN ISO 20846

[0127] For evaluating the capability of separating water from fuels containing of the respective mixtures of additives, the corresponding standard test method according to ASTM D 1094 - 07 (2019) was applied. For this test, at room temperature a glass cylinder was filled with 20 ml of water phosphate buffer and 80 ml of the fuel and then shaken for 2 minutes. After the emulsion generated has been allowed to settle, phase separation and interface between the phases was ranked with a rating after 5 and 10 minutes as follows:

Separation

Rating	Appearance
(1)	Complete absence of all emulsions and/or precipitates within either layer or upon the fuel layer.

(continued)

Rating	Appearance
(2)	Same as (1), except small air bubbles or small water droplets in the fuel layer.
(3)	Emulsions and/or precipitates within either layer or upon the fuel layer, and/or droplets in the water layer or adhering to the cylinder walls, excluding the walls above the fuel layer.

Interface Conditions

Rating	Appearance
(1)	Clear and clean
(1b)	Clear bubbles covering not more than an estimated 50 % of the interface and no shreds, lace, or film at the interface
(2)	Shred, lace, or film at interface
(3)	Loose lace or slight scum, or both
(4)	Tight lace or heavy scum, or both

[0128] For a pass of the test the rating should be 1b or better.

[0129] The dehazing formulation was prepared in a solvent (Solvent Naphtha) and the formulation added to the respective fuel in the amounts given in the tables. All amounts are given in ppm by weight (mg additive per kg fuel).

											5 min		10 min	
Example	PIBA	Carrier oil	Xylene (solvent)	Detergent	Dehazer	Fatty Acid 1	PIBSA	Oleic acid	Fatty Acid 2	Fatty Acid 3	Rating Interface	Rating Separation	Rating Interface	Rating Separation
1*	140.355	34.865	42.674	25	2						2	1	2	1
2*	140.355	34.865	42.674	25	1						4	3	4	3
3a	140.355	34.865	42.674	25	2	0.109					1b	1	1	1
3b	280.71	69.73	85.348	50	4	0.218					1b	1	1	1
3c	421.065	104.595	128.022	75	6	0.327					1b	1	1	1
4*	140.355	34.865	42.674	25	2		15				1	1	1	1
5	140.355	34.865	42.674	25	2			5			1	1	1	1
6	140.355	34.865	42.674	25	2				5		1b	1	1	1
7	140.355	34.865	42.674	25	2					5	1b	1	1	1

*): Comparative

PIBA: Polyisobutene amine, molecular weight approx. 1000 g/mol, commercially available as KEROCOM® PIBA 03 from BASF

Carrier oil: propoxylated tridecanol derived from trimerbutene (after hydroformylation and hydrogenation)

Detergent: reaction product of n-hexadecyldimethylamine with propylene oxide, with hydrolyzed polyisobutenyl succinic acid as counterion as described in EP 3004294 B1, Synthetic Example 6 (applied as 50 wt% solution in 2-ethylhexanol).

Dehazer: Tolad® 9360K, dehazer commercially available from Baker Hughes

Fatty Acid 1: mixed dimer acid, trimer acid and "synthetic" component, obtained from tall oil fatty acid by Diels-Alder self condensation (according to WO 2013/101256)

PIBSA: Hydrolyzed polyisobutenyl succinic acid anhydride (based upon polyisobutene with a molecular weight of 1000 g/mol) - comparative Dehazing Booster according to WO 2015/003961

Oleic acid

Fatty Acid 2: Mixture of 22% dimer fatty acid, 11% dodecyl succinic acid, and 3% oleic acid in Solvent Naphtha

Fatty Acid 3: tall oil fatty acid mixture

[0130] It can easily be seen that the carboxylic acids according to the invention pass the test using much smaller amounts amounts of 5 ppm or less compared to Example 4 (15 ppm polyisobutenyl succinic acid).

Claims

1. Use of mixtures of

(A) at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids
with

at least one additive with detergent action selected from the group consisting of

- quaternary nitrogen compounds (B) and
- polyisobutenylsuccinimides (G)

for improving or boosting the separation of water from fuel oils and gasoline fuels, preferably from gasoline fuels.

2. Use according to Claim 1, wherein the mixture of (A) and (B) or (G) is applied together with at least one dehazer as additive component (C) selected from

(C1) alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins;
(C2) alkoxylated phenol formaldehyde resins.

3. Use according to any one of the preceding claims, wherein compound (B) is of the formula

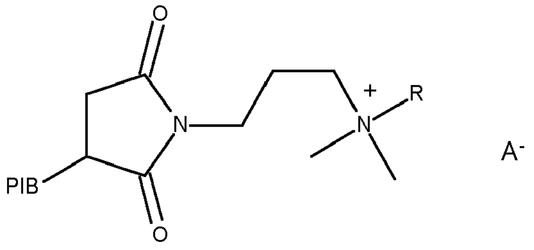
$^{+}NR^1R^2R^3R^4\ A^-$

in which

A^- stands for an anion, preferably a carboxylate R^5COO^- or a carbonate $R^5O\text{-}COO^-$,
and
R^1, R^2, R^3, R^4, and R^5 independently of another are an organic residue with from 1 to 100 carbon atoms, substituted or unsubstituted, preferably unsubstituted, linear or branched alkyl, alkenyl or hydroxyalkyl residue with 1 to 100, more preferably 1 to 75, even more preferably 1 to 30, most preferably 1 to 25 and especially 1 to 20 carbon atoms,
R^5 additionally may be substituted or unsubstituted cycloalkyl or aryl residues bearing 5 to 20, preferably 5 to 12 carbon atoms.

4. Use according to any one of claims 1 or 2, wherein nitrogen compounds (B) are obtainable by addition of a compound which comprises 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 in the presence of an acid or in an acid-free manner, preferably with an epoxide, especially styrene or propylene oxide, in the absence of free acid, or with a carboxylic ester, e.g. dimethyl oxalate or methyl salicylate.

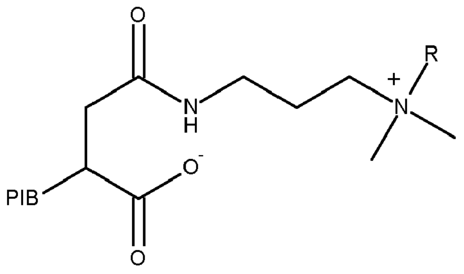
5. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for an C_1- to C_4-alkyl or hydroxy-Ci- to C_4-alkyl, preferably methyl or 2-hydroxypropyl, and
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate $R^5O\text{-}COO^-$ as defined above, more preferably acetate, salicylate or methyloxalate.

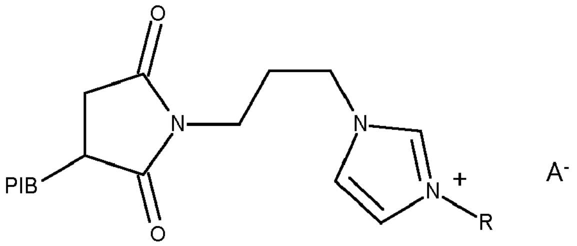
6. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for a hydroxy-Ci- to C_4-alkyl, preferably 2-hydroxypropyl.

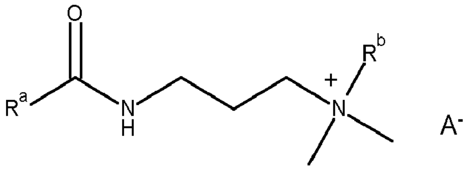
7. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol,
R stands for an C_1- to C_4-alkyl or hydroxy-C_1- to C_4-alkyl, preferably methyl, and
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate $R^5O\text{-}COO^-$ as defined above, more preferably salicylate or methyloxalate.

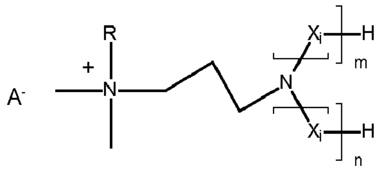
8. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula



wherein in this formula

R^a stands for C_1-C_{20}-alkyl, preferably C_9- to C_{17}-alkyl, more preferably for undecyl, tridecyl, pentadecyl or heptadecyl,
R^b stands for a hydroxy-Ci- to C_4-alkyl, preferably 2-hydroxypropyl or 2-hydroxybutyl, and
A^- stands for an anion, preferably carboxylate R^5COO^-, as defined above, more preferably R^5COO^- being a carboxylate of a fatty acid, especially A^- being acetate, 2-ethylhexanoate, oleate or polyisobutenyl succinate.

9. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula

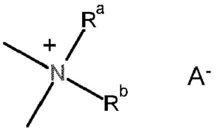


wherein in this formula

X_i for i = 1 to n and 1 to m are independently of another selected from the group consisting of $-CH_2\text{-}CH_2\text{-}O-$, $-CH_2\text{-}CH(CH_3)\text{-}O-$, $-CH(CH_3)\text{-}CH_2\text{-}O-$, $-CH_2\text{-}C(CH_3)_2\text{-}O-$, $-C(CH_3)_2\text{-}CH_2\text{-}O-$, $-CH_2\text{-}CH(C_2H_5)\text{-}O-$, $-CH(C_2H_5)\text{-}CH_2\text{-}O-$ and $-CH(CH_3)\text{-}CH(CH_3)\text{-}O-$, preferably selected from the group consisting of $-CH_2\text{-}CH(CH_3)\text{-}O-$, $-CH(CH_3)\text{-}CH_2\text{-}O-$, $-CH_2\text{-}C(CH_3)_2\text{-}O-$, $-C(CH_3)_2\text{-}CH_2\text{-}O-$, $-CH_2\text{-}CH(C_2H_5)\text{-}O-$, $-CH(C_2H_5)\text{-}CH_2\text{-}O-$ and $-CH(CH_3)\text{-}CH(CH_3)\text{-}O-$, more preferably selected from the group consisting of $-CH_2\text{-}CH(CH_3)\text{-}O-$, $- CH(CH_3)\text{-}CH_2\text{-}O-$, $-CH_2\text{-}C(CH_3)_2\text{-}O-$, $-C(CH_3)_2\text{-}CH_2\text{-}O-$, $-CH_2\text{-}CH(C_2H_5)\text{-}O-$ and $-CH(C_2H_5)\text{-}CH_2\text{-}O-$, most preferably selected from the group consisting of $-CH_2\text{-}CH(C_2H_5)\text{-}O-$, $-CH(C_2H_5)\text{-}CH_2\text{-}O-$, $-CH_2\text{-}CH(CH_3)\text{-}O-$ and $-CH(CH_3)\text{-}CH_2\text{-}O-$, and especially selected from the group consisting of $-CH_2\text{-}CH(CH_3)\text{-}O-$ and $-CH(CH_3)\text{-}CH_2\text{-}O-$,
m and n independently of another are positive integers, with the proviso that the sum (m + n) is from 2 to 50, preferably from 5 to 40, more preferably from 10 to 30, and especially from 15 to 25,
R stands for an C_1- to C_4-alkyl, preferably methyl, and
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate $R^5O\text{-}COO^-$ as defined above, more

preferably salicylate or methyloxalate.

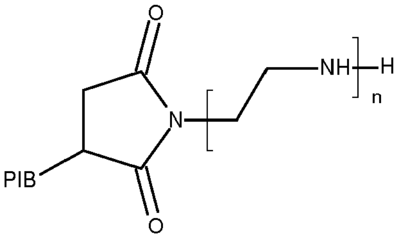
10. Use according to any one of the claims 1 or 2, wherein the nitrogen compound (B) is of formula



wherein in this formula

R^a and R^b independently of another stand for C_1-C_{20}-alkyl or hydroxy-Ci- to C_4-alkyl, preferably R^a stands for C_1-C_{20}-alkyl, preferably ethyl, n-butyl, n-octyl, n-dodecyl, tetradecyl or hexadecyl, and R^b stands for hydroxy-Ci- to C_4-alkyl, preferably 2-hydroxypropyl,
A^- stands for an anion, preferably carboxylate R^5COO^- or a carbonate R^5O-COO^- as defined above, more preferably C_{12}-C_{100}-alkyl- and -alkenyl succinic acid, especially dodecenyl succinic acid, hexadecenyl succinic acid, eicosenyl succinic acid, and polyisobutenyl succinic acid.

11. Use according to any one of the claims 1 or 2, wherein the polyisobutenylsuccinimide (G) is of formula



wherein in this formula

PIB stands for a polyisobutenyl residue having a number average molecular weight M_n of from 550 to 2300, preferably from 650 to 1500 and more preferably from 750 to 1300 g/mol, and
n stands for a positive integer of from 2 to 6, preferably 2 to 5, and more preferably 3 or 4.

12. Process for improving or boosting the separation of water from fuel oils and gasoline fuels by applying mixtures of

at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids (A)
with
at least one additive with detergent action selected from the group consisting of

- quaternary nitrogen compounds (B) and
- polyisobutenylsuccinimides (G)

to such water containing fuel oils and gasoline fuels and allowing the organic and aqueous phase to separate.

13. Process according to Claim 12, wherein the mixture is applied together with at least one dehazer as additive component (C) selected from

(C1) alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins;
(C2) alkoxylated phenol formaldehyde resins.

14. Use and process according to any one of the preceeding claims, wherein the at least one saturated or unsaturated monocarboxylic acid with from 9 to 30 carbon atoms or dimers of such unsaturated monocarboxylic acids (A) is present in the fuel in amounts of at most 5 ppm by weight, preferably up to 4, more preferably up to 3, even more preferably up to 2.5, and especially up to 2 ppm by weight.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 17 0691

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 2 960 319 A2 (AFTON CHEMICAL CORP [US]) 30 December 2015 (2015-12-30) * paragraphs [0016] - [0017], [0022] - [0027], [0030], [0038] - [0042], [0063], [0070]; claims 1, 4, 7; example 1 * -----	1-10, 12-14	INV. C10L1/14 ADD. C10L1/188 C10L1/198 C10L1/222 C10L1/224 C10L10/18
A	US 3 304 162 A (MARVEL JR HARRY D) 14 February 1967 (1967-02-14) * example 1: table 1: control 1; column 2, line 22 - line 27; claim 1; figure 1; examples 1, 2, 5 * -----	1-10, 12-14	
A	US 3 657 121 A (GANNON JOHN J ET AL) 18 April 1972 (1972-04-18) * examples 1-2; table 1 * -----	1-10, 12-14	
X	WO 2020/109568 A1 (TOTAL MARKETING SERVICES [FR]) 4 June 2020 (2020-06-04) * page 30, line 1 - line 4; claim 10; examples 1, 7-8; tables 7-9 * -----	1,3,4, 12-14	
A	WO 2021/063733 A1 (BASF SE [DE]) 8 April 2021 (2021-04-08) * comparative example 1; page 32 - page 33; claim 1; example 4; tables 1, 3a, 3b * -----	1-10, 12-14	**TECHNICAL FIELDS SEARCHED (IPC)** C10L
A	EP 3 019 579 A1 (BASF SE [DE]) 18 May 2016 (2016-05-18) * claims 1, 3 * -----	1-10, 12-14	

~~The present search report has been drawn up for all claims~~

1

Place of search	Date of completion of the search	Examiner
Munich	10 October 2022	Kaluza, Nora

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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Application Number

EP 22 17 0691

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

3-10(completely); 1, 2, 12-14(partially)

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION SHEET B

Application Number
EP 22 17 0691

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. claims: 3-10(completely); 1, 2, 12-14(partially)

   use of mixtures of a monocarboxylic acid or dimer acids thereof (A) and a quaternary nitrogen compound (B)

   \---

2. claims: 11(completely); 1, 2, 12-14(partially)

   use of mixtures of a monocarboxylic acid or dimer acids thereof (A) and polyisobutenylsuccinimides (G)

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 22 17 0691

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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10-10-2022

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		US 2019040332 A1	07-02-2019
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