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(54) **MEDIUM-CHAIN ALKANOLS IN ADDITIVE
CONCENTRATES FOR IMPROVING FOAM
REDUCTION IN FUEL OILS**

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(57) **ABSTRACT**

C₅- to C₁₅-alkanols are suitable for improving the defoamer action of a silicon-containing anti-foam in fuel oils, especially in biofuel oils, which comprise at least one additive with detergent action. Such alkanols are used in additive concentrates which also comprise aromatic hydrocarbons or hydrocarbon mixtures having a boiling point of 100 to 250° C. or C₅- to C₁₂-alkyl nitrates, and also silicon-containing antifoams, additives with detergent action and optionally commercial dehazers.

MEDIUM-CHAIN ALKANOLS IN ADDITIVE CONCENTRATES FOR IMPROVING FOAM REDUCTION IN FUEL OILS

[0001] The present invention relates to the use of medium-chain alkanols for improving the defoamer action of a silicon-containing antifoam in fuel oils which comprise at least one additive with detergent action. The present invention further relates to an additive concentrate and to the use thereof for improving foam reduction in fuel oils, said additive concentrate comprising medium-chain alkanols, aromatic hydrocarbons or hydrocarbon mixtures and/or alkyl nitrates, silicon-containing antifoams and additives with detergent action. The present application further provides a corresponding additized fuel oil.

[0002] Fuel oils generally comprise antifoams which are intended to prevent, or reduce to a tolerable degree, the foaming of the fuel oil in the course of movement or mechanical stress, for example when transferred or introduced into storage vessels or tanks. Foaming over, reduced fill levels, longer fill times and hence lower efficiency of gas stations are the main reasons why antifoams (also called defoamers) are now one of the standard components in modern multifunctional diesel additive packages. In this context, usually silicon-containing antifoams based on organosilicone chemistry, such as polysiloxanes or silicone oils, are customary.

[0003] For instance, WO 00/39254 (1) describes additive packages which are usable in fuel oils and which comprise, as an additive with detergent action, the reaction product of polyisobutenyl-succinic anhydride (with a polyisobutenyl chain with $M_n=950$) with tetraethylenepentamine, 2-ethylhexyl nitrate as a cetane number improver and 2-ethylhexanol as a solvent, in combination with a conventional organosilicone antifoam. The weight ratio of 2-ethylhexyl nitrate to 2-ethylhexanol is never above 3:1.

[0004] US 2010/0107479 A1 (2) discloses a diesel fuel additive package which, according to table 1 therein, comprises 42 mg/kg of the reaction product of polyisobutenylsuccinic anhydride with tetraethylenepentamine in a molar ratio of 1:1 as an additive with detergent action, 20 mg/kg of 2-ethylhexyl nitrate as a solvent, 132 mg/kg of an aromatic hydrocarbon mixture as a further solvent, and 8 mg/kg of a conventional siloxane antifoam.

[0005] EP 0 681 023 A1 (3) describes fuel oils, such as diesel fuels, kerosene, turbine fuels, heating oils and, among other substances, also biofuel oils comprising vegetable oils, which comprise metallic detergents such as alkali metal or alkaline earth metal salts of acids or phenols, antifoams such as water-soluble polyether-polysiloxane copolymers and ashless dispersants such as polyisobutenylsuccinimides, and may optionally have further components such as solvents, for example aromatic hydrocarbons, oil-soluble alcohols, demulsifiers, corrosion inhibitors, carrier liquids, antioxidants, metal deactivators, cold flow improvers or wax inhibitors.

[0006] However, the action of antifoams in fuel oils is still in need of improvement, especially when they are supplied to the fuel oils or diesel fuels in mixed form, in multifunctional diesel additive packages which comprise, as the main active components, ashless additives with detergent action. It was an object of the present invention to improve the defoamer action of the known antifoams, especially of the silicon-containing antifoams, and to provide a corresponding additive concen-

trate for use as an additive package in fuel oils, which improves foam reduction in fuel oils.

[0007] Accordingly, in a first aspect of the present invention, the use of a C_5 - to C_{15} -alkanol for improving the defoamer action of a silicon-containing antifoam in fuel oils which comprise at least one additive with detergent action has been found.

[0008] In addition, in a second aspect of the present invention, an additive concentrate has been found, which comprises

[0009] (A) 0.1 to 10% by weight, especially 1 to 8% by weight, in particular 3 to 6% by weight, of at least one C_5 - to C_{15} -alkanol,

[0010] (B) 0.5 to 80% by weight, especially 5 to 75% by weight, in particular 15 to 70% by weight, of either (i) at least one aromatic hydrocarbon or hydrocarbon mixture having a boiling point or a predominant boiling range within the temperature range from 100° C. to 250° C. or (ii) at least one C_5 - to C_{12} -alkyl nitrate or (iii) a mixture of (i) and (ii), with the proviso that the amount of component (B) is at least five times the amount of the C_5 - to C_{15} -alkanol of component (A),

[0011] (C) 0.01 to 2% by weight, especially 0.1 to 1.5% by weight, in particular 0.4 to 1.3% by weight, of at least one silicon-containing antifoam,

[0012] (D) 1 to 30% by weight, especially 7 to 29% by weight, in particular 15 to 28% by weight, of at least one additive with detergent action and

[0013] (E) 0 to 5% by weight, especially 0.1 to 5% by weight, in particular 1 to 3.5% by weight, of at least one commercial dehazer,

where the sum of components (A) to (E) is 100% by weight in each case, and with the proviso that at least one of the following criteria is additionally met:

[0014] (γ) the amount of the additive with detergent action in component (D) is at least ten times, especially at least fifteen times, the amount of the silicon-containing antifoam in component (C);

[0015] (δ) the amount of the C_5 - to C_{15} -alkanol of component (A) is at least three times, especially at least four times, the amount of the silicon-containing antifoam of component (C).

[0016] Preferably, both criteria (γ) and (δ) are met.

[0017] The present invention owes the improved action to the use of particular medium-chain alkanols and in particular to the precisely balanced ratio of components (A), (B), (C) and (D). The inventive use of the median-chain alkanols mentioned has an advantageous effect on the foaming characteristics especially in fuel oils which comprise biofuel oils or consist thereof.

[0018] Medium-chain alkanols, which constitute component (A) in the inventive additive concentrate, are understood to mean C_5 - to C_{15} -alkanols, especially C_6 - to C_{13} -alkanols, in particular C_8 - to C_{11} -alkanols, which are linear or preferably branched. In a preferred embodiment, in both aspects of the present invention, n-octanol, 2-ethylhexanol, n-nonanol, 2-propylheptanol, n-decanol, n-undecanol, n-dodecanol, n-tridecanol or isotridecanol is used. It is also possible to use a mixture of the alkanols mentioned. Very particular preference is given to 2-ethylhexanol.

[0019] Silicon-containing antifoams of component (C) are understood here to mean all known antifoams which are customary in the mineral oils sector, are of organic structure and comprise one or more silicon atoms incorporated within

the molecule. They may, for example, be polysiloxanes or silicone oils. In a preferred embodiment, in both aspects of the present invention, polyether-modified polysiloxanes are used. These may have, for example, the structure of a polyether-polysiloxane copolymer.

[0020] Additives with detergent action in component (D) refer in the context of the present invention to those compounds whose action in an internal combustion engine, especially a diesel engine, consists predominantly or at least essentially of eliminating and/or preventing deposits. The detergents are preferably amphiphilic substances which have at least one hydrophobic hydrocarbyl radical having a number-average molecular weight (M_n) of 85 to 20 000, especially of 300 to 5000, in particular of 500 to 2500, and at least one polar moiety.

[0021] The additives with detergent action here are preferably selected from:

[0022] (i) compounds with moieties which are derived from succinic anhydride and have hydroxyl and/or amino and/or amido and/or imido groups;

[0023] (ii) nitrogen compounds with acid-free quaternization, 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 then quaternizing;

[0024] (iii) polytetrahydrobenzoxazines and bistetrahydrobenzoxazines

[0025] Additives comprising moieties which are derived from succinic anhydride and have hydroxyl and/or amino and/or amido and/or imido groups according to the above group (i) are preferably corresponding derivatives of polyisobutenylsuccinic anhydride, which are obtainable by reaction of conventional or high-reactivity polyisobutene with $M_n=300$ to 5000, in particular with $M_n=500$ to 2500, with maleic anhydride by the thermal route or via the chlorinated polyisobutene. Of particular interest in this context are derivatives with aliphatic polyamines such as ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine. The moieties with hydroxyl and/or amino and/or amido and/or imido groups are, for example, carboxylic acid groups, acid amides, acid amides of di- or polyamines, which also have free amine groups in addition to their amide function, succinic acid derivatives with an acid and an imide function, carboximides with monoamines, carboximides with di- or polyamines, which also have free amine groups in addition to the imide function, and diimides which are formed by the reaction of di- or polyamines with two succinic acid derivatives. Such fuel additives are described especially in U.S. Pat. No. 4,849,572.

[0026] Nitrogen compounds with acid-free quaternization according to the above group (ii), which 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 in the absence of free acid, are described in EP patent application 10 168 622.8. Suitable compounds having at least one oxygen- or nitrogen-containing group reactive with an anhydride and additionally at least one quaternizable amino group are especially polyamines with at least one primary or secondary amino group and at least one tertiary amino group. Useful polycarboxylic anhydrides are especially dicarboxylic acids such as

succinic acid with a relatively long-chain hydrocarbyl substituent, preferably with 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 is a polyisobutenylsuccinic monoamide and which is subsequently quaternized with styrene oxide in the absence of free acid at 70° C.

[0027] Polytetrahydrobenzoxazines and bistetrahydrobenzoxazines according to the above group (iii) are described in EP patent application 10 194 307.4. Such polytetrahydrobenzoxazines and bistetrahydrobenzoxazines are obtainable by successively reacting, in a first reaction step a C_1 - to C_{20} -alkylenediamine having two primary amino functions, for example 1,2-ethylenediamine, with a C_1 - to C_{12} -aldehyde, e.g. formaldehyde, and a C_1 - to C_8 -alkanol at a temperature of 20 to 80° C. while eliminating and removing water, both the aldehyde and the alcohol being used in more than twice the molar amount, especially both in four times the molar amount, compared to the diamine, in a second reaction step reacting the condensation product thus obtained with a phenol which bears at least one long-chain substituent having 6 to 3000 carbon atoms, for example a tert-octyl, n-nonyl, n-dodecyl or polyisobutyl radical with an M_n of 1000, in a stoichiometric ratio to the originally used alkylenediamine of 1.2:1 to 3:1 at a temperature of 30 to 120° C., and optionally in a third reaction step heating the bistetrahydrobenzoxazine thus obtained to a temperature of 125 to 280° C. for at least 10 minutes.

[0028] Particular preference is given as the at least one additive with detergent action, in both aspects of the present invention, to a compound having moieties which are derived from succinic anhydride and have hydroxyl and/or amino and/or amido and/or imido groups, but especially a compound from group (i) which is a polyisobutenyl-substituted succinimide.

[0029] Fuel oils shall be understood in the context of the present invention to mean especially middle distillate fuels, especially diesel fuels. However, use of the present invention in heating oil or kerosene is also possible. Diesel fuels or middle distillate fuels are typically mineral oil raffinates which generally have a boiling range from 100 to 400° C. These are usually distillates with a 95% point up to 360° C. or even higher. However, they 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 by coal gasification or gas liquefaction ["gas to liquid" (GTL) fuels] are suitable. Also suitable are mixtures of the aforementioned diesel fuels with renewable fuels (biofuel oils) such as biodiesel or bioethanol. Of particular interest at present are diesel fuels with a low sulfur content, i.e. with a sulfur content of less than 0.05% by weight, preferably of less than 0.02% by weight, particularly of less than 0.005% by weight and especially of less than 0.001% by weight of sulfur. Diesel fuels may also comprise water, for example in an amount up to 20% by weight, for example in the form of diesel-water microemulsions, or in the form of what is called "white diesel".

[0030] In a preferred embodiment, the C₅- to C₁₅-alkanols or the inventive additive concentrate, in the context of the present invention, is used in fuel oils which consist

[0031] (a) to an extent of 0.1 to 100%, preferably to an extent of 0.1 to less than 100% by weight, especially to an extent of 10 to 95% by weight, in particular to an extent of 30 to 90% by weight, of at least one biofuel oil based on fatty acid esters, and

[0032] (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, in particular to an extent of 10 to 70%, of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

[0033] The fuel oils may of course also consist to an extent of 100% by weight of at least one biofuel oil (a) based on fatty acid esters.

[0034] The fuel oil component (a) is usually also referred to as "biodiesel". This preferably comprises essentially alkyl esters of fatty acids which derive from vegetable and/or animal oils and/or fats. Alkyl esters are typically understood to mean lower alkyl esters, especially C₁- to C₄-alkyl esters, which are obtainable by transesterifying the glycerides, especially triglycerides, which occur in vegetable and/or animal oils and/or fats by means of lower alcohols, for example ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol or especially methanol ("FAME").

[0035] Examples of vegetable oils which can be converted to corresponding alkyl esters and can thus serve as a basis for 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 the shea tree nut; additionally useable are also arachis oil, jatropha oil and linseed oil. The extraction of these oils and the conversion thereof to the alkyl esters are known or can be inferred from the prior art.

[0036] It is also possible to convert vegetable oils which have already been used, for example used deep fat frier oil, optionally after an appropriate purification, to alkyl esters, and for them thus to serve as a basis for biodiesel.

[0037] Vegetable fats are likewise usable in principle as a source for biodiesel, but play a minor role.

[0038] Examples of animal fats and oils which are converted to corresponding alkyl esters and can thus serve as a basis for biodiesel are fish oil, bovine tallow, porcine tallow and similar fats and oils which are obtained as wastes in the slaughter or utilization of farm animals or wild animals.

[0039] The parent saturated or unsaturated fatty acids of the vegetable and/or animal oils and/or fats mentioned, which usually have 12 to 22 carbon atoms and may bear additional functional groups such as hydroxyl groups, and 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.

[0040] 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").

[0041] 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.

[0042] The fuel oil component (b) shall be understood in the context of the present invention to mean the abovementioned middle distillate fuels, especially diesel fuels, particularly those which boil within the range from 120 to 450° C.

[0043] In a preferred embodiment, the C₅- to C₁₅-alkanols or the inventive additive concentrate is used in the context of the present invention to improve the defoamer action of the silicon-containing antifoam in fuels in such a way that the improvement is to such a degree that at least one of the following criteria is met:

[0044] (α) reduction in the foam volume with respect to the defoamer action of the same silicon-containing antifoam in the same fuel oil in the absence of a C₅- to C₁₅-alkanol by at least 10%, especially by at least 14%, determined by the BNPe NF-M 07-075 foam test;

[0045] (β) reduction in the foam collapse time with respect to the defoamer action of the same silicon-containing antifoam in the same fuel oil in the absence of a C₅- to C₁₅-alkanol by at least 20%, especially by at least 35%, determined by the BNPe NF-M 07-075 foam test.

[0046] Preferably, both criteria (α) and (β) are met.

[0047] The BNPe NF-M 07-075 foam test is a standard test method for determining the foam volume and the foam collapse time of fuel oil samples. For this purpose, a test apparatus standardized according to this standard is used.

[0048] The inventive additive concentrate comprises, as component (B), in the function as an essentially nonpolar solvent which displays the desired defoamer action in interplay with component (A) as a polar solvent, as a first alternative (i) one or more aromatic hydrocarbons, for example toluene, xylenes or homologous mono- or dialkylbenzenes, and technical solvent mixtures which consist of aromatic hydrocarbons or comprise aromatic hydrocarbons as main components and are named Shellsol® (manufacturer: Royal Dutch/Shell Group), Exxsol® or Solvesso® (manufacturer: ExxonMobil) or Solvent Naphtha.

[0049] A second alternative (ii) for component (B) is that of C₅- to C₁₂-alkyl nitrates, which are intended to function as a cetane number improver or ignition accelerator in the fuel oil. Such alkyl nitrates are especially nitrate esters of unsubstituted or substituted aliphatic or else cycloaliphatic alcohols, usually having 5 to 10 carbon atoms. The alkyl group in these nitrate esters may be linear or branched, saturated or else unsaturated. Typical examples of such nitrate esters are 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 with an n-propyl or isopropyl radical in the 2 position of the alkyl chain, as described in WO 2008/092809. Additionally suitable are also, for example, nitrate esters of alkoxy-substituted aliphatic alcohols, such as 2-ethoxyethyl nitrate, 2-(2-ethoxyethoxy)ethyl nitrate, 1-methoxypropyl nitrate or 4-ethoxybutyl nitrate. Additionally suitable are also diol nitrates such as 1,6-hexamethylene dinitrate. Among the alkyl nitrates mentioned, 2-ethylhexyl nitrate is the most commonly used cetane number improver and is also preferred for the present invention.

[0050] Another, third alternative (iii) for component (B) is that of mixtures of (i) and (iii), for example mixtures of 1 to 99

parts by weight of (i) and 99 to 1 parts by weight of (ii), especially of 10 to 90 parts by weight of (i) and 90 to 10 parts by weight of (ii), in particular of 25 to 75 parts by weight of (i) and 75 to 25 parts by weight of (ii), where the aromatic hydrocarbons (i) and the alkyl nitrates (ii) together add up to the amounts mentioned in the inventive additive concentrate.

[0051] Dehazers suitable as coadditives of component (E) are, for example, alkoxyated phenol-formaldehyde condensates.

[0052] The inventive additive concentrate is typically added to the fuel oil in such an amount that the additive with detergent action of component (D) or a mixture of a plurality of such additives with detergent action is present in the fuel oil in an amount of 10 to 2000 ppm by weight, especially of 20 to 1000 ppm by weight, in particular of 30 to 500 ppm by weight.

[0053] The inventive additive concentrate or the fuel oil additized therewith, i.e. corresponding diesel fuels or middle distillate fuels or the mixtures of biofuel oils and middle distillates of fossil, vegetable or animal origin mentioned, may further comprise other customary coadditives, especially cold flow improvers, corrosion inhibitors, demulsifiers, antioxidants and stabilizers, metal deactivators, antistats, lubricity improvers, dyes (markers) and/or further solvents and diluents.

[0054] Cold flow improvers suitable as further coadditives are, for example, copolymers of ethylene with at least one further unsaturated monomer, in particular ethylene-vinyl acetate copolymers.

[0055] Corrosion inhibitors suitable as further coadditives are, for example, succinic esters, in particular with polyols, fatty acid derivatives, e.g. oleic esters, oligomerized fatty acids and substituted ethanolamines.

[0056] Demulsifiers suitable as further coadditives are, for example, the alkali metal and alkaline earth metal salts of alkyl-substituted phenol- and naphthalenesulfonates and the alkali metal and alkaline earth metal salts of fatty acid, and additionally alcohol alkoxyates, e.g. alcohol ethoxyates, phenol alkoxyates, e.g. tert-butylphenol ethoxyates or tert-pentylphenol ethoxyates, fatty acid, alkylphenols, condensation products of ethylene oxide and propylene oxide, e.g. ethylene oxide-propylene oxide block copolymers, polyethyleneimines and polysiloxanes.

[0057] Antioxidants suitable as further coadditives are, for example, substituted phenols, e.g. 2,6-di-tert-butylphenol and 2,6-di-tert-butyl-3-methylphenol, and also phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine.

[0058] Metal deactivators suitable as further coadditives are, for example, salicylic acid derivatives, e.g. N,N'-disalicylidene-1,2-propanediamine.

[0059] A lubricity improver suitable as a further coadditive is, for example, glyceryl monooleate.

[0060] When the coadditives mentioned and/or further solvents or diluents are additionally used, they are used in the amounts customary therefor.

[0061] The present invention also provides an additized fuel oil which comprises a major amount of base fuel oil which consists

[0062] (a) to an extent of 0.1 to 100% by weight of at least one biofuel oil based on fatty acid esters, and

[0063] (b) to an extent of 0 to 99.9% by weight of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters,

and a minor amount of the inventive additive concentrate.

[0064] The examples which follow are intended to illustrate the present invention without restricting it.

EXAMPLES

[0065] In a diesel fuel ("DF 1") which was typical of the European market, conformed to the standard EN 590 and comprised a proportion of 7% by weight of biodiesel (FAME), the foaming characteristics were determined by the BNPe NF-M 07-075 foam test:

[0066] An additive formulation ("AF A", for comparison) composed of 25% by weight of a commercial polyisobutenyl-substituted succinimide (Kerocom® PIBSI from BASF SE) as an additive with detergent action, 72% by weight of Solvesso® 150 as an aromatic hydrocarbon mixture, 1% by weight of a commercial silicon-containing antifoam and 2% by weight of a commercial dehazer were added in a dosage of 200 mg/kg to the abovementioned fuel DF 1. The foam volume and the foam collapse time of the fuel additized with AF A were determined.

[0067] A further additive formulation ("AF B", according to the present invention) composed of 25% by weight of a commercial polyisobutenyl-substituted succinimide (Kerocom® PIBSI from BASF SE) as an additive with detergent action, 67% by weight of Solvesso® 150 as an aromatic hydrocarbon mixture, 5% by weight of 2-ethylhexanol, 1% by weight of a commercial silicon-containing antifoam and 2% by weight of a commercial dehazer were added in a dosage of 200 mg/kg to the abovementioned fuel DF 1. The foam volume and the foam collapse time of the fuel additized with AF A were determined.

[0068] The following table shows the results of the determinations:

Fuel	Foam volume	Foam collapse time
Unadditized DF 1	95 ml	35 sec
AF A (for comparison)	35 ml	10 sec
AF B (inventive)	30 ml	6 sec

1. The use of a C₅- to C₁₅-alkanol for improving the defoamer action of a silicon-containing antifoam in fuel oils which comprise at least one additive with detergent action.

2. The use according to claim 1 in fuel oils which consist (a) to an extent of 0.1 to less than 100% by weight of at least one biofuel oil based on fatty acid esters, and

(b) to an extent of more than 0 to 99.9% by weight of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters.

3. The use according to claim 1 or 2, wherein the defoamer action of the silicon-containing antifoam is improved to such an extent that at least one of the following criteria is met:

(α) reduction in the foam volume with respect to the defoamer action of the same silicon-containing antifoam in the same fuel oil in the absence of a C₅- to C₁₅-alkanol by at least 10%, determined by the BNPe NF-M 07-075 foam test;

(β) reduction in the foam collapse time with respect to the defoamer action of the same silicon-containing antifoam in the same fuel oil in the absence of a C₅- to C₁₅-alkanol by at least 20%, determined by the BNPe NF-M 07-075 foam test.

4. The use according to claims 1 to 3, wherein the C₅- to C₁₅-alkanol is n-octanol, 2-ethylhexanol, n-nonanol, 2-propylheptanol, n-decanol, n-undecanol, n-dodecanol, n-tridecanol or isotridecanol.

5. The use according to claims 1 to 4, wherein the silicon-containing antifoam is a polyether-modified polysiloxane.

6. The use according to claims 1 to 5, wherein the additive with detergent action is a compound with moieties which are derived from succinic anhydride and have hydroxyl and/or amino and/or amido and/or imido groups.

7. An additive concentrate comprising

(A) 0.1 to 10% by weight of at least one C₅- to C₁₅-alkanol,

(B) 0.5 to 80% by weight of either (i) at least one aromatic hydrocarbon or hydrocarbon mixture having a boiling point or a predominant boiling range within the temperature range from 100° C. to 250° C. or (ii) at least one C₅- to C₁₂-alkyl nitrate or (iii) a mixture of (i) and (ii), with the proviso that the amount of component (B) is at least five times the amount of the C₅- to C₁₅-alkanol of component (A),

(C) 0.01 to 2% by weight of at least one silicon-containing antifoam,

(D) 1 to 30% by weight of at least one additive with detergent action and

(E) 0 to 5% by weight of at least one commercial dehazer, where the sum of components (A) to (E) is 100% by weight in each case, and with the proviso that at least one of the following criteria is additionally met:

(γ) the amount of the additive with detergent action in component (D) is at least ten times the amount of the silicon-containing antifoam in component (C);

(δ) the amount of the C₅- to C₁₅-alkanol of component (A) is at least three times the amount of the silicon-containing antifoam of component (C).

8. The additive concentrate according to claim 7, wherein the C₅- to C₁₅-alkanol is n-octanol, 2-ethylhexanol, n-nonanol, 2-propylheptanol, n-decanol, n-undecanol, n-dodecanol, n-tridecanol or isotridecanol.

9. The additive concentrate according to claim 7 or 8, wherein the silicon-containing antifoam is a polyether-modified polysiloxane.

10. The additive concentrate according to claims 7 to 9, wherein the additive with detergent action is a compound with moieties which are derived from succinic anhydride and have hydroxyl and/or amino and/or amido and/or imido groups.

11. The use of the additive concentrate according to claims 7 to 10 for improving foam reduction in fuel oils.

12. An additized fuel oil comprising a major amount of base fuel oil which consists

(a) to an extent of 0.1 to 100% by weight of at least one biofuel oil based on fatty acid esters, and

(b) to an extent of 0 to 99.9% by weight of middle distillates of fossil origin and/or of vegetable and/or animal origin, which are essentially hydrocarbon mixtures and are free of fatty acid esters, and a minor amount of the additive concentrate according to claims 7 to 10.

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