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(71) Applicant: **BASF SE**
67056 Ludwigshafen am Rhein (DE)

(72) Inventors:
• **MEZGER, Jochen**
67308 Lautersheim (DE)
• **REHBERGER, Hubert**
67056 Ludwigshafen am Rhein (DE)

(74) Representative: **BASF IP Association**
BASF SE
GBI - Z078
67056 Ludwigshafen (DE)

(54) **NOVEL DIESEL FUEL ADDITIVE PACKAGES**

(57) The present invention concerns stabilised Diesel fuel additive packages, Diesel fuels comprising such

Diesel fuel additive packages, and a method for stabilising Diesel fuel additive packages.

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Description

[0001] The present invention concerns stabilised Diesel fuel additive packages, Diesel fuels comprising such Diesel fuel additive packages, and a method for stabilising Diesel fuel additive packages.

[0002] Fuel additive packages for Diesel fuels often comprise cold flow improvers in order to slow or prevent the agglomeration and settling of solid paraffins at the fuel's cloud point ("CP") and lower temperatures. It is thought that, during cooling, the platelet-shaped n-paraffin crystals form a kind of "house of cards structure" and the middle distillate fuel ceases to flow even though its predominant portion is still liquid. The precipitated n-paraffins in the temperature range between cloud point and pour point ("PP") trap the liquid portion and considerably impair the flowability of the middle distillate fuels; the n-paraffins can block filters and cause irregular or completely interrupted fuel supply to the combustion units. Similar disruptions occur in the case of light heating oils.

[0003] It has long been known that suitable additives can modify the crystal growth of the heavier n-paraffins in middle distillate fuels that precipitate out first, upon cooling. Additives of good efficacy prevent middle distillate fuels from already solidifying at temperatures a few degrees Celsius below the temperature at which the first paraffin crystals crystallize out. Instead, fine, readily crystallizing, separate paraffin crystals are formed, which, even when the temperature is lowered further, pass through the filters in motor vehicles and heating systems, or at least form a filter cake which is permeable to the liquid portion of the middle distillates, so that disruption-free operation is assured. The efficacy of the flow improvers is typically expressed, as in accordance with European standard EN 116 or US standard ASTM D6371, indirectly by measuring the fuel's cold filter plugging point ("CFPP"). Cold flow improvers or middle distillate flow improvers ("MDFIs") of this kind which are used have long included, for example, ethylene-vinyl carboxylate copolymers such as ethylene-vinyl acetate copolymers ("EVA").

[0004] One disadvantage of these additives when used in middle distillate fuels is that the paraffin crystals modified in this way, because of their higher density compared to the liquid portion, have a tendency to settle out more and more at the base of the fuel container, for example the reservoir tank, in the course of storage of the middle distillate fuel. This results in formation of a liquid low-heavy paraffin phase in the upper part of the vessel and a biphasic heavy paraffin-rich layer at the base. Since the fuel is usually drawn off not very far above the base of the container both in motor vehicle tanks and in storage or supply tanks belonging to mineral oil dealers, there is the risk that the high concentration of solid paraffins will lead to blockages of filters and metering units. The further the storage temperature drops below the precipitation temperature of the paraffins, the greater this risk becomes, since the amount of paraffin precipitated increases with falling temperature. The additional use of paraffin dispersants or wax anti-settling additives ("WASAs") can reduce the problems outlined.

[0005] Such middle distillate flow improvers and wax anti-settling additives and combination thereof are collectively referred to as wax anti-settling flow improvers ("WAFIs").

[0006] Furthermore, Diesel fuels comprise deposit control additives (DCA) for reducing or removing deposits from injectors in modern direct-injection diesel engines, where the fuel is injected and distributed ultra finely (nebulized) by a multi-hole injection nozzle which reaches directly into the combustion chamber in the engine, instead of being introduced into a prechamber or swirl chamber as in the case of the conventional (chamber) diesel engine. The advantage of the direct-injection diesel engines lies in their high performance for diesel engines and nevertheless low fuel consumption. Moreover, these engines achieve a very high torque even at low speeds.

[0007] The injection nozzle holes are susceptible to formation of deposits, such as Internal Diesel Injector Deposits (IDID), which are successfully removed or their formation be suppressed by quaternary ammonium salts. However, it is difficult to achieve stable formulations with quaternary ammonium salts since such quaternary ammonium salts comprise a polar moiety in a nonpolar environment such as Diesel fuels. Therefore, additionally to the existing stability problem caused by heavy n-paraffins, the stability issues are augmented by the presence of quaternary ammonium salts.

[0008] The combination of such deposit control additives and wax anti-settling flow improvers often lead to unstable additive package formulations, recognisable by turbidity, precipitation or even solidification of the packages. In order to achieve stability of such additive package formulations, the content of solvent is dramatically increased to maintain solubility of potential precipitations.

[0009] Therefore, the problem underlying the present invention was to increase the stability of diesel fuel additive packages comprising deposit control additives and wax anti-settling flow improvers thereby reducing the amount of solvent to be used in such packages.

[0010] The problem was solved by Diesel fuel additive packages comprising

(A) at least one quaternary ammonium compound,

(B) at least one wax anti-settling flow improvers selected from the group consisting of

- (Ba) copolymers of olefins and one or more vinyl esters and/or (meth)acrylic esters
- (Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically

unsaturated dicarboxylic acids

- (Bc) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids and their derivatives
- (Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols
- (Be) reaction products of alkenyl-spiro-bislactones with amines,

(C) at least one saturated or unsaturated C₈- to C₁₈-carboxylic acid, preferably at least one saturated branched C₈- to C₁₈-monocarboxylic acid, more preferably at least one saturated branched C₈- to C₁₆-monocarboxylic acid, even more preferably at least one saturated branched C₈- to C₁₂-monocarboxylic acid.

[0011] With the presence of the carboxylic acid compound (C) it is possible to increase the stability of Diesel fuels comprising components (A) and (B).

[0012] The components are described in more detail as follows:

(A) quaternary ammonium compound

[0013] The quaternary ammonium compounds (A) are preferably of the formula



in which

A- stands for an anion, preferably a carboxylate R⁵COO⁻ or a carbonate R⁵O-COO⁻, and

R¹, R², R³, R⁴, and R⁵ 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,

R⁵ additionally may be substituted or unsubstituted cycloalkyl or aryl residues bearing 5 to 20, preferably 5 to 12 carbon atoms.

[0014] It is also possible that the anion may have a multiple negative charge, 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.

[0015] 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.

[0016] In the organic residues the carbon atoms may be interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, and may be substituted by C₆-C₁₂-aryl, C₅-C₁₂-cycloalkyl or a five- or six-membered, oxygen-, nitrogen- and/or sulfur-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 sulfur 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.

[0017] Two of the residues R¹ to R⁴ 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).

[0018] In this case the ammonium cation may be a morpholinium, piperidinium, piperazinium, pyrrolidinium, imidazolinium or pyridinium cation.

[0019] In these definitions

C₁-C₂₀-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, methoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonyl, 2-ethoxycarbonyl, 2-butoxycarbonyl, 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-octylox-

yethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxylisopropyl, 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-aminoethyl, 2-methylaminoethyl, 2-methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminohexyl, 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

C₂-C₂₀-alkyl interrupted by one or more oxygen and/or sulfur 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-dioxaundecyl, 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.

[0020] 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-C₁-C₄-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.

[0021] The number of oxygen and/or sulfur 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.

[0022] Furthermore, there is generally at least one carbon atom, preferably at least two carbon atoms, between any two heteroatoms.

[0023] Substituted and unsubstituted imino groups can be, for example, imino, methylimino, isopropylimino, n-butylimino or tert-butylimino.

[0024] Furthermore,

functional groups can be carboxy, carboxamide, hydroxy, di(C₁-C₄-alkyl)amino, C₁-C₄-alkyloxycarbonyl, cyano or C₁-C₄-alkyloxy,

C₆-C₁₂-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-diphenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methyl-naphthyl, isopropyl-naphthyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 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,

C₅-C₁₂-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 sulfur-containing heterocycle is, for example, furyl, thienyl, pyrrol, pyridyl, indolyl, benzoxazolyl, dioxolyl, dioxyl, benzimidazolyl, benzothiazolyl, dimethylpyridyl, methylquinolyl, dimethylpyrrol, methoxyfuryl, dimethoxypyridyl, difluoropyridyl, methylthienyl, isopropylthienyl or tert-butylthienyl and

C₁ to C₄-alkyl is, for example, methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl or tert-butyl.

[0025] The residues R¹ to R⁵ are preferably C₂-C₁₈-alkyl or C₆-C₁₂-aryl, more preferably C₄-C₁₆-alkyl or C₆-C₁₂-aryl, and even more preferably C₄-C₁₆-alkyl or C₆-aryl.

[0026] The residues R¹ to R⁵ may be saturated or unsaturated, preferably saturated.

[0027] Preferred residues R¹ to R⁵ do not bear any heteroatoms other than carbon of hydrogen.

[0028] Preferred examples of R¹ to R⁴ 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.

[0029] In a preferred embodiment at least one of the residues R¹ to R⁴ is selected from the group consisting of 2-hydroxyethyl, hydroxyprop-1-yl, hydroxyprop-2-yl, 2-hydroxybutyl or 2-hydroxy-2-phenylethyl.

[0030] In one embodiment R⁵ 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 10000, 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.

[0031] 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-C₁-C₄-alkyl ester, phthalic acid mono-C₁-C₄-alkyl ester, C₁₂-C₁₀₀-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.

[0032] In an especially 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.

[0033] Further quaternized nitrogen compounds suitable as compounds (A) 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;

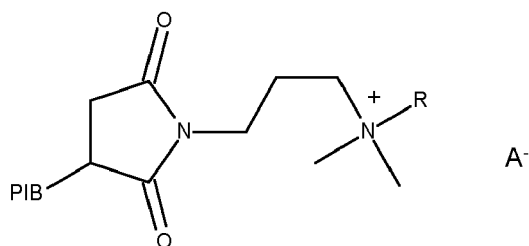
WO 2013/064689 A1, page 18, line 16 to page 29, line 8; and

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.

[0034] In one embodiment, the quaternized ammonium compound (A) is of formula



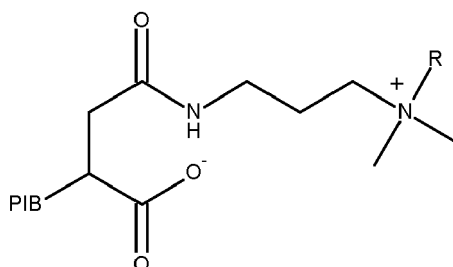
wherein in this formula

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 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.

[0035] In another preferred embodiment, the quaternized ammonium compound (A) is of formula

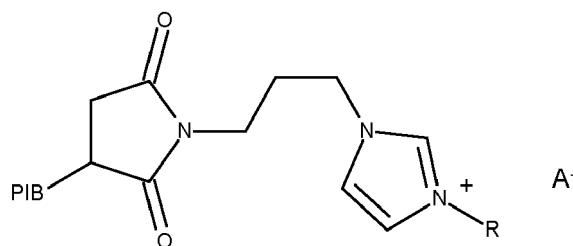


wherein in this formula

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- C_1 - to C_4 -alkyl, preferably 2-hydroxypropyl.

[0036] In another embodiment, the quaternized compound (A) is of formula



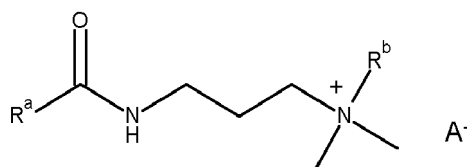
wherein in this formula

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-COO^- as defined above, more preferably salicylate or methyloxalate.

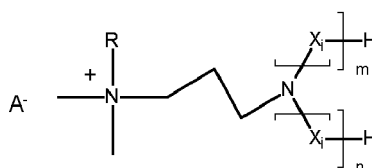
[0037] In another embodiment, the quaternized ammonium compound (A) is of formula



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.

[0038] In one embodiment, the quaternized ammonium compound (A) is of formula



wherein in this formula

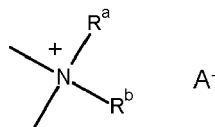
X_i for $i = 1$ to n and 1 to m are independently of another selected from the group consisting of $-\text{CH}_2-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{O}-$, $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{O}-$, $-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-$ and $-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{O}-$, preferably selected from the group consisting of $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{O}-$, $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{O}-$, $-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-$ and $-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{O}-$, more preferably selected from the group consisting of $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$, $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{C}(\text{CH}_3)_2-\text{O}-$, $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{O}-$ and $-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-$, most preferably selected from the group consisting of $-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{O}-$, $-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{O}-$, $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$ and $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$, and especially selected from the group consisting of $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-$ and $-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{O}-$,

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 $\text{R}^5\text{O}-\text{COO}^-$ as defined above, more preferably salicylate or methyloxalate.

[0039] In another preferred embodiment, the quaternized ammonium compound (A) is of formula



wherein in this formula

R^a and R^b independently of another stand for C_1 - C_{20} -alkyl or hydroxy- C_1 - 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- C_1 - to C_4 -alkyl, preferably 2-hydroxypropyl,

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

(B) wax anti-settling flow improvers

[0040] Component (B) is at least one wax anti-settling flow improvers selected from the group consisting of

- (Ba) copolymers of a C₂- to C₄₀-olefin with at least one further ethylenically unsaturated monomer
- (Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically unsaturated dicarboxylic acids
- (Bc) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids and their derivatives
- (Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols, and
- (Be) reaction products of alkenyl-spiro-bis lactones with amines.

(Ba) copolymers of a C₂- to C₄₀-olefin with at least one further ethylenically unsaturated monomer

[0041] Suitable C₂- to C₄₀-olefin monomers for the copolymers of class (Ba) are, for example, those having 2 to 20 and especially 2 to 10 carbon atoms, and 1 to 3 and preferably 1 or 2 carbon-carbon double bonds, especially having one carbon-carbon double bond. In the latter case, the carbon-carbon double bond may be arranged either terminally (α -olefins) or internally. However, preference is given to α -olefins, particular preference to α -olefins having 2 to 6 carbon atoms, for example propene, 1-butene, 1-pentene, 1-hexene and in particular, ethylene.

[0042] In the copolymers of class (Ba), the at least one other ethylenically unsaturated monomer is preferably selected from vinyl esters (alkenyl carboxylates), (meth)acrylic esters and other olefins.

[0043] When other olefins are also copolymerized, they are preferably higher in molecular weight than the above-mentioned C₂- to C₄₀-olefin base monomers. When, for example, the olefin base monomer used is ethylene or propene, suitable further olefins are especially C₁₀- to C₄₀- α -olefins. Other olefins are, in most cases, only additionally copolymerized when monomers with carboxylic ester functions are also used.

[0044] Suitable (meth)acrylic esters are, for example, esters of (meth)acrylic acid with C₁- to C₂₀-alkanols, especially C₁- to C₁₀-alkanols, in particular with methanol, ethanol, propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, 2-ethylhexanol, nonanol and decanol, and structural isomers thereof.

[0045] Suitable vinyl esters (alkenyl carboxylates) are, for example, C₂- to C₁₄-alkenyl esters, for example the vinyl and propenyl esters, of carboxylic acids having 2 to 21 carbon atoms, whose hydrocarbyl radical may be linear or branched. Among these, preference is given to the vinyl esters. Among the carboxylic acids with a branched hydrocarbyl radical, preference is given to those whose branch is in the α position to the carboxyl group, and the α -carbon atom is more preferably tertiary, i.e. the carboxylic acid is what is called a neocarboxylic acid. However, the hydrocarbyl radical of the carboxylic acid is preferably linear.

[0046] Examples of suitable alkenyl carboxylates are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl 2-ethylhexanoate, vinyl neopentanoate, vinyl hexanoate, vinyl neononanoate, vinyl neodecanoate and the corresponding propenyl esters, preference being given to the vinyl esters. A particularly preferred alkenyl carboxylate is vinyl acetate; typical copolymers of group (Ba) resulting therefrom are ethylene-vinyl acetate copolymers ("EVAs"), which are some of the most frequently used.

[0047] Ethylene-vinyl acetate copolymers usable particularly advantageously and the preparation thereof are described in WO 99/29748. Such ethylene-vinyl acetate copolymers e.g. comprise from 50 to 90 wt% ethylene and from 10 to 50 wt% vinyl acetate, preferably from 60 to 80 wt% ethylene and from 20 to 40 wt% vinyl acetate, and more preferably from 65 to 75 wt% ethylene and from 25 to 35 wt% vinyl acetate.

[0048] Suitable copolymers of class (Ba) are also those which comprise two or more different alkenyl carboxylates in copolymerized form, which differ in the alkenyl function and/or in the carboxylic acid group. Likewise suitable are copolymers which, as well as the alkenyl carboxylate(s), comprise at least one olefin and/or at least one (meth)acrylic ester in copolymerized form.

[0049] Terpolymers of a C₂- to C₄₀- α -olefin, a C₁- to C₂₀-alkyl ester of an ethylenically unsaturated monocarboxylic acid having 3 to 15 carbon atoms and a C₂- to C₁₄-alkenyl ester of a saturated monocarboxylic acid having 2 to 21 carbon atoms are also suitable as copolymers of class (Ba). Terpolymers of this kind are described in WO 2005/054314. A typical terpolymer of this kind is formed from ethylene, 2-ethylhexyl acrylate or 2-propylheptyl acrylate and vinyl acetate, e.g. from 50 to 70 wt% ethylene, from 15 to 25 wt% vinyl acetate, and from 10 to 20 wt% ethylhexyl acrylate.

[0050] The at least one or the further ethylenically unsaturated monomer(s) are copolymerized in the copolymers of class (Ba) in an amount of preferably 1 to 50% by weight, especially 10 to 45% by weight and in particular 20 to 40% by weight, based on the overall copolymer. The main proportion in terms of weight of the monomer units in the copolymers of class (Ba) therefore originates generally from the C₂- to C₄₀ base olefins.

[0051] The copolymers of class (Ba) preferably have a number-average molecular weight Mn of 1000 to 20 000, more

preferably of 1000 to 10 000 and especially of 1000 to 8000.

(Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically unsaturated dicarboxylic acids

[0052] Further preferred examples of polar nitrogen-containing compounds are copolymers of alpha-olefins with maleic anhydride and optionally further comonomers which are further reacted with primary or secondary amines. In one embodiment, the polar nitrogen-containing compounds are copolymers of C₁₀- to C₂₀-alpha-olefins with maleic anhydride which are further reacted with primary or secondary C₈-C₁₆-alkyl amines which are bound via amide- and/or imide-groups. Examples are disclosed in EP 1526167 A designated as component B), especially those in Table 4 thereof, or in EP 1857529 designated as component B) which are incorporated by reference.

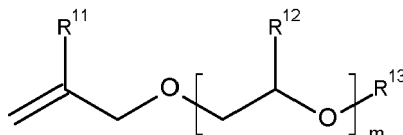
[0053] Further preferred copolymers are disclosed in WO 16/83130, which are incorporated by reference are copolymers of unsaturated dicarboxylic acids, C₆- to C₂₀-alpha olefins, C₆- to C₂₀-alkylesters of acrylic acid or methacrylic acid, and optionally further copolymerizable monomers which are further reacted with dialkylamines bearing C₁₇- to C₃₀-alkyl groups. Especially preferred are Examples 1 to 10 in Table A of WO 16/83130.

[0054] Further especially preferred copolymers are disclosed in WO 17/202642 which are incorporated by reference are copolymers of unsaturated dicarboxylic acids, C₆- to C₂₀-alpha olefins, optionally C₆- to C₂₀-alkylesters of acrylic acid or methacrylic acid, and optionally further copolymerizable monomers which are further reacted with dialkylamines bearing C₁₇- to C₃₀-alkyl groups. The content of C₆- to C₂₀-alkylesters of acrylic acid or methacrylic acid is less than according to WO 16/83130 or may preferably even be 0 (zero). Especially preferred are Examples 1, 2, 3, and 4 of WO 17/202642.

[0055] The copolymers (Bb) comprise amides and imides of ethylenically unsaturated dicarboxylic acids. Preferred dicarboxylic acids are maleic acid, fumaric acid and itaconic acid, and especially maleic anhydride. Particularly suitable comonomers are monoolefins (Bb1) having from 10 to 20, in particular having from 12 to 18, carbon atoms. These monoolefins are preferably linear and the double bond is preferably terminal, as, for example, in dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene and octadecene. The molar ratio of dicarboxamide/imide to olefin or olefins in the polymer is preferably in the range from 1:1.5 to 1.5:1, and is especially equimolar.

[0056] It is possible for copolymer (Bb) also to contain minor amounts of up to 20 mol %, preferably <10 mol %, especially <5 mol %, of further comonomers which are copolymerizable with ethylenically unsaturated dicarboxamides/imides and the olefins mentioned, for example olefins having from 2 to 50 carbon atoms, allyl polyglycol ethers, C₁-C₃₀-alkyl (meth)acrylates, vinylaromatics or C₁-C₂₀-alkyl vinyl ethers. Equally, minor amounts of poly(isobutylenes) having molecular weights of up to 5000 g/mol are used, preference being given to highly reactive variants having a high proportion of terminal vinylidene groups.

[0057] Allyl polyglycol ethers correspond to the general formula



where

- R¹¹ is hydrogen or methyl,
- R¹² is hydrogen or C₁-C₄-alkyl,
- m is a number from 1 to 100,
- R¹³ is C₁-C₂₄-alkyl, C₅-C₂₀-cycloalkyl, C₆-C₁₈-aryl or -C(O)-R¹⁴,
- R¹⁴ is C₁-C₄₀-alkyl, C₅-C₁₀-cycloalkyl or C₆-C₁₈-aryl.

[0058] The copolymers (Bb) are prepared preferably at temperatures between 50 and 220 °C, in particular from 100 to 190 °C. The preferred preparation process is solvent-free bulk polymerization, but it is also possible to carry out the polymerization in the presence of aprotic solvent such as benzene, toluene, xylene or of higher-boiling aromatic, aliphatic or isovalphatic solvents or solvent mixtures such as kerosene or Solvent Naphtha. Particular preference is given to polymerizing in a small amount of moderating, aliphatic or isovalphatic solvents. The proportion of solvent in the polymerization mixture is generally between 10 and 90% by weight, preferably between 35 and 60% by weight. In the solution polymerization, the reaction temperature may be adjusted particularly simply by the boiling point of the solvent or by working under reduced or elevated pressure.

[0059] The weight average molecular mass Mw of the copolymers (Bb) is generally between 1200 and 200 000 g/mol, in particular between 2000 and 100 000 g/mol, measured by means of gel permeation chromatography (GPC) against

polystyrene standards in THF. Copolymers (Bb) have to be oil-soluble in doses relevant in practice, i.e. they have to dissolve without residue at 50 °C in the oil to be additized.

[0060] The reaction of the monomers is initiated by free radical-forming initiators (free-radical chain starters). This substance class includes, for example, oxygen, hydroperoxides and peroxides, for example cumene hydroperoxide, t-butyl hydroperoxide, dilauroyl peroxide, dibenzoyl peroxide, bis(2-ethylhexyl) peroxodicarbonate, t-butyl perpivalate, t-butyl permaleate, t-butyl perbenzoate, dicumyl peroxide, t-butyl cumyl peroxide, di(t-butyl) peroxide, and also azo compounds, for example 2-2'-azobis(2-methylpropanonitrile) or 2,2'-azobis(2-methylbutyronitrile). The initiators are used individually or as a mixture of two or more substances in amounts of from 0.01 to 20% by weight, preferably from 0.05 to 10% by weight, based on the monomer mixture.

[0061] The copolymers (Bb) may be prepared either by reacting maleic acid, fumaric acid and/or itaconic acid or their anhydrides with the corresponding amine and subsequently copolymerizing, or by copolymerizing olefin or olefins with at least one unsaturated dicarboxylic acid or derivative thereof, for example itaconic anhydride and/or maleic anhydride and subsequently reacting with amines. Preference is given to carrying out a copolymerization with anhydrides and converting the resulting copolymer to an amide and/or an imide after the preparation.

[0062] In both cases, the reaction with amines is effected, for example, by reacting with from 0.8 to 2.5 mol of amine per mole of anhydride, preferably with from 1.0 to 2.0 mol of amine per mole of anhydride, at from 50 to 300 °C. When approx. 1 mol of amine is used per mole of anhydride, monoamides are formed preferentially at reaction temperatures of from approx. 50 to 100 °C and additionally bear one carboxyl group per amide group. At higher reaction temperatures of from approx. 100 to 250 °C, imides are formed preferentially from primary amines with elimination of water. When larger amounts of amine are used, preferably 2 mol of amine per mole of anhydride, amide-ammonium salts are formed at from approx. 50 to 200 °C and diamides at higher temperatures of, for example, 100-300 °C, preferably 120-250 °C. The water of reaction may be distilled off by means of an inert gas stream or removed by means of azeotropic distillation in the presence of an organic solvent. To this end, preferably 20-80%, in particular 30-70%, especially 35-55% by weight of at least one organic solvent is used. Here, copolymers (diluted to 50% in solvent) having acid numbers of 30-70 mg KOH/g, preferably of 40-60 mg KOH/g, are regarded as monoamides. Corresponding copolymers having acid numbers of less than 40 mg, especially less than 30 mg KOH/g, are regarded as diamides or imides. Particular preference is given to monoamides and diamides. Suitable amines are primary and secondary amines having one or two C₈-C₁₆-alkyl radicals. They may bear one, two or three amino groups which are bonded via alkylene radicals having two or three carbon atoms. Preference is given to monoamines. In particular, they bear linear alkyl radicals, but may also contain minor amounts, for example up to 30% by weight, preferably up to 20% by weight and especially up to 10% by weight of branched amines (in the 1- or 2-position). Either shorter- or longer-chain amines may be used, but their proportion is preferably below 20 mol % and especially below 10 mol %, for example between 1 and 5 mol %, based on the total amount of the amines used.

[0063] Particularly preferred primary amines are octylamine, 2-ethylhexylamine, decylamine, undecylamine, dodecylamine, n-tridecylamine, isotridecylamine, tetradecylamine, pentadecylamine, hexadecylamine and mixtures thereof.

[0064] Preferred secondary amines are dioctylamine, dinonylamine, didecylamine, didodecylamine, ditetradecylamine, dihexadecylamine, and also amines having different alkyl chain lengths, for example N-octyl-N-decylamine, N-decyl-N-dodecylamine, N-decyl-N-tetradecylamine, N-decyl-N-hexadecylamine, N-dodecyl-N-tetradecylamine, N-dodecyl-N-hexadecylamine, N-tetradecyl-N-hexadecylamine. Also suitable in accordance with the invention are secondary amines which, in addition to a C₈-C₁₆-alkyl radical, bear shorter side chains having from 1 to 5 carbon atoms, for example methyl or ethyl groups. Particularly preferred copolymers (Bb) contain monoamides and diamides of primary monoamines.

[0065] In a preferred embodiment the copolymer (Bb) obtainable by copolymerization of

(Bb1) at least one unsaturated dicarboxylic acid or derivatives thereof,

(Bb2) at least one α -olefin having from at least 6 up to and including 20 carbon atoms,

(Bb3) optionally at least one C₃- to C₂₀-alkyl ester of acrylic acid or methacrylic acid or a mixture of such alkyl esters and

(Bb4) optionally one or more further copolymerizable monomers other than monomers (Bb1), (Bb2) and (Bb3),

with a molar incorporation ratio of (Bb1):(Bb2):(Bb3):(Bb4) of 1:0.5 to 2.0:0 to 2.0:0 to 0.1, preferably 1:0.5 to 2.0:0 to less than 0.5:0 to 0.1, and more preferably 1:0.5 to 2.0:0:0 to 0.1

followed by the reaction with at least one dialkylamine (Bb5), where the two alkyl radicals in the at least one dialkylamine (Bb5) are independently alkyl radicals having at least 17 up to 30 carbon atoms.

[0066] In this embodiment monomer (Bb1) is preferably maleic acid, fumaric acid, 2-methylmaleic acid, 2,3-dimethylmaleic acid, 2-methylfumaric acid, 2,3-dimethylfumaric acid, methylenemalononic acid and tetrahydrophthalic acid, preferably maleic acid and fumaric acid and more preferably maleic acid, and derivatives thereof.

[0067] Monomer (Bb1) is especially maleic anhydride.

[0068] Derivatives are understood to mean

- the anhydrides in question, in monomeric or else polymeric form,
- mono- or dialkyl esters, preferably mono- or di-C₁-C₄-alkyl esters, more preferably mono- or dimethyl esters or the corresponding mono- or diethyl esters,
- mixed esters, preferably mixed esters having different C₁-C₄-alkyl components, more preferably mixed methyl ethyl esters.

[0069] Monomer (Bb2) is at least one linear 1-alkene, preferably selected from the group consisting of 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene and 1-eicosene, of which preference is given to 1-decene, 1-dodecene, 1-tetradecene and 1-hexadecene and particular preference to 1-dodecene.

[0070] Optional monomer (Bb3) is at least one, preferably one to four, more preferably one to three, even more preferably one or two and especially exactly one C₃- to C₂₀-alkyl ester(s) of acrylic acid or methacrylic acid, preferably of acrylic acid, or a mixture of such alkyl esters. The alkyl radical in each case may be straight-chain or branched.

[0071] Suitable C₃- to C₂₀-alkyl esters of acrylic acid or methacrylic acid, preferably of acrylic acid, for component (Bb3) are preferably the esters of acrylic acid and methacrylic acid with C₃- to C₁₈-alkanols, preferably with C₄- to C₁₈-alkanols, more preferably with C₈- to C₁₆-alkanols, even more preferably C₁₀- to C₁₄-alkanols and especially C₁₂-alkanols, for example with n-propanol, isopropanol, n-butanol, sec-butanol, isobutanol, tert-butanol, n-pentanol, tert-pentanol, n-hexanol, n-heptanol, n-octanol, 2-ethylhexanol, n-nonanol, isononanol, n-decanol, 2-propylheptanol, n-undecanol, isoundecanol, n-dodecanol, n-tridecanol, isotridecanol, 3,3,5,5,7-pentamethyloctanol, n-tetradecanol, n-pentadecanol, n-hexadecanol, n-heptadecanol, iso-heptadecanol, 3,3,5,5,7,7,9-heptamethyldecanol, n-octadecanol and n-eicosanol.

[0072] In a preferred embodiment no monomer (Bb3) is present.

[0073] Preferably no further monomers (Bb4) are present.

[0074] Preferred dialkylamines (Bb5) are di-n-octadecylamine, di-n-nonadecylamine and di-n-eicosylamine.

[0075] The molar ratio of dialkylamine (Bb5) based on incorporated units of the dicarboxylic acid (Bb1) in the copolymer is preferably at least 1.1:1, more preferably 1.2 to 2.0:1, even more preferably 1.3 to 1.8:1 and especially 1.3 to 1.7:1.

[0076] The copolymer (Bb), after reaction with component (Bb5), preferably has a weight-average molecular weight (M_w) in the range from 2000 to 20 000, more preferably from 2200 to 10000 and most preferably from 2500 to 8000 and especially 2500 to 6000 g/mol (determined in each case by gel permeation chromatography against polystyrene as standard). The polydispersity is preferably up to 5, more preferably 2 to 5, even more preferably 2 to 4 and especially 2 to 3.

(Be) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids and their derivatives

[0077] Components of class (Bc) are oil-soluble polar nitrogen compounds which may be either ionic or nonionic and preferably have at least one substituent, especially at least two substituents, in the form of a tertiary nitrogen atom of the general formula $>NR^7$ in which R^7 is a C₈- to C₄₀-hydrocarbyl radical. The nitrogen substituents may also be protonated, i.e. be in cationic form. Examples of such nitrogen compounds are ammonium salts and/or amides which are obtainable by the reaction of at least one amine substituted by at least one hydrocarbyl radical with a carboxylic acid having 1 to 4 carboxyl groups or with a suitable derivative thereof. The amines preferably comprise at least one linear C₈- to C₄₀-alkyl radical. Primary amines suitable for preparing the polar nitrogen compounds mentioned are, for example, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tetradecylamine and the higher linear homologs; secondary amines suitable for this purpose are, for example, dioctadecylamine and methylbehnylamine. Also suitable for this purpose are amine mixtures, especially amine mixtures obtainable on the industrial scale, such as fatty amines or hydrogenated tallamines, as described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 6th Edition, "Amines, aliphatic" chapter. Acids suitable for the reaction are, for example, cyclohexane-1,2-dicarboxylic acid, cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid, naphthalenedicarboxylic acid, phthalic acid, isophthalic acid, terephthalic acid, and succinic acids substituted by long-chain hydrocarbyl radicals.

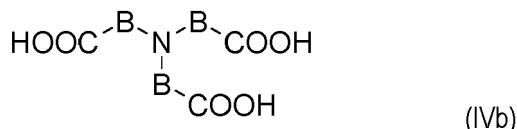
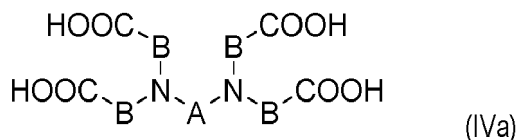
[0078] Examples are reaction products of phthalic anhydride with amines, especially dialkylamines, as described in US 4211534.

[0079] More particularly, the component of class (Bc) is an oil-soluble reaction product of poly(C₂- to C₂₀-carboxylic acids) having at least one tertiary amino group with primary or secondary amines. The poly(C₂- to C₂₀-carboxylic acids) which have at least one tertiary amino group and form the basis of this reaction product comprise preferably at least 3

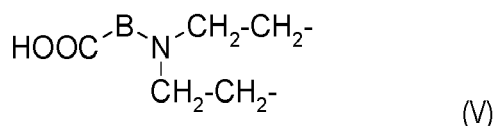
carboxyl groups, especially 3 to 12 and in particular 3 to 5 carboxyl groups. The carboxylic acid units in the polycarboxylic acids have preferably 2 to 10 carbon atoms, and are especially acetic acid units. The carboxylic acid units are suitably bonded to the polycarboxylic acids, usually via one or more carbon and/or nitrogen atoms. They are preferably attached to

tertiary nitrogen atoms which, in the case of a plurality of nitrogen atoms, are bonded via hydrocarbon chains.

[0080] The component of class (Bc) is preferably an oil-soluble reaction product based on poly(C₂- to C₂₀-carboxylic acids) which have at least one tertiary amino group and are of the general formula (IVa) or IVb



in which the variable A is a straight-chain or branched C₂- to C₆-alkylene group or the moiety of the formula (V)



and the variable B is a C₁- to C₁₉-alkylene group. The compounds of the general formulae (IVa) and (IVb) especially have the properties of a WASA.

[0081] Moreover, the preferred oil-soluble reaction product of component (Bc), especially that of the general formula (IVa) or IVb, is an amide, an amide-ammonium salt or an ammonium salt in which no, one or more carboxylic acid groups have been converted to amide groups.

[0082] Straight-chain or branched C₂- to C₆-alkylene groups of the variable A are, for example, 1,1-ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,3-butylene, 1,4-butylene, 2-methyl-1,3-propylene, 1,5-pentylene, 2-methyl-1,4-butylene, 2,2-dimethyl-1,3-propylene, 1,6-hexylene (hexamethylene) and especially 1,2-ethylene. The variable A comprises preferably 2 to 4 and especially 2 or 3 carbon atoms.

[0083] C₁- to C₁₉-alkylene groups of the variable B are, for example, methylene, 1,2-ethylene, 1,3-propylene, 1,4-butylene, hexamethylene, octamethylene, decamethylene, dodecamethylene, tetradecamethylene, hexadecamethylene, octadecamethylene, nonadecamethylene and especially methylene. The variable B comprises preferably 1 to 10 and especially 1 to 4 carbon atoms.

[0084] The primary and secondary amines as a reaction partner for the polycarboxylic acids to form component (Bc) are typically monoamines, especially aliphatic monoamines. These primary and secondary amines may be selected from a multitude of amines which bear hydrocarbyl radicals which may optionally be bonded to one another.

[0085] These parent amines of the oil-soluble reaction products of component (Bc) are usually secondary amines and have the general formula HN(R⁸)₂ in which the two variables R⁸ are each independently straight-chain or branched C₁₀- to C₃₀-alkyl radicals, especially C₁₄- to C₂₄-alkyl radicals. These relatively long-chain alkyl radicals are preferably straight-chain or only slightly branched. In general, the secondary amines mentioned, with regard to their relatively long-chain alkyl radicals, derive from naturally occurring fatty acids and from derivatives thereof. The two R⁸ radicals are preferably identical.

[0086] The secondary amines mentioned may be bonded to the polycarboxylic acids by means of amide structures or in the form of the ammonium salts; it is also possible for only a portion to be present as amide structures and another portion as ammonium salts. Preferably only few, if any, free acid groups are present. The oil-soluble reaction products of component (Bc) are preferably present completely in the form of the amide structures.

[0087] Typical examples of such components (Bc) are reaction products of nitrilotriacetic acid, of ethylenediaminetetraacetic acid or of propylene-1,2-diaminetetraacetic acid with in each case 0.5 to 1.5 mol per carboxyl group, especially 0.8 to 1.2 mol per carboxyl group, of a di-C₁₀- to C₂₄-alkyl amine, preferably dioleamine, dipalmitamine, dicocoamine, distearylamine, dibehenylamine or especially ditallamine. A particularly preferred component (Bc) is the reaction product of 1 mol of ethylenediaminetetraacetic acid and 4 mol of hydrogenated ditallamine.

[0088] Further typical examples of component (Bc) include the N,N-dialkylammonium salts of 2-N',N'-dialkylamido-benzoates, for example the reaction product of 1 mol of phthalic anhydride and 2 mol of ditallamine, the latter being

hydrogenated or unhydrogenated, and the reaction product of 1 mol of an alkenylspirobis lactone with 2 mol of a dialkylamine, for example ditallamine and/or tallamine, the latter two being hydrogenated or unhydrogenated.

[0089] Further typical structure types for the component of class (Bc) are cyclic compounds with tertiary amino groups or condensates of long-chain primary or secondary amines with carboxylic acid-containing polymers, as described in WO 93/18115.

[0090] Particular preferred paraffin dispersants comprise reaction products of secondary fatty amines having from 20 to 44 carbon atoms, in particular dicoconut amine; ditallow fat amine, distearylamine and dibehenylamine with carboxylic acids and their derivatives. Particularly useful paraffin dispersants have been found to be those which are obtained by reacting aliphatic or aromatic amines, preferably long-chain aliphatic amines, with aliphatic or aromatic mono-, di-, tri- or tetracarboxylic acids or their anhydrides (cf. U.S. Pat. No. 4,211,534). Equally suitable as paraffin dispersants are amides and ammonium salts of aminoalkylenepolycarboxylic acids, such as nitrilotriacetic acid or ethylenediaminetetraacetic acid, with secondary amines (cf. EP 0 398 101).

[0091] Optionally and preferably such components (Bc), especially the reaction product of 1 mol of ethylenediaminetetraacetic acid and 4 mol of hydrogenated ditallamine, may be applied together with reaction products of maleic anhydride and amines and/or reaction products of fatty acids and ethylene diamine oligomers, preferably with both reaction products of maleic anhydride and amines as well as reaction products of fatty acids and ethylene diamine oligomers.

[0092] Reaction products of maleic anhydride and mono amines are prepared by reacting maleic anhydride with C₈₋₃₀-alkylamines, preferably primary C₈-C₁₈-alkylamines, in a molar ratio of 1:1 at from 70 to 100°C by the process described in DE-A-1149843 and EP-A-106234; suitable primary amines are all amines defined within these limits, for example straight-chain or branched octyl-, nonyl-, decyl-, undecyl-, dodecyl-, tridecyl-, tetradecyl-, pentadecyl-, hexadecyl-, heptadecyl- and octadecylamine and mixtures of these amines. The reaction product of one mole of maleic anhydride and one mole of tridecylamine is particularly preferred.

[0093] Reaction products of saturated or unsaturated C₁₂-C₂₄-fatty acids and ethylene diamine oligomers are prepared by reacting at least one fatty acid or a mixture of fatty acids with ethylene diamine or oligomers thereof.

[0094] The fatty acids are preferably unsaturated and preferably comprise 14 to 22, and more preferably 16 to 20 carbon atoms. Examples for suitable fatty acids are listed below under compound (C). Preferred are hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, and mixtures thereof, and especially oleic acid, linoleic acid, and linolaidic acid. Oleic acid is preferred.

[0095] The ethylene diamine oligomers may be ethylene diamine, diethylene triamine, triethylene tetraamine, and tetraethylene pentaamine, preferably diethylene triamine or triethylene tetraamine, and more preferably diethylene triamine.

[0096] Fatty acid and diamine are reacted in a molar ratio of from 1 : 1 to 3:1, preferably 1.5 : 1 to 2.5 : 1, more preferably around 2 : 1, and very preferably 2:1.

[0097] The reaction product comprises a mixture of several products, e.g. amides and imidazolines.

(Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols

[0098] Other paraffin dispersants are copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols (cf. EP 0 154 177).

(Be) reaction products of alkenyl-spiro-bis lactones with amines

[0099] Products (Be) are the reaction products of alkenyl-spiro-bis lactones with amines (cf. EP 0 413 279 B1).

[0100] Further components (B) may be reaction products of terpolymers based on α,β -unsaturated dicarboxylic anhydrides, α,β -unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols according to EP-A-0 606 055 A2.

[0101] Carboxylic acid compound (C) is at least one saturated or unsaturated C₈- to C₁₈-carboxylic acid, preferably at least one saturated branched C₈- to C₁₈-monocarboxylic acid, more preferably at least one saturated branched C₈- to C₁₆-monocarboxylic acid, even more preferably at least one saturated branched C₈- to C₁₂-monocarboxylic acid.

[0102] In case of unsaturated carboxylic acids, the carboxylic acid may be one- or multifold unsaturated, however, compound (C) is preferably saturated.

[0103] Very preferred examples of branched non-fatty acids as monocarboxylic acids (C) are 2-ethyl hexanoic acid, 2,2-dimethylhexanoic acid (neooctanoic acid, Versatic Acid 8), 2,2-dimethylheptanoic acid (neononanoic acid, Versatic Acid 9), isononanoic acid, 2-propyl heptanoic acid, 2,2-dimethyloctanoic acid (neodecanoic acid, Versatic Acid 10), neoundecanoic acid (Versatic Acid 11), neododecanoic acid, and neotridecanoic acid (Versatic Acid 13). The neoalkanoic acids comprising 8 to 13 carbon atoms may be mixtures of isomers and not necessarily pure isomers.

[0104] For example, neodecanoic acid may be a mixture of carboxylic acids (CAS 26896-20-8) comprising 2,2,3,5-tetramethylhexanoic acid, 2,4-dimethyl-2-isopropylpentanoic acid, 2,5-dimethyl-2-ethylhexanoic acid, 2,2-dimethyloctanoic acid, and/or 2,2-diethylhexanoic acid. It is a feature of such neoalkanoic acids that the carboxylic acid group is bound to a carbon atom (quaternary carbon atom) which further bears three alkyl groups, preferably one methyl group and two

alkyl groups. The C₈- to C₁₃-neoalkanoic acids constitute a preferred embodiment of the present invention.

[0105] In another preferred embodiment, the carboxylic acid (C) is isononanoic acid. 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.

[0106] Further, less preferred examples for linear saturated or unsaturated carboxylic acid compounds (C) are dodecanoic acid (lauric acid), tridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, erucic acid, arachidic acid, behenic acid, lignoceric acid and cerotic acid, preferred are tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, erucic acid, arachidic acid, and behenic acid, very preferred are hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, and mixtures thereof, and especially oleic acid, linoleic acid, and linolaidic acid. Oleic acid is preferred.

[0107] It is also possible to use a mixture of aliphatic monocarboxylic acids, especially from natural and renewable sources, e.g. animal or preferably vegetable oil. Such mixtures of aliphatic mono-carboxylic acids are usually obtained by saponification of natural oils and yield mixtures of aliphatic monocarboxylic acids with different number of carbon atoms depending on the source and origin of the natural oil. Preferred are linseed oil, coconut fat, palm kernel oil, palm oil, soy bean oil, peanut oil, cocoa butter, shea butter, cotton seed oil, corn oil, sunflower oil, rapeseed oil or castor oil.

[0108] Possible is also a composition of tall oil fatty acids which usually comprises palmitic acid, oleic acid, and linoleic acid.

(D) Olefin-carboxylic acid copolymer (optional)

[0109] Optional copolymer (D) is a copolymer with a molecular weight Mn of from 0.5 to 10 kDa with a content of free acid groups in the copolymer of from 1 to 8 mmol/g of copolymer, more preferably from 2 to 7.5, even more preferably from 3 to 7 mmol/g of copolymer.

[0110] The olefin-carboxylic acid copolymer (D) is a copolymer obtainable by

- in a first reaction step (I) copolymerizing

(Da) at least one ethylenically unsaturated mono- or dicarboxylic acid or derivatives thereof, preferably a dicarboxylic acid,

(Db) at least one α -olefin having from at least 12 up to and including 30 carbon atoms,

(Dc) optionally at least one further aliphatic or cycloaliphatic olefin which has at least 4 carbon atoms and is different than (Db) and

(Dd) optionally one or more further copolymerizable monomers other than monomers (Da), (Db) and (Dc), selected from the group consisting of

(Dda) vinyl esters,

(Ddb) vinyl ethers,

(Ddc) (meth)acrylic esters of alcohols having at least 5 carbon atoms,

(Ddd) allyl alcohols or ethers thereof,

(Dde) N-vinyl compounds selected from the group consisting of vinyl compounds of heterocycles containing at least one nitrogen atom, N-vinylamides or N-vinylactams,

(Ddf) ethylenically unsaturated aromatics,

(Ddg) α,β -ethylenically unsaturated nitriles,

(Ddh) (meth)acrylamides and

(Ddi) allylamines,

followed by

- in a second optional reaction step (II) partly or fully hydrolyzing and/or saponifying anhydride or carboxylic ester functionalities present in the copolymer obtained from (I), the second reaction step being run at least when the copolymer obtained from reaction step (I) does not comprise any free carboxylic functionalities.

Description of the copolymer (D)

[0111] The monomer (Da) is at least one, preferably one to three, more preferably one or two and most preferably exactly one ethylenically unsaturated, preferably α,β -ethylenically unsaturated, mono- or dicarboxylic acid(s) or derivatives thereof, preferably a dicarboxylic acid or derivatives thereof.

[0112] Derivatives are understood to mean

- the corresponding anhydrides in monomeric or else polymeric form,
- mono- or dialkyl esters, preferably mono- or di-C₁-C₄-alkyl esters, more preferably mono- or dimethyl esters or the corresponding mono- or diethyl esters, and
- mixed esters, preferably mixed esters having different C₁-C₄ alkyl components, more preferably mixed methyl ethyl esters.

[0113] Preferably, the derivatives are anhydrides in monomeric form or di-C₁-C₄-alkyl esters, more preferably anhydrides in monomeric form.

[0114] In the context of this document, C₁-C₄-alkyl is understood to mean methyl, ethyl, iso-propyl, n-propyl, n-butyl, isobutyl, sec-butyl and tert-butyl, preferably methyl and ethyl, more preferably methyl.

[0115] Examples of α,β -ethylenically unsaturated mono- or dicarboxylic acids are those mono- or dicarboxylic acids or derivatives thereof in which the carboxyl group or, in the case of dicarboxylic acids, at least one carboxyl group, preferably both carboxyl groups, is/are conjugated to the ethylenically unsaturated double bond.

[0116] Examples of ethylenically unsaturated mono- or dicarboxylic acids that are not α,β -ethylenically unsaturated are cis-5-norbornene-endo-2,3-dicarboxylic anhydride, exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride and cis-4-cyclohexene-1,2-dicarboxylic anhydride.

[0117] Examples of α,β -ethylenically unsaturated monocarboxylic acids are acrylic acid, methacrylic acid, crotonic acid and ethylacrylic acid, preferably acrylic acid and methacrylic acid, referred to in this document as (meth)acrylic acid for short, and more preferably acrylic acid.

[0118] Particularly preferred derivatives of α,β -ethylenically unsaturated monocarboxylic acids are methyl acrylate, ethyl acrylate, n-butyl acrylate and methyl methacrylate.

[0119] Examples of dicarboxylic acids are maleic acid, fumaric acid, itaconic acid (2-methylenebutanedioic acid), citraconic acid (2-methylmaleic acid), glutaconic acid (pent-2-ene-1,5-dicarboxylic acid), 2,3-dimethylmaleic acid, 2-methylfumaric acid, 2,3-dimethylfumaric acid, methylenemalononic acid and tetrahydrophthalic acid, preferably maleic acid and fumaric acid and more preferably maleic acid and derivatives thereof.

[0120] More particularly, monomer (Da) is maleic anhydride.

[0121] Monomer (Db) is at least one, preferably one to four, more preferably one to three, even more preferably one or two and most preferably exactly one α -olefin(s) having from at least 12 up to and including 30 carbon atoms. The α -olefins (Db) preferably have at least 14, more preferably at least 16 and most preferably at least 18 carbon atoms. Preferably, the α -olefins (Db) have up to and including 28, more preferably up to and including 26 and most preferably up to and including 24 carbon atoms.

[0122] Preferably, the α -olefins may be one or more linear or branched, preferably linear, 1-alkene.

[0123] Examples of these are 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-docosene, 1-tetracosene, 1-hexacosene, preference being given to 1-octadecene, 1-eicosene, 1-docosene and 1-tetracosene, and mixtures thereof.

[0124] Further examples of α -olefin (Db) are those olefins which are oligomers or polymers of C₂ to C₁₂ olefins, preferably of C₃ to C₁₀ olefins, more preferably of C₄ to C₆ olefins. Examples thereof are ethene, propene, 1-butene, 2-butene, isobutene, pentene isomers and hexene isomers, preference being given to ethene, propene, 1-butene, 2-butene and isobutene.

[0125] Named examples of α -olefins (Db) include oligomers and polymers of propene, 1-butene, 2-butene, isobutene, and mixtures thereof, particularly oligomers and polymers of propene or isobutene or of mixtures of 1-butene and 2-butene. Among the oligomers, preference is given to the trimers, tetramers, pentamers and hexamers, and mixtures thereof.

[0126] In addition to the olefin (Db), it is optionally possible to incorporate at least one, preferably one to four, more preferably one to three, even more preferably one or two and especially exactly one further aliphatic or cycloaliphatic

olefin(s) (Dc) which has/have at least 4 carbon atoms and is/are different than (Db) by polymerization into the inventive copolymer.

[0127] The olefins (Dc) may be olefins having a terminal (α -)double bond or those having a non-terminal double bond, preferably having an α -double bond. The olefin (Dc) preferably comprises olefins having 4 to fewer than 12 or more than 30 carbon atoms. If the olefin (Dc) is an olefin having 12 to 30 carbon atoms, this olefin (Dc) does not have an α -double bond.

[0128] Examples of aliphatic olefins (Dc) are 1-butene, 2-butene, isobutene, pentene isomers, hexene isomers, heptene isomers, octene isomers, nonene isomers, decene isomers, undecene isomers and mixtures thereof.

[0129] Examples of cycloaliphatic olefins (Dc) are cyclopentene, cyclohexene, cyclooctene, cyclodecene, cyclododecene, α - or β -pinene and mixtures thereof, limonene and norbornene.

[0130] Further examples of olefins (Dc) are polymers having more than 30 carbon atoms of propene, 1-butene, 2-butene or isobutene or of olefin mixtures comprising the latter, preferably of isobutene or of olefin mixtures comprising the latter, more preferably having a mean molecular weight M_w in the range from 500 to 5000 g/mol, preferably 650 to 3000 and more preferably 800 to 1500 g/mol.

[0131] Preferably, the oligomers or polymers comprising isobutene in copolymerized form have a high content of terminal ethylenic double bonds (α -double bonds), for example at least 50 mol%, preferably at least 60 mol%, more preferably at least 70 mol% and most preferably at least 80 mol%.

[0132] For the preparation of such oligomers or polymers comprising isobutene in copolymerized form, suitable isobutene sources are either pure isobutene or isobutene-containing C4 hydrocarbon streams, for example C4 raffinates, especially "raffinate 1", C4 cuts from isobutane dehydrogenation, C4 cuts from steamcrackers and from FCC crackers (fluid catalyzed cracking), provided that they have substantially been freed of 1,3-butadiene present therein. A C4 hydrocarbon stream from an FCC refinery unit is also known as a "b/b" stream. Further suitable isobutene-containing C4 hydrocarbon streams are, for example, the product stream of a propylene-isobutane cooxidation or the product stream from a metathesis unit, which are generally used after customary purification and/or concentration. Suitable C4 hydrocarbon streams comprise generally less than 500 ppm, preferably less than 200 ppm, of butadiene. The presence of 1-butene and of cis- and trans-2-butene is substantially uncritical. Typically, the isobutene concentration in said C4 hydrocarbon streams is in the range from 40% to 60% by weight. For instance, raffinate 1 generally consists essentially of 30% to 50% by weight of isobutene, 10% to 50% by weight of 1-butene, 10% to 40% by weight of cis- and trans-2-butene and 2% to 35% by weight of butanes; in the polymerization process the unbranched butenes in the raffinate 1 are generally virtually inert, and only the isobutene is polymerized.

[0133] In a preferred embodiment, the monomer source used for polymerization is a technical C4 hydrocarbon stream having an isobutene content of 1% to 100% by weight, especially of 1% to 99% by weight, in particular of 1% to 90% by weight, more preferably of 30% to 60% by weight, especially a raffinate 1 stream, a b/b stream from an FCC refinery unit, a product stream from a propylene-isobutane cooxidation or a product stream from a metathesis unit.

[0134] Especially when a raffinate 1 stream is used as isobutene source, the use of water as the sole initiator or as further initiator has been found to be useful, particularly when polymerization is effected at temperatures of -20°C to $+30^{\circ}\text{C}$, especially of 0°C to $+20^{\circ}\text{C}$. At temperatures of -20°C to $+30^{\circ}\text{C}$, especially of 0°C to $+20^{\circ}\text{C}$, however, it is possible to dispense with the use of an initiator when using a raffinate 1 stream as isobutene source.

[0135] Said isobutene-containing monomer mixture may comprise small amounts of contaminants such as water, carboxylic acids or mineral acids without causing any critical yield or selectivity losses. It is appropriate to the purpose to avoid accumulation of these impurities by removing such harmful substances from the isobutene-containing monomer mixture, for example, by adsorption on solid adsorbents such as activated carbon, molecular sieves or ion exchangers.

[0136] It is also possible, albeit less preferable, to convert monomer mixtures of isobutene or of the isobutene-containing hydrocarbon mixture with olefinically unsaturated monomers copolymerizable with isobutene. If monomer mixtures of isobutene with suitable comonomers are to be copolymerized, the monomer mixture comprises preferably at least 5% by weight, more preferably at least 10% by weight and especially at least 20% by weight of isobutene, and preferably at most 95% by weight, more preferably at most 90% by weight and especially at most 80% by weight of comonomers.

[0137] In a preferred embodiment, the mixture of the olefins (Db) and optionally (Dc), averaged to their molar amounts, have at least 12 carbon atoms, preferably at least 14, more preferably at least 16 and most preferably at least 17 carbon atoms.

[0138] For example, a 2:3 mixture of docosene and tetradecene has an averaged value for the carbon atoms of $0.4 \times 22 + 0.6 \times 14 = 17.2$.

[0139] The upper limit is less relevant and is generally not more than 60 carbon atoms, preferably not more than 55, more preferably not more than 50, even more preferably not more than 45 and especially not more than 40 carbon atoms.

[0140] The optional monomer (Dd) is at least one monomer, preferably one to three, more preferably one or two and most preferably exactly one monomer(s) selected from the group consisting of

(Dda) vinyl esters,
(Ddb) vinyl ethers,

(Ddc) (meth)acrylic esters of alcohols having at least 5 carbon atoms,
 (Ddd) allyl alcohols or ethers thereof,
 (Dde) N-vinyl compounds selected from the group consisting of vinyl compounds of heterocycles containing at least one nitrogen atom, N-vinylamides or N-vinylactams,
 5 (Ddf) ethylenically unsaturated aromatics and
 (Ddg) α,β -ethylenically unsaturated nitriles,
 (Ddh) (meth)acrylamides and
 (Ddi) allylamines.

10 **[0141]** Examples of vinyl esters (Dda) are vinyl esters of C_2 - to C_{12} -carboxylic acids, preferably vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pentanoate, vinyl hexanoate, vinyl octanoate, vinyl 2-ethylhexanoate, vinyl decanoate, and vinyl esters of Versatic Acids 5 to 10, preferably vinyl esters of 2,2-dimethylpropionic acid (pivalic acid, Versatic Acid 5), 2,2-dimethylbutyric acid (neohexanoic acid, Versatic Acid 6), 2,2-dimethylpentanoic acid (neoheptanoic acid, Versatic Acid 7), 2,2-dimethylhexanoic acid (neooctanoic acid, Versatic Acid 8), 2,2-dimethylheptanoic acid (neononanoic acid, Versatic Acid 9) or 2,2-dimethyloctanoic acid (neodecanoic acid, Versatic Acid 10).

15 **[0142]** Examples of vinyl ethers (Ddb) are vinyl ethers of C_1 - to C_{12} -alkanols, preferably vinyl ethers of methanol, ethanol, iso-propanol, n-propanol, n-butanol, iso-butanol, sec-butanol, tert-butanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol) or 2-ethylhexanol.

20 **[0143]** Preferred (meth)acrylic esters (Ddc) are (meth)acrylic esters of C_5 - to C_{12} -alkanols, preferably of n-pentanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol), 2-ethyl-hexanol or 2-propylheptanol. Particular preference is given to pentyl acrylate, 2-ethylhexyl acrylate, 2-propylheptyl acrylate.

[0144] Examples of monomers (Ddd) are allyl alcohols and allyl ethers of C_2 - to C_{12} -alkanols, preferably allyl ethers of methanol, ethanol, iso-propanol, n-propanol, n-butanol, iso-butanol, sec-butanol, tert-butanol, n-hexanol, n-heptanol, n-octanol, n-decanol, n-dodecanol (lauryl alcohol) or 2-ethylhexanol.

25 **[0145]** Examples of vinyl compounds (Dde) of heterocycles comprising at least one nitrogen atom are N-vinylpyridine, N-vinylimidazole and N-vinylmorpholine.

[0146] Preferred compounds (Dde) are N-vinylamides or N-vinylactams.

[0147] Examples of N-vinylamides or N-vinylactams (Dde) are N-vinylformamide, N-vinylacetamide, N-vinylpyrrolidone and N-vinylcaprolactam.

30 **[0148]** Examples of ethylenically unsaturated aromatics (Ddf) are styrene and α -methylstyrene.

[0149] Examples of α,β -ethylenically unsaturated nitriles (Ddg) are acrylonitrile and methacrylonitrile.

[0150] Examples of (meth)acrylamides (Ddh) are acrylamide and methacrylamide.

[0151] Examples of allylamines (Ddi) are allylamine, dialkylallylamine and trialkylallylammonium halides.

[0152] Preferred monomers (Dd) are (Dda), (Ddb), (Ddc), (Dde) and/or (Ddf), more preferably (Dda), (Ddb) and/or (Ddc), even more preferably (Dda) and/or (Ddc) and especially (Ddc).

35 **[0153]** The incorporation ratio of the monomers (Da) and (Db) and optionally (Dc) and optionally (Dd) in the polymer obtained from reaction step (I) is generally as follows:

The molar ratio of (Da)/((Db) and (Dc)) (in total) is generally from 10:1 to 1:10, preferably 8:1 to 1:8, more preferably 5:1 to 1:5, even more preferably 3:1 to 1:3, particularly 2:1 to 1:2 and especially 1.5:1 to 1:1.5. In the preferred particular case of maleic anhydride as monomer (Da), the molar incorporation ratio of maleic anhydride to monomers ((Db) and (Dc)) (in total) is about 1:1.

[0154] The molar ratio of obligatory monomer (Db) to monomer (Dc), if present, is generally of 1:0.05 to 10, preferably of 1:0.1 to 6, more preferably of 1:0.2 to 4, even more preferably of 1:0.3 to 2.5 and especially 1:0.5 to 1.5.

[0155] In a preferred embodiment, no optional monomer (Dc) is present in addition to monomer (Db).

45 **[0156]** The proportion of one or more of the monomers (Dd), if present, based on the amount of the monomers (Da), (Db) and optionally (Dc) (in total) is generally 5 to 200 mol%, preferably 10 to 150 mol%, more preferably 15 to 100 mol%, even more preferably 20 to 50 mol% and especially 0 to 25 mol%.

[0157] In a preferred embodiment, no optional monomer (Dd) is present.

[0158] In a second reaction step (II), the anhydride or carboxylic ester functionalities present in the copolymer obtained from (I) are partly or fully hydrolyzed and/or saponified.

[0159] Reaction step (II) is obligatory in case the copolymer obtained from reaction step (I) does not comprise free carboxylic acid groups.

[0160] Hydrolyzation of anhydride groups is preferred over saponification of ester groups.

55 **[0161]** Preferably, 10% to 100% of the anhydride or carboxylic ester functionalities present are hydrolyzed and/or saponified, preferably at least 20%, more preferably at least 30%, even more preferably at least 50% and particularly at least 75% and especially at least 85%.

[0162] For a hydrolysis, based on the anhydride functionalities present, the amount of water that corresponds to the desired hydrolysis level is added and the copolymer obtained from (I) is heated in the presence of the added water. In

general, a temperature of preferably 20 to 150°C is sufficient for the purpose, preferably 60 to 100°C. If required, the reaction can be conducted under pressure in order to prevent the escape of water. Under these reaction conditions, in general, the anhydride functionalities in the copolymer are converted selectively, whereas any carboxylic ester functionalities present in the copolymer react at least only to a minor degree, if at all.

[0163] For a saponification, the copolymer is reacted with an amount of a strong base corresponding to the desired saponification level in the presence of water.

[0164] Strong bases used may preferably be hydroxides, oxides, carbonates or hydrogencarbonates of alkali metals or alkaline earth metals.

[0165] The copolymer obtained from (I) is then heated in the presence of the added water and the strong base. In general, a temperature of preferably 20 to 130°C is sufficient for the purpose, preferably 50 to 110°C. If required, the reaction can be conducted under pressure.

[0166] It is also possible to hydrolyze the carboxylic ester functionalities with water in the presence of an acid. Acids used are preferably mineral acids, carboxylic acids, sulfonic acids or phosphorus acids having a pKa of not more than 5, more preferably not more than 4.

[0167] Examples are acetic acid, formic acid, oxalic acid, salicylic acid, substituted succinic acids, aromatically substituted or unsubstituted benzenesulfonic acids, sulfuric acid, nitric acid, hydrochloric acid or phosphoric acid; the use of acidic ion exchange resins is also conceivable.

[0168] In a preferred embodiment for anhydrides, especially maleic anhydride being monomers (Da), such anhydride moieties are partly or fully, especially fully hydrolysed while potentially existing ester groups in the copolymer remain intact.

In this case no saponification in step (II) takes place.

[0169] The copolymer obtained from (I) is then heated in the presence of the added water and the acid. In general, a temperature of preferably 40 to 200°C is sufficient for the purpose, preferably 80 to 150°C. If required, the reaction can be conducted under pressure.

[0170] Should the copolymers obtained from step (II) still comprise residues of acid anions, it may be preferable to remove these acid anions from the copolymer with the aid of an ion exchanger and preferably exchange them for hydroxide ions or carboxylate ions, more preferably hydroxide ions. This is the case especially when the acid anions present in the copolymer are halides or contain sulfur or nitrogen.

[0171] In a preferred embodiment copolymer (D) is a copolymer of maleic anhydride and a mixture of C₂₀ to C₂₄ alpha-olefins in essentially equimolar amounts which is afterward completely hydrolysed.

[0172] The copolymer obtained from reaction step (II) generally has a weight-average molecular weight Mw of 0.5 to 20 kDa, preferably 0.6 to 15, more preferably 0.7 to 7, even more preferably 1 to 7 and especially 1.5 to 4 kDa (determined by gel permeation chromatography with tetrahydrofuran and polystyrene as standard).

[0173] The number-average molecular weight Mn is usually from 0.5 to 10 kDa, preferably 0.6 to 5, more preferably 0.7 to 4, even more preferably 0.8 to 3 and especially 1 to 2 kDa (determined by gel permeation chromatography with tetrahydrofuran and polystyrene as standard).

[0174] The polydispersity is generally from 1 to 10, preferably from 1.1 to 8, more preferably from 1.2 to 7, even more preferably from 1.3 to 5 and especially from 1.5 to 3.

[0175] The content of acid groups in the copolymer is preferably from 1 to 8 mmol/g of copolymer, more preferably from 2 to 7.5, even more preferably from 3 to 7 mmol/g of copolymer.

[0176] In a preferred embodiment, the copolymers comprise a high proportion of adjacent carboxylic acid groups, which is determined by a measurement of adjacency. For this purpose, a sample of the copolymer is heat-treated between two Teflon films at a temperature of 290°C for a period of 30 minutes and an FTIR spectrum is recorded at a bubble-free site. The IR spectrum of Teflon is subtracted from the spectra obtained, the layer thickness is determined and the content of cyclic anhydride is determined.

[0177] In a preferred embodiment, the adjacency is at least 10%, preferably at least 15%, more preferably at least 20%, even more preferably at least 25% and especially at least 30%.

[0178] The olefin-carboxylic acid copolymer (D) is applied in the form of the free acid, i.e. COOH groups are present, or in the form of the anhydride which may be an intramolecular anhydride or an intermolecular anhydride linking two dicarboxylic acid molecules together, preferably in the form of a free acid. To a minor extent, some of the carboxylic functions may be present in salt form, e.g. as alkali or alkaline metal 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%. A single olefin-carboxylic acid copolymer (D) or a mixture of different olefin-carboxylic acid copolymers (D) may be used.

(E) Other additives

[0179] The Diesel fuel additive packages according to the present invention may, as coadditives, further comprise

customary additive components in amounts customary therefor, especially corrosion inhibitors, further demulsifiers, antioxidants and stabilizers, metal deactivators, antistats, friction modifiers, antifoams, dyes (markers) and/or diluents and solvents.

[0180] Corrosion inhibitors suitable as other coadditives are, for example, succinic esters, in particular with polyols, fatty acid derivatives, for example oleic esters, oligomerized fatty acids and substituted ethanolamines.

[0181] Demulsifiers suitable as other coadditives are, for example, the alkali metal and alkaline earth metal salts of alkylsubstituted 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.

[0182] Antifoams suitable as other coadditives are, for example, polyether-modified poly-siloxanes.

[0183] Antioxidants suitable as other 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.

[0184] Metal deactivators suitable as other coadditives are, for example, salicylic acid derivatives, e.g. N,N'-disalicylidene-1,2-propanediamine.

[0185] A lubricity improver suitable as a other coadditive is, for example, glyceryl mono-oleate.

[0186] Preferred examples for dehazers exhibiting emulsifying action are

- alkoxylation copolymers of ethylene oxide, propylene oxide, butylene oxide, styrene oxide and/or other oxides, e.g. epoxy based resins, and
- alkoxyated phenol formaldehyde resins.

[0187] These or other dehazer components 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.

[0188] In a further preferred embodiment of the present invention, the fuel oils additionally comprise as additive component 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 $R^aR^bCH-CH_2-O-NO_2$ 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.

[0189] Suitable solvents and diluents as other additives, 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.

Fuel

[0190] 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, albeit less preferable. 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.

[0191] 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.

[0192] In one embodiment, the fuel oil comprises

(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 the above-mentioned middle distillate fuels, especially diesel fuels, especially those which boil in the range from 120 to 450°C, 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.

[0193] Such 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 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").

[0194] 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.

[0195] 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.

[0196] Vegetable fats can in principle likewise be used as a source for biodiesel, but play a minor role.

[0197] 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.

[0198] 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.

[0199] 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").

[0200] 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.

[0201] In a further preferred embodiment, the fuel additive package according to the present invention is used 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.

[0202] Polycyclic aromatic hydrocarbons in (β) shall be understood to mean polyaromatic hydrocarbons according to standard EN 12916 and are determined according to this standard.

Composition of the additive package

[0203] Another subject matter of the present invention are fuel oils, preferably Diesel fuels comprising compounds (A), (B), (C), and optionally (B) in amounts as follows:

The quaternary ammonium compound (A) 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.

[0204] The wax anti-settling flow improver component (B) is present in the fuel oils typically in an amount of from 10 to 5000 ppm by weight, preferably of 20 to 3000 ppm by weight, especially of 30 to 2000 ppm by weight and in particular of 50 to 1000 ppm by weight.

[0205] Carboxylic acid compound (C) is added to the fuels so that the middle distillate fuels comprise the compound in an amount of typically 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.

[0206] Copolymer (D) is optional in the fuel oils according to the present invention. Hence, in one embodiment of the present invention no copolymer (D) is present in the fuels.

[0207] In a preferred embodiment of the present invention the fuel oils comprise said olefin-carboxylic acid copolymer (D) in an amount of from 1 to 1000 ppm by weight, preferably of from 2 to 500 ppm by weight, more preferably of from 3 to 300 ppm by weight, most preferably of from 5 to 200 ppm by weight, for example of from 10 to 100 ppm by weight.

[0208] One or more dehazers as other additive component (E), 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.

[0209] The cetane number improver (E) or a mixture of a plurality of cetane number improvers is present in the fuel oils normally in an amount of from 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.

[0210] Subject matter of the present invention is also a fuel additive concentrate suitable for use in fuel oils, especially in diesel fuel, comprising

(A) 5 to 40% by weight, preferably 10 to 35% by weight, more preferably 15 to 30% by weight, of at least one quaternary ammonium compound;

(B) 10 to 80% by weight, preferably 15 to 70% by weight, more preferably 20 to 60% by weight wax anti-settling flow improver

(C) 1 to 15% by weight, preferably 2 to 10% by weight, more preferably 3 to 10% by weight C₈- to C₁₈-carboxylic acid

(D) 0.01 to 25% by weight, preferably 0.05 to 20% by weight, more preferably 0.1 to 15% by weight, of olefin-carboxylic acid copolymer;

(E) 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 other additive (E), preferably selected from the group consisting of corrosion inhibitors, demulsifiers, antioxidants, stabilizers, metal deactivators, antistats, friction modifiers, antifoams, and dyes (markers);

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;

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.

[0211] In each case, the sum of components (A), (B), (C), (D) and (E) results in 100%.

Examples

Formulations

[0212] The following formulations were prepared:

	Formulation 1 (Inventive)	Formulation 2 (Comparative)	Formulation 3 (Comparative)
	[wt%]	[wt%]	[wt%]
Compound (A) *)	3.75	3.75	3.75
Compound (D) **)	1.667	1.667	1.667
Dehazer ***)	0.25	0.25	0.25

(continued)

	Formulation 1 (Inventive)	Formulation 2 (Comparative)	Formulation 3 (Comparative)
	[wt%]	[wt%]	[wt%]
Antioxidant ****)	7.5	7.5	7.5
MDFI *****)	16.46	17.31	14.77
WASA *****)	4.38	4.60	3.94
Neodecanoic Acid	1.08	--	--
Solvent *****)	64.917	64.917	68.08
Sum	100	100	100
*) Quaternary Ammonium Compound (A): Reaction product of polyisobutenyl succinic acid anhydride (based upon polyisobutene with a molecular weight of 1000 g/mol) with 3-(N,N-dimethylamino) propane-1-amine (DMAPA) with consecutive quaternization with propylene oxide in an analogous matter as described in WO 2012/004300 A1, Synthetic Example 1 (applied as 50 wt% solution in 2-ethylhexanol). **) Hydrolyzed copolymer of a mixture of C₂₀ to C₂₄ alpha-olefins with maleic acid anhydride, Mn: 1500 g/mol, Mw: 3200 g/mol, 40% solution in Solvesso, as described in EP 3099720 B1, Synthetic Example 2. ***) Commercially available dehazer ****) Phenolic antioxidant (Benzenepropanoic acid, 3,5-bis (1,1-dimethyl-ethyl)-4-hydroxy-C7-C9 branched alkyl esters, CAS No. 125643-61-0) *****) Middle distillate flow improver *****) Wax anti-settling additive *****) Commercially available solvent (Solvesso 150)			

Example 1 - Stability

[0213] The Formulations 1 to 3 were cooled to minus 20 °C and their appearance was visually determined:

	Appearance
Formulation 1 (Inventive)	Liquid/turbid
Formulation 2 (Comparative)	Solid
Formulation 3 (Comparative)	Solid

[0214] It can easily be seen that solidification cannot simply be resolved by the use of more solvent and less compound (B) as in Formulation 3 vs. Formulation 2.

[0215] In contrast, addition of compound (C) according to the invention in minor amounts of approx. 1 wt% yields a formulation which is still liquid at minus 20 °C.

Example 2 - CFPP Tests

[0216] The cloud point (CP) according to ISO 3015 and the Cold filter plugging point ("CFPP") according to EN 116 of the additized fuel samples were determined. For this purpose, the additized fuel samples were stored in 500 ml glass cylinders, in order to determine the delta CP after being cooled at minus 13 °C in a cold bath for 16 hours. For each sample, the CP was again determined to ISO 3015 on the 20% by volume base phase separated off at minus 13 °C.

[0217] The smaller the deviation of the CP of the 20% by volume base phase from the original CP (delta CP) for the respective fuel sample, the better the dispersion of the paraffins.

[0218] The smaller the delta CP and the lower the CFPP, the better the cold flow characteristics of a diesel fuel.

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		CFPP [°C] without additive	CFPP [°C] @300ppm additive	
	Biodiesel content (soybean oil methyl ester, SME)		Formulation 2 (Comparative)	Formulation 1 (Inventive)
Fuel 1	0%	-10	-31	-30
Fuel 1	5%	-12	-28	-29
Fuel 1	15%	-9	-25	-27
Fuel 2	0%	-18	-22	-23
Fuel 2	5%		-23	-21
Fuel 2	15%		-19	-19
Fuel 1: B0 Diesel from OMV, density at 15 °C: 832.2 kg/m ³ , viscosity at 15 °C 3.92 mm ² /s, CP: -8.9 °C, PP: -15 °C, CFPP: -10 °C Fuel 2: B0 Diesel, for DW10 test according to CEC RF-79-07 Batch 11, density at 15 °C: 836.7 kg/m ³ , CFPP: -18°C				

[0219] It can easily be seen that addition of compound (C) according to the invention does not significantly affect fuel properties with regard to CFPP values both for pure fossil fuels as well as for fuels comprising biodiesel.

Example 3 - Filtration

[0220] Determination of cold filter blocking tendency (FBT) was conducted according to IP 618 at standard test operating temperatures 3 °C and -1 °C.

[0221] Fuel 3 (B0 Diesel, for DW10 test according to CEC RF-79-07 Batch 12, density at 15 °C: 835.2 kg/m³, CFPP: -20°C)

Additive	Dosage	FBT 3 °C	FBT -1 °C
	mg/kg		
--	0	1.03	1.02
Formulation 1 (Inventive)	1200	1.03	1.06
Formulation 1 (Inventive)	2400	1.06	1.12
Formulation 2 (Comparative)	1200	1.09	1.09
Formulation 2 (Comparative)	2400	1.05	1.06

[0222] Fuel 4 (85% Fuel 3 + 15% SME (density 884.2 kg/m³, CFPP: -2 °C))

Additive	Dosage	FBT 3 °C	FBT -1 °C
	mg/kg		
--	0	1.04	1.02
Formulation 1 (Inventive)	1200	1.04	1.08
Formulation 1 (Inventive)	2400	1.06	1.08
Formulation 2 (Comparative)	1200	1.09	1.10
Formulation 2 (Comparative)	2400	1.11	1.15

[0223] It can easily be seen that addition of compound (C) according to the invention does not significantly affect fuel properties with regard to filtration both for pure fossil fuels as well as for fuels comprising biodiesel.

Claims

1. Diesel fuel additive packages comprising

(A) at least one quaternary ammonium compound,

(B) at least one wax anti-settling flow improvers selected from the group consisting of

- (Ba) copolymers of olefins and one or more vinyl esters and/or (meth)acrylic esters
- (Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically unsaturated dicarboxylic acids
- (Bc) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids and their derivatives
- (Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols
- (Be) reaction products of alkenyl-spiro-bislactones with amines,

(C) at least one saturated or unsaturated C₈- to C₁₈-carboxylic acid, preferably at least one saturated branched C₈- to C₁₈-monocarboxylic acid, more preferably preferably at least one saturated branched C₈- to C₁₆-monocarboxylic acid, even more preferably preferably at least one saturated branched C₈- to C₁₂-monocarboxylic acid.

2. Diesel fuel, comprising at least one Diesel fuel additive package according to Claim 1.

3. Process for stabilising Diesel fuel additive packages comprising

(A) at least one quaternary ammonium compound,

(B) at least one wax anti-settling flow improvers selected from the group consisting of

- (Ba) copolymers of olefins and one or more vinyl esters and/or (meth)acrylic esters
- (Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically unsaturated dicarboxylic acids
- (Bc) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids and their derivatives
- (Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols
- (Be) reaction products of alkenyl-spiro-bislactones with amines,

by admixing at least one saturated or unsaturated C₈- to C₁₈-carboxylic acid (C), preferably at least one saturated branched C₈- to C₁₈-monocarboxylic acid, more preferably at least one saturated branched C₈- to C₁₆-monocarboxylic acid, even more preferably at least one saturated branched C₈- to C₁₂-monocarboxylic acid to said Diesel fuel additive packages.

4. Use of at least one saturated or unsaturated C₈- to C₁₈-carboxylic acid (C), preferably at least one saturated branched C₈- to C₁₈-monocarboxylic acid, more preferably at least one saturated branched C₈- to C₁₆-monocarboxylic acid, even more preferably at least one saturated branched C₈- to C₁₂-monocarboxylic acid for stabilising Diesel fuel additive packages comprising

(A) at least one quaternary ammonium compound,

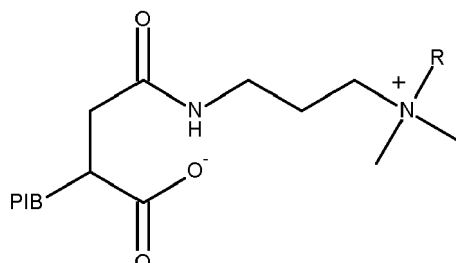
(B) at least one wax anti-settling flow improvers selected from the group consisting of

- (Ba) copolymers of olefins and one or more vinyl esters and/or (meth)acrylic esters
- (Bb) copolymers of monoolefins having from 10 to 20 carbon atoms and amides and imides of ethylenically unsaturated dicarboxylic acids
- (Bc) reaction products of secondary fatty amines having from 20 to 44 carbon atoms with carboxylic acids

and their derivatives

- (Bd) copolymers of maleic anhydride and α,β -unsaturated compounds which may optionally be reacted with primary monoalkylamines and/or aliphatic alcohols
- (Be) reaction products of alkenyl-spiro-bis lactones with amines.

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5. Additive package, fuel, process, and use according to any one of the preceding claims, wherein the quaternized ammonium compound (A) is of formula

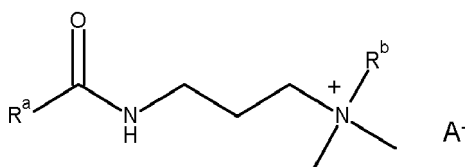


wherein in this formula

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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- C_1 - to C_4 -alkyl, preferably 2-hydroxypropyl.

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6. Additive package, fuel, process, and use according to any one of the claims 1 to 4, wherein the quaternized ammonium compound (A) is of formula



wherein in this formula

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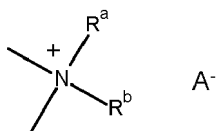
R^a stands for C_1 - C_{20} -alkyl, preferably C_9 - to C_{17} -alkyl, more preferably for undecyl, tridecyl, pentadecyl or heptadecyl,

R^b stands for a hydroxy- C_1 - to C_4 -alkyl, preferably 2-hydroxypropyl or 2-hydroxybutyl, and

40

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.

- 45
7. Additive package, fuel, process, and use according to any one of the claims 1 to 4, wherein the quaternized ammonium compound (A) is of formula



wherein in this formula

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R^a and R^b independently of another stand for C_1 - C_{20} -alkyl or hydroxy- C_1 - 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- C_1 - 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.

8. Additive package, fuel, process, and use according to any one of the preceding claims, wherein component (B) comprises at least one copolymer (Ba) of a C₂- to C₄₀-olefin with at least one further ethylenically unsaturated monomer, preferably selected from vinyl esters (alkenyl carboxylates), (meth)acrylic esters and further olefins.

9. Additive package, fuel, process, and use according to any one of the claims 1 to 7, wherein component (B) comprises at least one copolymer (Bb) obtainable by copolymerization of

(Bb1) at least one unsaturated dicarboxylic acid or derivatives thereof,

(Bb2) at least one α -olefin having from at least 6 up to and including 20 carbon atoms,

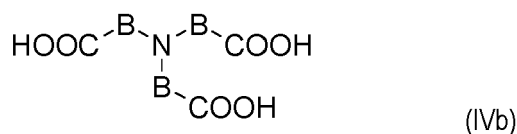
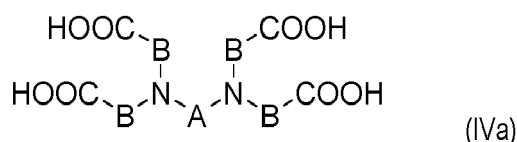
(Bb3) optionally at least one C₃- to C₂₀-alkyl ester of acrylic acid or methacrylic acid or a mixture of such alkyl esters and

(Bb4) optionally one or more further copolymerizable monomers other than monomers (Bb1), (Bb2) and (Bb3), with a molar incorporation ratio of (Bb1):(Bb2):(Bb3):(Bb4) of 1:0.5 to 2.0:0 to 2.0:0 to 0.1, preferably 1:0.5 to 2.0:0 to less than 0.5:0 to 0.1, and more preferably 1:0.5 to 2.0:0:0 to 0.1

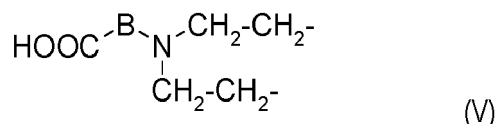
followed by the reaction with at least one dialkylamine (Bb5), where the two alkyl radicals in the at least one dialkylamine (Bb5) are independently alkyl radicals having at least 17 up to 30 carbon atoms.

10. Additive package, fuel, process, and use according to any one of the claims 1 to 7, wherein component (B) comprises at least one reaction product based on

poly(C₂- to C₂₀-carboxylic acids) which have at least one tertiary amino group and are of the general formula (IVa) or IVb



in which the variable A is a straight-chain or branched C₂- to C₆-alkylene group or the moiety of the formula (V)



and the variable B is a C₁- to C₁₉-alkylene group, with secondary amines having the general formula HN(R⁸)₂ in which the two variables R⁸ are each independently straight-chain or branched C₁₀- to C₃₀-alkyl radicals, especially C₁₄- to C₂₄-alkyl radicals.

11. Additive package, fuel, process, and use according to any one of the preceding claims, further comprising at least one copolymer (D) obtainable by

- in a first reaction step (I) copolymerizing

(Da) at least one ethylenically unsaturated mono- or dicarboxylic acid or derivatives thereof, preferably a dicarboxylic acid,

(Db) at least one α -olefin having from at least 12 up to and including 30 carbon atoms,

(Dc) optionally at least one further aliphatic or cycloaliphatic olefin which has at least 4 carbon atoms and is different than (Db) and

(Dd) optionally one or more further copolymerizable monomers other than monomers (Da), (Db) and (Dc), selected from the group consisting of

(Dda) vinyl esters,

(Ddb) vinyl ethers,
 (Ddc) (meth)acrylic esters of alcohols having at least 5 carbon atoms,
 (Ddd) allyl alcohols or ethers thereof,
 (Dde) N-vinyl compounds selected from the group consisting of vinyl compounds of heterocycles containing
 at least one nitrogen atom, N-vinylamides or N-vinylactams,
 (Ddf) ethylenically unsaturated aromatics,
 (Ddg) α,β -ethylenically unsaturated nitriles,
 (Ddh) (meth)acrylamides and
 (Ddi) allylamines,
 followed by

- in a second optional reaction step (II) partly or fully hydrolyzing and/or saponifying anhydride or carboxylic ester functionalities present in the copolymer obtained from (I), the second reaction step being run at least when the copolymer obtained from reaction step (I) does not comprise any free carboxylic functionalities.

12. Additive package, fuel, process, and use according to any one of the preceding claims, wherein the carboxylic acid (C) is selected from the group consisting of linear saturated or unsaturated carboxylic acid compounds (C) are dodecanoic acid (lauric acid), tridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, erucic acid, arachidic acid, behenic acid, lignoceric acid and cerotic acid, preferred are tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, erucic acid, arachidic acid, and behenic acid, very preferred are hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid), isostearic acid, oleic acid, linoleic acid, linolaidic acid, and mixtures thereof, and especially oleic acid, linoleic acid, and linolaidic acid, preferably oleic acid.

13. Additive package, fuel, process, and use according to any one of the claims 1 to 11, wherein the carboxylic acid (C) is at least one saturated branched C_8 - to C_{12} -monocarboxylic acid.

14. Additive package, fuel, process, and use according to any one of the claims 1 to 11, wherein the carboxylic acid (C) is selected from the group consisting of 2-ethyl hexanoic acid, 2,2-dimethylhexanoic acid (neooctanoic acid, Versatic Acid 8), 2,2-dimethylheptanoic acid (neononanoic acid, Versatic Acid 9), isononanoic acid, 2-propyl heptanoic acid, 2,2-dimethyloctanoic acid (neodecanoic acid, Versatic Acid 10), neoundecanoic acid (Versatic Acid 11), neododecanoic acid, and neotridecanoic acid (Versatic Acid 13).

15. Additive package, fuel, process, and use according to any one of the preceding claims, wherein the fuel oil comprises

(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, preferably C_1 - to C_4 -alkyl esters of fatty acids which derive from vegetable and/or animal oils and/or fats, 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 distillate fuels, especially diesel fuels, especially those which boil in the range from 120 to 450°C, 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.



EUROPEAN SEARCH REPORT

Application Number

EP 24 18 9383

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