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(54) **COMPOSITION OF FUEL OILS**

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(57) **ABSTRACT**

The present invention relates to a fuel oil additive comprising

A) a copolymer of ethylene and from 13 to 17 mol % of at least one acrylic ester or vinyl ester having a C_1-C_{18}-alkyl radical and a melt viscosity V_{140} of not more than 80 mPas, and

B) a comb polymer comprising structural units formed from

B1) at least one olefin as monomer 1, which bears at least one C_8-C_{18}-alkyl radical on the olefinic double bond, and

B2) at least one ethylenically unsaturated dicarboxylic acid as monomer 2, which bears at least one C_8-C_{16}-alkyl radical bonded via an ester group,

in which the parameter Q

$$Q = \sum_i w_{1i} \cdot n_{1i} + \sum_j w_{2j} \cdot n_{2j}$$

in which

w_1 is the molar proportion of the individual chain lengths n_1 in the alkyl radicals of monomer 1,

w_2 is the molar proportion of the individual chain lengths n_2 in the alkyl radicals of the ester groups of monomer 2,

n_1 are the individual chain lengths in the alkyl radicals of monomer 1,

n_2 are the individual chain lengths in the alkyl radicals of the ester groups of monomer 2,

i is the serial variable for the chain lengths in the alkyl radicals of monomer 1, and

is the serial variable for the chain lengths in the alkyl radicals of the ester groups of monomer 2

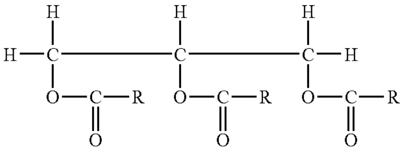
assumes values of from 23 to 27.

COMPOSITION OF FUEL OILS

[0001] The present invention relates to an additive, to its use as a cold flow improver for vegetable or animal fuel oils and to correspondingly additized fuel oils.

[0002] In view of decreasing world crude oil reserves and the discussion about the environmentally damaging consequences of the use of fossil and mineral fuels, there is increasing interest in alternative energy sources based on renewable raw materials. These include in particular natural oils and fats of vegetable or animal origin. These are generally triglycerides of fatty acids having from 10 to 24 carbon atoms and a calorific value comparable to conventional fuels, but are at the same time regarded as being less harmful to the environment. Biofuels, i.e. fuels derived from animal or vegetable material, are obtained from renewable sources and, when they are combusted, therefore generate only as much CO_2 as had previously been converted to biomass. It has been reported that less carbon dioxide is formed in the course of combustion than by the equivalent amount of crude oil distillate fuel, for example diesel fuel, and that very little sulfur dioxide is formed. In addition, they are biodegradable.

[0003] Oils obtained from animal or vegetable material are mainly metabolism products which include triglycerides of monocarboxylic acids, and generally correspond to the formula



$$\mathrm{H-\overset{H}{\underset{O-\underset{\displaystyle O}{\overset{\|}{C}}-R}{C}}-\overset{H}{\underset{O-\underset{\displaystyle O}{\overset{\|}{C}}-R}{C}}-\overset{H}{\underset{O-\underset{\displaystyle O}{\overset{\|}{C}}-R}{C}}-H}$$

where R is an aliphatic radical which has from 10 to 25 carbon atoms and may be saturated or unsaturated.

[0004] In general, such oils contain glycerides from a series of acids whose number and type vary with the source of the oil, and they may additionally contain phosphoglycerides. Such oils can be obtained by processes known from the prior art.

[0005] As a consequence of the sometimes unsatisfactory physical properties of the triglycerides, the industry has applied itself to converting the naturally occurring triglycerides to fatty acid esters of lower alcohols such as methanol or ethanol.

[0006] A hindrance to the use of triglycerides and also fatty acid esters of lower monohydric alcohols as a replacement for diesel fuel, alone or in a mixture with diesel fuel, has been found to be their flow behavior at low temperatures. The cause of this is the high uniformity of these oils in comparison to mineral oil middle distillates. For example, rapeseed oil methyl ester (RME) has a cold filter plugging point (CFPP) of −14° C. It has hitherto been impossible using the prior art additives to reliably attain a CFPP value of −20° C. required for use as a winter diesel in Central Europe, or of −22° C. or lower for special applications. This problem is worsened when oils are used which comprise relatively large amounts of saturated fatty acid esters, as are present, for example, in sunflower oil methyl ester, used oil methyl ester or soybean oil methyl ester.

[0007] EP-A-0 665 873 discloses a fuel oil composition which includes a biofuel, a fuel oil based on crude oil and an additive which comprises (a) an oil-soluble ethylene copolymer or (b) a comb polymer or (c) a polar nitrogen compound or (d) a compound in which at least one substantially linear alkyl group having from 10 to 30 carbon atoms is bonded to a nonpolymeric organic radical, in order to provide at least one linear chain of atoms which includes the carbon atoms of the alkyl groups and one or more nonterminal oxygen atoms, or (e) one or more of components (a), (b), (c) and (d).

[0008] EP-A-0 629 231 discloses a composition which comprises a relatively large proportion of oil which consists substantially of alkyl esters of fatty acids which are derived from vegetable or animal oils or both, mixed with a small proportion of mineral oil cold flow improvers, which comprises one or more of the following:

[0009] (I) comb polymer, the copolymer (which may be esterified) of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, or polymer or copolymer of α-olefin, or fumarate or itaconate polymer or copolymer,

[0010] (II) polyoxyalkylene ester, ester/ether or a mixture thereof,

[0011] (III) ethylene/unsaturated ester copolymer,

[0012] (IV) polar, organic, nitrogen-containing paraffin crystal growth inhibitor,

[0013] (V) hydrocarbon polymer,

[0014] (VI) sulfur-carboxyl compounds and

[0015] (VII) aromatic pour point depressant modified with hydrocarbon radicals,

with the proviso that the composition does not comprise any mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid which are derived from alcohols having from 1 to 22 carbon atoms.

[0016] EP-A-0 543 356 discloses a process for preparing compositions having improved low temperature performance for use as fuels or lubricants, starting from the esters of naturally occurring long-chain fatty acids with monohydric C_1-C_6-alcohols (FAE), which comprises

[0017] a) adding PPD additives (pour point depressants) known per se and used for improving the low temperature performance of mineral oils in amounts of from 0.0001 to 10% by weight, based on the long-chain fatty acid esters FAE and

[0018] b) cooling the nonadditized long-chain fatty acid esters FAE to a temperature below the cold filter plugging point and

[0019] c) removing the resulting precipitates (FAN).

[0020] DE-A-40 40 317 discloses mixtures of fatty acid lower alkyl esters having improved cold stability comprising

[0021] a) from 58 to 95% by weight of at least one ester within the iodine number range from 50 to 150 and being derived from fatty acids having from 12 to 22 carbon atoms and lower aliphatic alcohols having from 1 to 4 carbon atoms,

[0022] b) from 4 to 40% by weight of at least one ester of fatty acids having from 6 to 14 carbon atoms and lower aliphatic alcohols having from 1 to 4 carbon atoms and

[0023] c) from 0.1 to 2% by weight of at least one polymeric ester.

[0024] EP-A-0 153 176 discloses the use of polymers based on unsaturated dialkyl C_4-C_8-dicarboxylates having an average alkyl chain length of from 12 to 14 as cold flow improvers for certain crude oil distillate fuel oils. Mentioned as suitable comonomers are unsaturated esters, in particular vinyl acetate, but also α-olefins.

[0025] EP-A-0 153 177 discloses an additive concentrate which comprises a combination of

[0026] I) a copolymer having at least 25% by weight of an n-alkyl ester of a monoethylenically unsaturated C_4-C_8 mono- or dicarboxylic acid, the average number of carbon atoms in the n-alkyl radicals being 12-14, and another unsaturated ester or an olefin, with

[0027] II) another low temperature flow improver for distillate fuel oils.

[0028] EP-A-1 491 614 discloses oils of vegetable or animal origin and their blends with crude oil distillate fuel oils, which comprise an ethylene-vinyl ester copolymer which contains at least 17 mol % of vinyl ester and has a degree of branching of 5 or more alkyl branches per 100 methylene groups to improve their low temperature properties.

[0029] With the known additives, it is often impossible to reliably adjust fatty acid esters, especially those which comprise a total of more than 7% by weight of palmitic acid methyl ester and stearic acid methyl ester, to a CFPP of −10° C. which is required for use as winter diesel in Southern Central Europe and of −20° C. in Northern Central Europe, and of −22° C. and lower for specific applications. An additional problem with the existing additives is a lack of cold transition stability of the additized oils, i.e. the set CFPP value of the oils rises gradually when the oil is stored for a prolonged period at varying temperatures in the region of its cloud point or lower. Moreover, especially oils having a high content of palmitic acid methyl ester and stearic acid methyl ester exhibit a strong tendency to sedimentation in the course of storage at low temperatures. It is known from practice that sedimentation of the additized fatty acid esters which occurs in laboratory experiments under cold conditions, in spite of the CFPP being attained, can lead to filter blockages in the engine and the fuel is thus not suitable for use in transport.

[0030] It was therefore an object of the invention to provide additives for improving the cold flow behavior of fatty acid esters which are derived, for example, from rapeseed oil, used oil, sunflower oil and/or soybean oil and which comprise, at least 7% by weight of palmitic acid methyl ester and stearic acid methyl ester, to set CFPP values of −10° C. or −20° C. or lower which remain constant even in the course of prolonged storage of the oil in the region of its cloud point and lower. Moreover, these additives should contribute to preventing the sedimentation tendency of these oils, such that, even after storage of the fatty acid esters for several days, they remain homogeneous and free-flowing and their CFPP does not change either.

[0031] It has now been found that, surprisingly, an additive comprising ethylene copolymers and comb polymers is an outstanding flow improver for such fatty acid esters.

[0032] The invention provides an additive comprising

[0033] mA) a copolymer of ethylene and from 13 to 17 mol % of at least one acrylic ester or vinyl ester having a C_1-C_{18}-alkyl radical and a melt viscosity V_{140} of not more than 80 mpas, and

[0034] B) a comb polymer comprising structural units formed from

[0035] B1) at least one olefin as monomer 1, which bears at least one C_8-C_{18}-alkyl radical on the olefinic double bond, and

[0036] B2) at least one ethylenically unsaturated dicarboxylic acid as monomer 2, which bears at least one C_8-C_{16}-alkyl radical bonded via an ester group,

[0037] in which the parameter Q

$$Q=\sum_i w_{1i}\cdot n_{1i}+\sum_j w_{2j}\cdot n_{2j}$$

[0038] in which

[0039] w_1 is the molar proportion of the individual chain lengths n_1 in the alkyl radicals of monomer 1,

[0040] w_2 is the molar proportion of the individual chain lengths n_2 in the alkyl radicals of the ester groups of monomer 2,

[0041] n_1 are the individual chain lengths in the alkyl radicals of monomer 1,

[0042] n_2 are the individual chain lengths in the alkyl radicals of the ester groups of monomer 2,

[0043] i is the serial variable for the chain lengths in the alkyl radicals of monomer 1, and

[0044] j is the serial variable for the chain lengths in the alkyl radicals of the ester groups of monomer 2

[0045] assumes values of from 23 to 27.

[0046] The invention further provides a fuel oil composition comprising a fuel oil of animal or vegetable origin and the above-defined additive.

[0047] The invention further provides for the use of the above-defined additive for improving the cold flow properties of fuel oils of animal or vegetable origin.

[0048] The invention further provides a process for improving the cold flow properties of fuel oils of animal or vegetable origin by adding the above-defined additive to fuel oils of animal or vegetable origin.

[0049] In a preferred embodiment of the invention, Q assumes values of from 24 to 26.

[0050] Chain length of olefins is understood here to mean the chain length of the monomeric olefin minus the two olefinically bonded carbon atoms. In olefins with nonterminal double bonds, for example olefins with vinylidene moiety, the chain length is equal to the total chain length of the olefin minus the two olefinically bonded carbon atoms.

[0051] When the polymers formed from the olefins B1) and the dicarboxylates B2) rather than the monomeric olefins are considered, the chain length is the length of the alkyl radicals which—introduced into the polymer by the olefin—depart from the polymer backbone.

[0052] Suitable ethylene copolymers A) are preferably those which contain from 13 to 17 mol % of one or more vinyl esters and/or (meth)acrylic esters and from 83 to 87% by weight of ethylene. Particular preference is given to ethylene copolymers having from 15 to 17 mol % of at least one vinyl ester. Suitable vinyl esters derive from fatty acids having linear or branched alkyl groups having from 1 to 30 carbon atoms. Preferred ethylene copolymers have a melt viscosity V_{140} of at least 5 mPas, preferably from 10 to 80 mPas, in particular from 20 to 60 mPas.

[0053] Examples of suitable vinyl esters are vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl heptanoate, vinyl octanoate, vinyl laurate and vinyl stearate, and esters of vinyl alcohol based on branched fatty acids, such as vinyl isobutyrate, vinyl pivalate, vinyl 2-ethylhexanoate, vinyl isononanoate, vinyl neononanoate, vinyl neodecanoate and vinyl neoundecanoate. Likewise suitable as comonomers are esters of acrylic acid and methacrylic acid having from 1 to 20 carbon atoms in the alkyl radical, such as methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth) acrylate, n- and isobutyl(meth)acrylate, hexyl(meth)acrylate, octyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, decyl (meth)acrylate, dodecyl(meth)acrylate, tetradecyl(meth) acrylate, hexadecyl(meth)acrylate, octadecyl(meth)acrylate. Also suitable are mixtures of two, three, four or even more of these comonomers.

[0054] Further preferred copolymers contain, in addition to ethylene and from 13 to 17 mol % of vinyl esters, also from 0.5 to 10 mol % of olefins having from 3 to 10 carbon atoms, for example propene, butene, isobutylene, hexene, 4-methylpentene, octene, diisobutylene and/or norbornene.

[0055] The copolymers A preferably have weight-average molecular weights Mw, measured by means of gel permeation chromatography (GPC) against polystyrene standards in THF of from 1000 to 10 000 g/mol, in particular from 1500 to 5000 g/mol. Their degrees of branching determined by means of ^1H NMR spectroscopy (400 MHz with $CDCl_3$ as the solvent) are preferably less than 6 $CH_3/100$ CH_2 groups, in particular less than 5 $CH_3/100$ CH_2 groups. The methyl groups stem from the short-chain and long-chain branches, and not from copolymerized comonomers.

[0056] The copolymers (A) can be prepared by customary copolymerization processes, for example suspension polymerization, solution polymerization, gas phase polymerization or high pressure bulk polymerization. Preference is given to carrying out the high pressure bulk polymerization at pressures of from 50 to 400 MPa, preferably from 100 to 300 MPa, and temperatures from 100 to 300° C., preferably from 150 to 250° C. In a particularly preferred preparation variant, the polymerization is effected in a multizone reactor in which the temperature difference between the peroxide feeds along the tubular reactor is kept to a minimum, i.e. <50° C., preferably <30° C., in particular <15° C. The temperature maxima in the individual reaction zones preferably differ by less than 30° C., more preferably by less than 20° C. and especially by less than 10° C.

[0057] The reaction of the monomers is initiated by free radical-forming initiators (free radical chain initiators). This substance class includes, for example, oxygen, hydroperoxides, peroxides and azo compounds, such as 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, 2,2'-azobis(2-methyl-propanonitrile), 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.

[0058] The high-pressure bulk polymerization is carried out in known high-pressure reactors, for example autoclaves or tubular reactors, batchwise or continuously; tubular reactors have been found to be particularly useful. Solvents such as aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, benzene or toluene may be present in the reaction mixture. Preference is given to the substantially solvent-free procedure. In a preferred embodiment of the polymerization, the mixture of the monomers, the initiator and, if used, the moderator, is fed to a tubular reactor via the reactor entrance and also via one or more side branches. Preferred moderators are, for example, hydrogen, saturated and unsaturated hydrocarbons, for example propane or propene, aldehydes, for example propionaldehyde, n-butyraldehyde or isobutyraldehyde, ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, and alcohols, for example butanol. The comonomers and also the moderators may be metered into the reactor either together with ethylene or else separately via sidestreams. The monomer streams may have different compositions (EP-A-0 271 738 and EP-A-0 922 716).

[0059] Examples of suitable co- or terpolymers include:

[0060] ethylene-vinyl acetate copolymers having 10-40% by weight of vinyl acetate and 60-90% by weight of ethylene;

[0061] the ethylene-vinyl acetate-hexene terpolymers known from DE-A-34 43 475;

[0062] the ethylene-vinyl acetate-diisobutylene terpolymers described in EP-A-0 203 554;

[0063] the mixture of an ethylene-vinyl acetate-diisobutylene terpolymer and an ethylene/vinyl acetate copolymer known from EP-A-0 254 284;

[0064] the mixtures of an ethylene-vinyl acetate copolymer and an ethylene-vinyl acetate-N-vinylpyrrolidone terpolymer known from EP-A-0 405 270;

[0065] the ethylene/vinyl acetate/isobutyl vinyl ether terpolymers described in EP-A-0 463 518;

[0066] the ethylene/vinyl acetate/vinyl neononanoate or vinyl neodecanoate terpolymers which, apart from ethylene, contain 10-35% by weight of vinyl acetate and 1-25% by weight of the particular neo compound, known from EP-A-0 493 769;

[0067] the terpolymers of ethylene, a first vinyl ester having up to 4 carbon atoms and a second vinyl ester which is derived from a branched carboxylic acid having up to 7 carbon atoms or a branched but nontertiary carboxylic acid having from 8 to 15 carbon atoms, described in EP-A-0 778 875;

[0068] the terpolymers of ethylene, the vinyl ester of one or more aliphatic C_2- to C_{20}-monocarboxylic acids and 4-methylpentene-1, described in DE-A-196 20 118;

[0069] the terpolymers of ethylene, the vinyl ester of one or more aliphatic C_2- to C_{20}-monocarboxylic acids and bicyclo[2.2.1]hept-2-ene, disclosed in DE-A-196 20 119;

[0070] the terpolymers of ethylene and at least one olefinically unsaturated comonomer which contains one or more hydroxyl groups, described in EP-A-0 926 168.

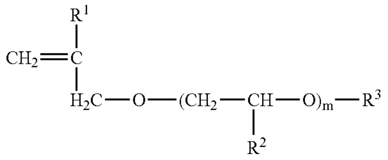
[0071] Preference is given to using mixtures of identical or different ethylene copolymers. The polymers on which the mixtures are based more preferably differ in at least one characteristic. For example, they may contain different comonomers, different comonomer contents, molecular weights and/or degrees of branching. The mixing ratio of the different ethylene copolymers is preferably between 20:1 and 1:20, preferably from 10:1 to 1:10, in particular from 5:1 to 1:5.

[0072] The copolymers B are preferably derived from dicarboxylic acids B2 and their derivatives such as esters and anhydrides. Preference is given to maleic acid, fumaric acid, itaconic acid and especially maleic anhydride.

[0073] Particularly suitable comonomers are monoolefins B1 having from 10 to 20, in particular having from 12-18, carbon atoms. These are preferably linear and the double bond is preferably terminal, as, for example, in dodecene, tridecene, tetradecene, pentadecene, hexadecene, heptadecene and octadecene.

[0074] The molar ratio of dicarboxylic acids/derivitives to olefin or olefins in the polymer is preferably in the range from 1:1.5 to 1.5:1, and is especially equimolar. It is possible for copolymers B also to contain minor amounts of up to 20 mol %, preferably <10 mol %, especially <5 mol %, of further comonomers apart from B1 and B2 which are copolymerizable with dicarboxylic acids/derivatives and the olefins mentioned. These comonomers are, for example olefins having from 2 to 50 carbon atoms, allyl polyglycol ethers, C_1-C_{30}-alkyl(meth)acrylates, vinylaromatics or C_1-C_{20}-alkyl vinyl ethers. Equally, minor amounts of poly (isobutylenes) having molecular weights of up to 5000 g/mol are used with preferance, preference being given to highly reactive variants having a high proportion of terminal vinylidene groups. These further comonomers are not taken into account in the calculation of the factor Q which is critical for the effectiveness.

[0075] Allyl polyglycol ethers correspond to the general formula



$$CH_2{=}C(R^1)\text{—}H_2C\text{—}O\text{—}(CH_2\text{—}CH(R^2)\text{—}O)_m\text{—}R^3$$

where

[0076] R^1 is hydrogen or methyl,

[0077] R^2 is hydrogen or C_1-C_4-alkyl,

[0078] m is a number from 1 to 100,

[0079] R^3 is C_1-C_{24}-alkyl, C_5-C_{20}-cycloalkyl, C_6-C_{18}-aryl or —C(O)—R^4,

[0080] R^4 is C_1-C_{40}-alkyl, C_5-C_{10}-cycloalkyl or C_6-C_{18}-aryl.

[0081] The inventive copolymers B) 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 isoaliphatic solvents or solvent mixtures such as kerosene or Solvent Naphtha. Particular preference is given to polymerizing in a small amount of moderating, aliphatic or isoaliphatic 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.

[0082] The average molecular mass Mw of the inventive copolymers B 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. Inventive copolymers B 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.

[0083] 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.

[0084] The copolymers may be prepared either by reacting maleic acid, fumaric acid and/or itaconic acid or their anhydrides with the corresponding alcohol 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 alcohols. Preference is given to carrying out a copolymerization with anhydrides and converting the resulting copolymer to an ester and/or a diester after the preparation.

[0085] In both cases, this esterification is effected, for example, by reacting with from 0.8 to 2.5 mol of alcohol per mole of anhydride, preferably with from 1.0 to 2.0 mol of alcohol per mole of anhydride, at from 50 to 300° C. When approx. 1 mol of alcohol is used per mole of anhydride, monoesters are formed. Here, esterification temperatures of from approx. 70 to 120° C. are preferred. When larger amounts of alcohol are used, preferably 2 mol of alcohol per mole of anhydride, diesters are formed at 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 having acid numbers of 30-70 mg KOH/g, preferably of 40-60 mg KOH/g, are regarded as monoesters. Copolymers having acid numbers of less than 40 mg, especially less than 30 mg KOH/g, are regarded as diesters. Particular preference is given to monoesters.

[0086] Suitable alcohols are, in particular, linear, 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 alcohols (in the 1- or 2-position). Particular preference is given to octanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol and hexadecanol.

[0087] The use of mixtures of different olefins in the polymerization and mixtures of different alcohols in the esterification allows the effectiveness to be adjusted further to specific fatty acid ester compositions.

[0088] Particularly preferred copolymers B contain monoesters of primary alcohols as monomer B2.

[0089] The use of mixtures of different olefins in the polymerization and mixtures of different alcohols in the esterification allows the effectiveness to be further adapted to specific fatty acid ester compositions.

[0090] In a preferred embodiment, the additives, as well as constituents A and B, may also comprise polymers and copolymers based on C_{10}-C_{24}-alkyl acrylates or methacrylates (constituent C). These poly(alkyl acrylates) and methacrylates have molecular weights Mw of from 800 to 1 000 000 g/mol, and derive preferably from caprylic alcohol, capric alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, palmitoleyl alcohol, stearyl alcohol or mixtures thereof, for example coconut alcohol, palm alcohol, tallow fat alcohol or behenyl alcohol.

[0091] In a preferred embodiment, mixtures of different copolymers B are used, the mean (weight average) of the parameter Q of the mixture components assuming values of from 23 to 27 and preferably values of from 24 to 26.

[0092] The mixing ratio of the inventive additive constituents A and B is (in parts by weight) from 20:1 to 1:20, preferably from 10:1 to 1:10, in particular from 5:1 to 1:5. The proportion of component C in the formulations composed of A, B and C may be up to 40% by weight; it is preferably less than 20% by weight, in particular between 1 and 10% by weight, based on the total weight of A, B and C.

[0093] The inventive additives are added to oils in amounts of from 0.001 to 5% by weight, preferably from 0.005 to 1 % by weight and especially from 0.01 to 0.6% by weight. They may be used as such or else dissolved or dispersed in solvents, for example aliphatic and/or aromatic hydrocarbons or hydrocarbon mixtures, for example toluene, xylene, ethylbenzene, decane, pentadecane, petroleum fractions, kerosene, naphtha, diesel, heating oil, isoparaffins or commercial solvent mixtures such as Solvent Naphtha, ®Hydrosol A 200 N, ®Shellsol A 150 ND, ®Caromax 20 LN, ®Shellsol AB, ®Solvesso 150, ®Solvesso 150 ND, ®Solvesso 200, ®Exxsol, ®Isopar and ®Shellsol D types. They are preferably dissolved in fuel oil of animal or vegetable origin based on fatty acid alkyl esters. The inventive additives preferably comprise 1-80%, especially 10-70%, in particular 25-60%, of solvent.

[0094] In a preferred embodiment, the fuel oil, which is frequently also referred to as biodiesel or biofuel, comprises fatty acid alkyl esters composed of fatty acids having from 12 to 24 carbon atoms and alcohols having from 1 to 4 carbon atoms. Typically, a relatively large portion of the fatty acids contains one, two or three double bonds.

[0095] Examples of oils which are derived from animal or vegetable material and in which the inventive additive can be used are rapeseed oil, coriander oil, soya oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustardseed oil, bovine tallow, bone oil, fish oils and used cooking oils. Further examples include oils which are derived from wheat, jute, sesame, shea tree nut, arachis oil and linseed oil. The fatty acid alkyl esters also referred to as biodiesel can be derived from these oils by processes disclosed by the prior art. Preference is given to rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, since it is obtainable in large amounts and is obtainable in a simple manner by extractive pressing of rapeseeds. In addition, preference is given to the likewise widely available oils of used oil, palm oil, sunflowers and soya, and also to their mixtures with rapeseed oil.

[0096] Particularly suitable biofuels are lower alkyl esters of fatty acids. These include, for example, commercially available mixtures of the ethyl, propyl, butyl and in particular methyl esters of fatty acids having from 14 to 22 carbon atoms, for example of lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinolic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, each of which preferably has an iodine number of from 50 to 150, in particular from 90 to 125. Mixtures having particularly advantageous properties are those which comprise mainly, i.e. comprise at least 50% by weight of, methyl esters of fatty acids having from 16 to 22 carbon atoms, and 1, 2 or 3 double bonds. The preferred lower alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linolenic acid and erucic acid.

[0097] Commercial mixtures of the type mentioned are obtained, for example, by hydrolyzing and esterifying, or by transesterifying, animal and vegetable fats and oils with lower aliphatic alcohols. Equally suitable as starting materials are used cooking oils. To prepare lower alkyl esters of fatty acids, it is advantageous to start from fats and oils having a high iodine number, for example sunflower oil, rapeseed oil, coriander oil, castor oil, soya oil, cottonseed oil, peanut oil or bovine tallow. Preference is given to lower alkyl esters of fatty acids based on a novel type of rapeseed oil, more than 80% by weight of whose fatty acid component is derived from unsaturated fatty acids having 18 carbon atoms.

[0098] A biofuel is therefore an oil which is obtained from vegetable or animal material or both or a derivative thereof which can be used as a fuel and in particular as a diesel or heating oil. Although many of the above oils can be used as biofuels, preference is given firstly to vegetable oil derivatives, particularly preferred biofuels being alkyl ester derivatives of rapeseed oil, cottonseed oil, soya oil, sunflower oil, olive oil or palm oil, and very particular preference is given to rapeseed oil methyl ester, sunflower oil methyl ester, palm oil methyl ester and soya oil methyl ester. Owing to the high demand for biofuels, ever more manufacturers are switching from fatty acid methyl esters to other raw material sources with higher availability. Mention should be made here particularly of used oil, which is used in the form of used oil methyl ester as biodiesel alone or in a blend with other fatty acid methyl esters, for example rapeseed oil methyl ester, sunflower oil methyl ester, palm oil methyl ester and soybean oil methyl ester. Mention should also be made of mixtures of rapeseed oil methyl ester with soybean oil methyl ester or rapeseed oil methyl ester with a mixture of soybean oil methyl ester and palm oil methyl ester or a mixture of soybean oil methyl ester and palm oil methyl ester.

[0099] The additive can be introduced to the oil to be additized by processes known in the prior art. When more than one additive component or coadditive component is to be used, such components can be introduced into the oil together or separately in any combination.

[0100] The inventive additives allow the CFPP value of biodiesel to be adjusted to values of −10° C. and below −20° C. and in some cases to values of below −25° C., as required for marketing for use especially in winter. Equally, the pour point of biodiesel is lowered by the addition of the inventive additives. The inventive additives are particularly advantageous in problematic oils which have a high proportion of esters of the saturated fatty acids palmitic acid and stearic acid of more than 7% by weight, as present, for example, in fatty acid methyl esters obtained from used oil, sunflowers and soybean. It is thus also possible with the inventive additives to adjust mixtures of rapeseed oil methyl ester and/or used oil methyl ester and/or sunflower oil methyl ester and/or soybean oil methyl ester to CFPP values of −10° C. or −20° C. and lower. It is thus also possible with the inventive additives to adjust used oil methyl ester or sunflower oil methyl ester or soybean oil methyl ester to CFPP values of −10° C. or −20° C. and lower. In addition, the oils thus additized have a good cold transition stability, i.e. the CFPP value remains constant even in the case of storage under winter conditions, and do not tend to sediment at constant low temperatures (e.g. −10° C. or −22° C.).

[0101] To produce additive packages for specific solutions to problems, the inventive additives may also be used together with one or more oil-soluble coadditives which, even alone, improve the cold flow properties of crude oils, lubricant oils or fuel oils. Examples of such coadditives are polar compounds which bring about paraffin dispersancy (paraffin dispersants) and oil-soluble amphiphiles.

[0102] The inventive additives may be used in a mixture with paraffin dispersants. Paraffin dispersants reduce the size of the paraffin crystals and have the effect that the paraffin particles do not settle out but rather remain dispersed in colloidal form with significantly reduced sedimentation tendency. Useful paraffin dispersants have been found to be both low molecular weight and polymeric oil-soluble compounds having ionic or polar groups, for example amine salts and/or amides. 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). 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), and the reaction products of alkenyl-spiro-bislactones with amines (cf. EP 0 413 279 B1), and, according to EP-A-0 606 055 A2, reaction products of terpolymers based on α,β-unsaturated dicarboxylic anhydrides, α,β-unsaturated compounds and polyoxyalkylene ethers of lower unsaturated alcohols.

[0103] The mixing ratio (in parts by weight) of the inventive additives with paraffin dispersants is from 1:10 to 20:1, preferably from 1:1 to 10:1.

[0104] The oils treated with the inventive additive may also be added to middle distillates obtained from crude oil. The mixtures of biofuel and middle distillate thus obtained can in turn be admixed with cold additives such as flow improvers or wax dispersants, and also performance packages.

[0105] The mixing ratio between biofuel and middle distillates may be between 1:99 and 99:1. Particular preference is given to mixing ratios of biofuel:middle distillate=3:97 to 30:70.

[0106] Middle distillate refers in particular to those mineral oils which are obtained by distilling crude oil and boil within the range from 120 to 450° C., for example kerosene, jet fuel, diesel and heating oil. Preference is given to using those middle distillates which contain 0.05% by weight of sulfur and less, more preferably less than 350 ppm of sulfur, in particular less than 200 ppm of sulfur and in special cases less than 50 ppm of sulfur. They are generally those middle distillates which have been subjected to refining under hydrogenating conditions, and which therefore contain only small proportions of polyaromatic and polar compounds. They are preferably those middle distillates which have 95% distillation points below 370° C., in particular 350° C. and in special cases below 330° C. Suitable middle distillates are also synthetic fuels, as made available, for example, by the Fischer-Tropsch process.

[0107] The additives may be used alone or else together with other additives, for example with other pour point depressants or dewaxing aids, with antioxidants, cetane number improvers, dehazers, demulsifiers, detergents, dispersants, defoamers, dyes, corrosion inhibitors, conductivity improvers, sludge inhibitors, odorants and/or additives for lowering the cloud point.

EXAMPLES

[0108]

TABLE 1

Characterization of the ethylene copolymers used

Example	Comonomer(s)	V_{140}	CH_3/100 CH_2	Content of vinyl ester
A1 (C)	Ethylene/ VAC/ vinyl neodecanoate	110 mPas	4.2	13.3 mol %
A2	Ethylene/ VAC	35 mPas	3.9	16.6 mol %
A3 (C)	Ethylene/ VAC	154 mPas	3.0	16.7 mol %
A4 (C)	Ethylene/ VAC	125 mPas	3.0	13.8 mol %

VAC = vinyl acetate

[0109] The vinyl ester content was measured by means of pyrolysis and subsequent titration.

[0110] The viscosity (V_{140}) was measured with a Haake Reostress 600 viscometer.

[0111] The degree of branching ($CH_3/100CH_2$) was measured on a ^1H NMR unit at 400 MHz in $CDCl_3$, and calculated by means of integration of the individual signals.

TABLE 2

Characterization of the comb polymers used

Example	Comonomers	Alcohol	Q	Acid number [mg KOH/g]
B1	MSA-co-$C_{14}/_{16}$-α-olefin (1:0.5:0.5)	C_{12}/C_{16} alcohol (85%:15%)	25.6	49.9
B2	MSA-co-$C_{14}/_{16}$-α-olefin (1:0.5:0.5)	C_{12} alcohol	25.0	48.2
B3	MSA-co-$C_{14}/_{16}$-α-olefin (1:05:05)	C_{12} alcohol	23.0	51.1

TABLE 3

Acrylates	
C1	Poly(octadecyl acrylate), K value 32
C2	Poly(behenyl acrylate), K value 18

TABLE 4

Characterization of the test oils

Oil No.:	CFPP [° C.]	Composition
E1	−8	Soya Me/RME 30:70
E2	−7	RME/PME 85:15
E3	−11	RME/AME 60:40
E4	−10	RME/AME 50:50
E5	−8	RME/AME 40:60
E6	−8	RME/AME 45:55

SoyaME = soya methyl ester
RME = rapeseed oil methyl ester
PME = palm oil methyl ester
AME = used oil methyl ester

TABLE 5

Methyl ester distribution of the test oils

	E1	E2	E3	E4	E5	E6
C16:0	6.53	6.21	6.74	7.33	8.13	7.76
C18:0	1.19	2.36	2.71	2.97	3.32	3.16
C18:1	45.19	48.73	52.53	50.84	45.36	46.77
C18:2	36.33	28.77	26.45	28.17	32.27	31.00
C18:3	8.37	9.18	6.36	5.49	5.45	5.89
C20:1/2/3	0.79	1.25	1.14	1.04	0.97	1.03
C20:0	0.39	0.57	0.58	0.56	0.53	0.57
C22:0	0.15	0.39	0.48	0.51	0.50	0.49

[0112] In the tables which follow, the mixing ratio according to weight of the additives A, B and C is A:B=4:1, or, when C is present in the mixtures, A:B:C=4:1:0.2. The total amount of additive is evident from the top row of the table.

TABLE 6

CFPP testing in test oil E1

Ex.	Comb polymer	Ethylene copolymer	Polyacrylate	2000 ppm	3000 ppm	4000 ppm
1 (C)	B2	A4	—	−12	−13	−12
2 (C)	B2	A3	—	−16	−18	−10
3	B2	A2	—	−17	−18	−18
4	B1	A2	—	−14	−15	−17
5 (C)	B1	A1	—	−13	−13	−11
6 (C)	B2	A1	—	−11	−17	−11
7	B2	A2	C1	−18	−20	−20
8	B3	A2	—	−18	−20	−20

TABLE 7

CFPP testing in test oil E2

Ex.	Comb polymer	Ethylene copolymer	Poly-acrylate	2000 ppm	3000 ppm	4000 ppm
9	B1	A2	—	−7	−7	−11
10 (C)	B2	A3	—	−7	−10	−10
11	B1	A2	—	−7	−9	−12
12	B1	A2	C2	−9	−10	−12
13	B3	A2	—	−9	−9	−12

TABLE 8

CFPP testing in test oil E3

Ex.	Comb polymer	Ethylene copolymer	Poly-acrylate	2000 ppm	3000 ppm
14 (C)	B1	A1	—	−18	−11
15	B1	A2	—	−19	−20
16	B3	A2	—	−18	−20

TABLE 9

CFPP testing in test oil E4

Ex.	Comb polymer	Ethylene copolymer	Polyacrylate	2000 ppm	3000 ppm
17 (C)	B1	A1	—	−17	−10
18	B1	A2	—	−18	−20
19 (C)	B1	A4	—	−17	−10

TABLE 10

CFPP testing in test oil E5

Ex.	Comb polymer	Ethylene copolymer	Polyacrylate	2000 ppm	3000 ppm
20 (C)	B2	A1	—	−12	−9
21 (C)	B1	A1	—	−10	−9
22	B1	A2	—	−12	−19
23	B1	A2	C2	−13	−19
24 (C)	B1	A3	—	−10	−9

TABLE 11

CFPP testing in test oil E6

Ex.	Comb polymer	Ethylene copolymer	Polyacrylate	4000 ppm
25 (C)	B2	A1	—	−8
26 (C)	B1	A1	—	−9
27	B2	A2	—	−19
28 (C)	B1	A4	—	−8

1. A fuel oil additive comprising

A) a copolymer of ethylene and from 13 to 17 mol % of at least one acrylic ester or vinyl ester having a C_1-C_{18}-alkyl radical and a melt viscosity V_{140} of not more than 80 mPas, and

B) a comb polymer comprising structural units formed from

B1) at least one olefin as monomer 1, which bears at least one C_8-C_{18}-alkyl radical on the olefinic double bond, and

B2) at least one ethylenically unsaturated dicarboxylic acid as monomer 2, which bears at least one C_8-C_{16}-alkyl radical bonded via an ester group, in which the parameter Q

$$Q = \sum_i w_{1i} \cdot n_{1i} + \sum_j w_{2j} \cdot n_{2j}$$

in which

w_1 is the molar proportion of the individual chain lengths n_1 in the alkyl radicals of monomer 1,

w_2 is the molar proportion of the individual chain lengths n_2 in the alkyl radicals of the ester groups of monomer 2,

n_1 are the individual chain lengths in the alkyl radicals of monomer 1,

n_2 are the individual chain lengths in the alkyl radicals of the ester groups of monomer 2,

i is the serial variable for the chain lengths in the alkyl radicals of monomer 1, and

j is the serial variable for the chain lengths in the alkyl radicals of the ester groups of monomer 2

assumes values of from 23 to 27.

2. The fuel oil additive as claimed in claim **1**, wherein Q assumes values of from 24 to 26.

3. The fuel oil additive as claimed in claim **1**, wherein constituent A) comprises from 15 to 17 mol % of at least one vinyl ester.

4. The fuel oil additive of claim **1**, wherein constituent A) comprises from 0.5 to 10 mol % of olefins having from 3 to 10 carbon atoms.

5. The fuel oil additive of claim **1**, wherein component A) has a degree of branching of less than 6 CH_3/100 CH_2 groups, determined by means of ^1H NMR spectroscopy.

6. The fuel oil additive of claim **1**, wherein the constituent B1) is an α-olefin.

7. The fuel oil additive of claim **1**, wherein the monomer B1) and the comonomer B2) are present in copolymer B) in a molar ratio of between 1.5:1 and 1:1.5.

8. The fuel oil additive of claim **1**, wherein copolymer B, as well as comonomers B1) and B2), also comprises up to 20 mol % of a further comonomer other than B1) and B2), selected from the group consisting of an olefin having less than 10 and more than 20 carbon atoms, an allyl polyglycol ether, a C_1-C_{30}-alkyl(meth)acrylate, a vinylaromatic ether, a C_1-C_{20}-alkyl vinyl ether, and a polyisobutene having a molecular weight of up to 5000 g/mol.

9. The fuel oil additive of claim **1**, wherein constituent A) has a melt viscosity V_{140} of from 5 to 80 mPas.

10. The fuel oil additive of claim **1**, wherein constituent A) has a molecular weight Mw of from 1000 to 10 000 g/mol.

11. The fuel oil additive of claim **1**, in which constituent B) has a molecular weight of from 1200 to 200 000 g/mol.

12. A fuel oil composition comprising a fuel oil of vegetable or animal origin or a mixture thereof and a fuel oil additive as claimed in claim **1**.

13. The fuel oil composition as claimed in claim **12**, wherein the fuel oil comprises a mixture of fatty acid esters of C_1- to C_4-alcohols.

14. The fuel oil composition as claimed in claim **13**, wherein the fatty acid esters include stearic acid methyl ester and palmitic acid methyl ester in a proportion of at least 7% by weight.

15. A method for improving the cold behavior of a fuel oil of vegetable or animal origin or a mixture thereof, said method comprising adding the fuel oil additive of claim **1** to the fuel oil.

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