(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 491 614 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
04.04.2012 Bulletin 2012/14

(51) Int Cl.:
C10L 1/18 *(2006.01)* ***C10L 1/14*** *(2006.01)*

(21) Application number: **04076690.9**

(22) Date of filing: **09.06.2004**

(54) **Oil compositions**

Ölzusammensetzungen

Compositions d'huile

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LI LU MC NL PL PT RO SE SI SK TR

(30) Priority: **23.06.2003 EP 03253948**

(43) Date of publication of application:
29.12.2004 Bulletin 2004/53

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EP-A2- 1 380 635
WO-A-93/18115
US-A- 4 354 011
US-A- 4 623 684

- **PATENT ABSTRACTS OF JAPAN vol. 007, no. 242 (C-192), 27 October 1983 (1983-10-27) -& JP 58 129096 A (MITSUBISHI YUKA KK), 1 August 1983 (1983-08-01)**

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EP 1 491 614 B1

Description

[0001] This invention relates to the use of wax crystal modifying additives in oils obtained from animal or vegetable material or both, or derivatives thereof, or their mixtures with petroleum-based oils.

[0002] Oils obtained from animal or vegetable material are mainly metabolites comprising triglycerides of monocarboxylic acids, e.g. acids containing 10 to 25 carbon atoms which may be saturated or unsaturated.

[0003] Generally, such oils contain glycerides of a number of acids, the number and kind varying with the source of the oil, and may additionally contain phosphoglycerides. Such oils may be obtained by methods know in the art.

[0004] Examples of derivatives of such oils are alkyl esters, such as methyl esters, of fatty acids of the vegetable or animal oils. Such esters can be made by transesterification.

[0005] Reference within this specification to oils that are derived from animal or vegetable material therefore includes reference both to oils obtained from said animal or vegetable material or both, or to derivatives thereof.

[0006] FR-A-2,492,402 describes fuel compositions containing one or more fatty acid esters of animal and vegetable origin described by the general formula:

$$R^1\text{-COO-}R^2$$

where R^1 contains 5 to 23 carbon atoms, being a substantially linear saturated or unsaturated aliphatic radical and R^2 contains 1 to 12 carbon atoms, being a linear or branched, saturated or unsaturated, aliphatic radical. Such fuel compositions are described as particularly suitable for use in diesel engines, possessing a cetane-index range broadly equivalent to that of conventional diesel fuels derived from mineral oils.

[0007] However the usefulness of such fatty acid ester compositions as diesel fuels is limited by their low temperature properties. DE-A-4,040,317 discloses that at temperatures below -5°C, such fuels may solidify in supply lines due to inadequate filterability, and describes a process for improving the low temperature filterability involving the addition of mixtures of short chain methyl esters of fatty acids and selected polymeric materials, namely polymeric esters or copolymers of esters of acrylic and/or methacrylic acids derived from alcohols possessing 1 to 22 carbon atoms.

[0008] The low temperature properties of petroleum-based oils, i.e. mineral oils and their derivatives such as crude oil, lubricating oil and fuel oil, for example middle distillate fuel oil, are well documented in the art. Similarly, it is known to use additives to modify the wax crystal structure of these mineral oils and derivatives thereof. Examples of such additives and their use are described in US-A-3,048,479; GB-A-1,263,152; US-A-3,961,916; US-A-4,211,534; EP-A-153,176 and EP-A-153,177.

[0009] In contrast to said mineral oils and derivatives thereof, the low temperature properties of oils according to the present invention being oils derived from animal or vegetable material, are controlled predominantly by the precipitation of higher molecular weight fatty acid esters present as major constituents. Such fatty acid esters are frequently derived from mixtures of saturated and unsaturated fatty acids. By way of example only, the main components of rapeseed oil methyl ester are the methyl esters of oleic, linoleic, linolenic and erucic acids.

[0010] In general such unsaturated fatty acid derivatives predominate over their saturated analogues, although the exact proportions of individual components within a particular oil may vary as a result of seasonal fluctuations of the constituent fatty acids within the source material, or as a result of the particular method by which they are obtained.

[0011] This preponderance of ethylenically-unsaturated fatty acid esters provides such oils with crystallization behavior different from that of the aforementioned mineral oils, with the difference in crystal morphologies between these two classes of oil believed to result from the different structural configurations of the hydrocarbon chains of precipitating n-alkanes and unsaturated fatty acid esters respectively.

[0012] WO-A-93/18115 describes generally the use of cold flow additives typically used in petroleum fuels to improve the low temperature properties of oils derived from animal or vegetable oils. Among the additives described in WO-A-93/18115 are ethylene unsaturated ester copolymer flow improvers. Polymer A of WO-A-93/18115 at page 20 has about 16 mole% vinyl acetate.

[0013] EP 1 380 635 A2 having a priority date of 09.07.2002 and a publication date of 14.01.2004 describes additives suitable for addition to fuel oils of vegetable or animal origin comprising the combination of a copolymer of ethylene and 8-21 mol% of at least one acrylic or vinyl ester having a C_1 - C_{18} alkyl radical, and a comb polymer of at least one C_8-C_{16} alkyl ester of an ethylenically unsaturated dicarboxylic acid and at least one C_{10}-C_{20} olefin, wherein the sum Q

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

of the molar averages of the carbon chain distributions in the alkyl side chains of the olefins on the one hand and the fatty alcohols in the ester groups on the other hand is from 23 to 27, where w_1 and w_2 are the molar proportions of the individual chain lengths in the alkyl side chains of the olefins on the one hand and the fatty alcohols in the ester groups on the other hand, and n_1 and n_2 are the side chain lengths, in the case of olefins without the originally olefinically bonded carbon atoms, of the alkyl side chains of the olefins on the one hand and of the fatty alcohols in the ester groups on the other hand, and the serial variables i and j are the individual side chain lengths in the alkyl side chains of the olefins on the one hand and of the fatty alcohols in the ester groups on the other hand.

[0014] US 4,623,684 describes compositions comprising the combination of an oil-soluble ethylene backbone polymer and hydrocarbyl substituted carboxylic acylating agent derivatives, and hydrocarbon fuel compositions containing such combinations.

[0015] The present invention is based on the discovery that a certain limited category of ethylene-vinyl ester copolymers, i.e. those having a certain vinyl ester content and degree of branching, exhibit enhanced low temperature performance in fuel oils derived from animal or vegetable oils and mixtures of same with petroleum-based fuel oils.

[0016] In a first aspect the present invention provides a composition comprising a major proportion of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, or its mixtures with petroleum-based oils, wherein such mixtures comprise 95-5wt% of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof and 5-95wt% of petroleum-based oils, in admixture with a minor proportion of an ethylene-vinyl ester copolymer cold flow additive having 17-25 mole% vinyl ester units and containing 5 - 8 alkyl branches per 100 backbone methylenes, and having an Mn molecular weight in the range of 3,000 to 5,000 as measured by GPC using polystyrene standards. Preferably the polymer has a vinyl ester content of 17-19, mole%. The esters are those of monocarboxylic acids having 2 to 30, preferably 2 to 10 carbon atoms.

[0017] In a second aspect, the present invention provides the use of a copolymer as defined in relation to the first aspect to improve the low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, or its mixtures with petroleum-based oils.

[0018] In a third aspect, the present invention provides a method of improving the low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, the method including the step of adding a copolymer as defined in relation to the first aspect to the oil.

[0019] The following copolymers are preferred: ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, ethylene-vinyl 2-ethylhexanoate, or ethylene-vinyl octanoate copolymer.

[0020] They may also be in the form of mixture of two copolymers such as those described in US-A3,961,916. If desired, the copolymers may be derived from additional comonomers, e.g., they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is propylene or isobutylene.

[0021] The copolymers may be made by direct polymerisation of comonomers. Such copolymers may also be made by transesterification, or by hydrolysis and reesterification, of an ethylene unsaturated ester copolymer to give a different unsaturated ester copolymer. For example, ethylene-vinyl hexanoate and ethylene-vinyl 2-ethylhexanoate copolymers may be made this way, e.g., from an ethylene-vinyl acetate copolymer.

[0022] The polymers of this invention may be used in combination with conventional cold flow additives which may comprise one or more of the following:

(a) another ethylene-unsaturated ester copolymer;
(b) a comb polymer;
(c) polar nitrogen compounds;
(d) a compound containing a cyclic ring system;
(e) a hydrocarbon polymer;
(f) a polyoxyalkylene compound;
(g) a hydrocarbylated-aromatic pour point depressant; or
(h) alkyl phenol formaldehyde condensates.

[0023] The features of this invention will now be discussed in further detail.

OILS

[0024] Examples of oils derived from animal or vegetable material are rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, caster oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow and fish oils. Further examples include oils derived from corn, jute, sesame, shea nut, ground nut and linseed and may be derived therefrom by methods know in the art. Rapeseed oil, which is a mixture of fatty acids partially esterified with glycerol, is preferred as it is available in large quantities and can be obtained in a simple way by pressing from rapeseed.

[0025] As lower alkyl esters of fatty acids, consideration may be given to the following, for example as commercial mixtures: the ethyl, propyl, butyl and especially methyl esters of fatty acids with 12 to 22 carbon atoms, for example of lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid or erucic acid, which have an iodine number from 50 to 150, especially 90 to 125. Mixtures with particularly advantageous properties are those which contain mainly, i.e. to at least 20 wt.% methyl esters of fatty acids with 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.

[0026] Commercial mixtures of the stated kind are obtained for example by cleavage and esterification of animal and vegetable fats and oils by their transesterification with lower aliphatic alcohols. For production of lower alkyl esters of fatty acids it is advantageous to start from fats and oils with high iodine number, such as, for example, sunflower oil, rapeseed oil, coriander oil, castor oil, soyabean oil, cottonseed oil, peanut oil or beef tallow. Lower alkyl esters of fatty acids based on a new variety of rapeseed oil, the fatty acid component of which is derived to more than 80 wt.% from unsaturated fatty acids with 18 carbon atoms, are preferred.

[0027] Particularly preferred are oils according to this invention capable of being utilized as biofuels. Biofuels, i.e. fuels derived from animal or vegetable material, are believed to be less damaging to the environment on combustion, and are obtained from a renewable source. It has been reported that on combustion less carbon dioxide is formed than is formed by the equivalent quantity of petroleum distillate fuel, e.g. diesel fuel, and very little sulphur dioxide is formed. Certain derivatives of vegetable oil, e.g. those obtained by saponification and re-esterification with a monohydric alkyl alcohol, may be used as a substitute for diesel fuel. Rapeseed esters, for example, rapeseed oil methyl ester (RME), have been used neat on their own or in mixtures with petroleum distillate fuels. Thus, a biofuel is an oil obtained from vegetable or animal material, or both, or a derivative thereof, capable of being utilized as a fuel.

[0028] Whilst many of the above oils may be used as biofuels, preferred are vegetable oils or derivatives thereof, of which particularly preferred biofuels are rapeseed oil, cottonseed oil, soyabean oil, sunflower oil, olive oil, palm oil, or alkyl ester derivatives thereof, rapeseed oil methyl ester being especially preferred.

[0029] The invention is also applicable to mixtures comprising 95-5 wt.% of the aforesaid biofuels with 5-95 wt.% by weight of a petroleum based fuel. The petroleum based fuel oil may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet fuels, diesel fuels, heating oils and heavy fuel oils. Such distillate fuel oils generally boil in the range of 100-500 degrees Centigrade. The heating oil may be a straight atmospheric distillate, or may also contain vacuum gas oil or cracked gas oil or both. The fuels may also contain major or minor amounts of components derived from the Fischer-Tropsch process. Fischer-Tropsch fuels, also known as FT fuels, include those that are described as gas-to-liquid fuels and coal or biomass conversion fuels. To make such fuels, syngas ($CO + H_2$) is first generated and then converted to normal paraffins by a Fischer-Tropsch process. The normal paraffins may then be modified by processes such as catalytic cracking/reforming or isomerization, hydrocracking and hydroisomerisation to yield a variety of hydrocarbons such as iso-paraffins, cyclo-paraffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types such as those mentioned in this specification.

[0030] The concentration of the additive in the oil may for example be in the range of 1 to 10,000 ppm of additive (active ingredient) by weight per weight of fuel, for example 10 to 5,000 ppm such as 10 to 2000 ppm (active ingredient) by weight per weight of fuel.

[0031] The additive may be incorporated into bulk oil by methods such as those known in the art. Where more than one additive component or co-additive component is to be used, such components may be incorporated into the oil together or separately in any combination.

[0032] A concentrate comprising the additive dissolved or dispersed in carrier liquid (e.g. in solution) is convenient as a means of incorporating the additive. The concentrates of the present invention are convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt.%, more preferably 3 to 60 wt.%, most preferably 10 to 50 wt.% of the additives preferably in solution in oil. Examples of carrier liquid are organic solvents including hydrocarbon solvents, for example petroleum fractions such as naphtha, kerosene, diesel and heater oil; aromatic hydrocarbons such as aromatic fractions, e.g. those sold under the 'SOLVESSO' tradename; and paraffinic hydrocarbons such as hexane and pentane and isoparaffins. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the fuel.

[0033] The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

[0034] The conventional cold flow additives for use in combination with the polymers of the invention are defined in (A) - (H) below.

(A) Other ethylene-unsaturated ester copolymers, more especially one having, in addition to units derived from ethylene, units of the formula

$$-CR^7R^8-CHR^9-$$

where R^8 represents hydrogen or a methyl group; R^7 represents a - $OOCR^{10}$ or $COOR^{10}$ group wherein R^{10} represents hydrogen or a C_1 to C_{28}, preferably C_1 to C_9, straight or branched chain alkyl group, provided that R^{10} does not represent hydrogen when R^7 represents -$COOR^{10}$, and R^9 is hydrogen or -$COOR^{10}$.

These may comprise a copolymer of ethylene with an ethylenically unsaturated ester, or derivatives thereof. An example is a copolymer of ethylene with an ester of an unsaturated carboxylic acid. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, ethylene-vinyl 2-ethylhexanoate, or ethylene-vinyl octanoate copolymer is preferred.

Preferably, the copolymers contain from 0.3 up to 15mole%, preferably from 3.5 up to 15 mole% of the vinyl ester. They may also be in the form of mixtures of two copolymers such as those described in US-A3,961,916. If desired, the copolymers may be derived from additional comonomers, e.g. they may be terpolymers or tetrapolymers or higher polymers, for example where the additional comonomer is propylene or isobutylene.

The copolymers may be made by direct polymerisation of comonomers. Such copolymers may also be made by transesterification, or by hydrolysis and reesterification, of an ethylene unsaturated ester copolymer to give a different unsaturated ester copolymer. For example, ethylene-vinyl hexanoate and ethylene-vinyl 2-ethylhexanoate copolymers may be made this way, e.g. from an ethylene-vinyl acetate copolymer.

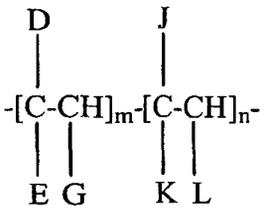
(B) Comb polymers.

Such polymers are polymers in which branches containing hydrocarbyl groups are pendant from a polymer backbone, and are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Platé and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

Generally, comb polymers have one or more long chain hydrocarbyl branches, e.g., oxyhydrocarbyl branches, normally having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

Advantageously, the comb polymer is a homopolymer or a copolymer wherein at least 25 and preferably at least 40, more preferably at least 50, molar per cent of the units of which have, side chains containing at least 6, and preferably at least 10, atoms.

As examples of preferred comb polymers there may be mentioned those of the general formula



wherein

D	= R^{11}, $COOR^{11}$, $OCOR^{11}$, $R^{12}COOR^{11}$, or OR^{11},
E	= H, CH_3, D, or R^{12},
G	= H or D
J	= H, R^{12}, $R^{12}COOR^{11}$, or an aryl or heterocyclic group,
K	= H, $COOR^{12}$, $OCOR^{12}$, OR^{12} or COOH,
L	= H, R^{12}, $COOR^{12}$, $OCOR^{12}$, COOH, or aryl,
$R^{11} \geq C_{10}$	hydrocarbyl,
$R^{12} \geq C_1$	hydrocarbyl or hydrocarbylene,

and m and n represent mole fractions, m being finite and preferably within the range of from 1.0 to 0.4, n being less than 1 and preferably in the range of from 0 to 0.6.

R^{11} advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, while R^{12} advantageously represents a hydrocarbyl or hydrocarbylene group with from 1 to 30 carbon atoms.

The comb polymer may contain units derived from other monomers if desired or required.

These comb polymers may be copolymers of maleic anhydride or fumaric or itaconic acids and another ethylenically unsaturated monomer, e.g., an α-olefin, including styrene, or an unsaturated ester, for example, vinyl acetate or homopolymer of fumaric or itaconic acids. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g., maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

The acid or anhydride group of the comb polymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, ndodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and noctadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecanl-ol or 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols.

It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the R^{12} refers to the average number of carbon atoms in the alkyl group; if alcohols that contain a branch at the 1 or 2 positions are used R^{12} refers to the straight chain backbone segment of the alcohol.

These comb polymers may especially be fumarate or itaconate polymers and copolymers such for example as those described in EP-A-153176, EP-A-153177 and - EP-A-225688, and WO 91/16407.

Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C_{14}/C_{16} alkyl groups, made, for example, by solution copolymerizing an equimolar mixture of fumaric acid and vinyl acetate and reacting the resulting copolymer with the alcohol or mixture of alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C_{14} and C_{16} alcohols. Furthermore, mixtures of the C_{14} ester with the mixed C_{14}/C_{16} ester may advantageously be used. In such mixtures, the ratio of C_{14} to C_{14}/C_{16} is advantageously in the range of from 1:1 to 4:1, preferably 2:1 to 7:2, and most preferably about 3:1, by weight. The particularly preferred comb polymers are those having a number average molecular weight, as measured by vapour phase osmometry, of 1,000 to 100,000, more especially 1,000 to 30,000.

Other suitable comb polymers are the polymers and copolymers of α-olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous. Other examples of comb polymers are hydrocarbon polymers, e.g., copolymers of ethylene and at least one α-olefin the α-olefin preferably having at most 20 carbon atoms, examples being n-decene-1 and n-dodecene-1. Preferably, the number average molecular weight of such a copolymer is at least 30,000 measured by GPC. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

(C) Polar nitrogen compounds.

Such compounds are oil-soluble polar nitrogen compounds carrying one or more, preferably two or more, substituents of the formula $>NR^{13}$, where R^{13} represents a hydrocarbyl group containing 8 to 40 atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. The oil soluble polar nitrogen compound is generally one capable of acting as a wax crystal growth inhibitor in fuels; it comprises, for example, one or more of the following compounds:

An amine salt and/or amide formed by reacting at least one molar proportion of a hydrocarbyl-substituted amine with a molar proportion of a hydrocarbyl acid having from 1 to 4 carboxylic acid groups or its anhydride, the substituent (s) of formula $>NR^{13}$ being of the formula $-NR^{13}R^{14}$ where R^{13} is defined as above and R^{14} represents hydrogen or R^{13}, provided that R^{13} and R^{14} may be the same or different, said substituents constituting part of the amine salt and/or amide groups of the compound.

Ester/amides may be used, containing 30 to 300, preferably 50 to 150, total carbon atoms. These nitrogen compounds are described in US Patent No. 4,211,534. Suitable amines are predominantly C_{12} to C_{40} primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble, normally containing about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8 to C_{40}, preferably C_{14} to C_{24}, alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but are preferably secondary. Tertiary and quaternary amines only form amine salts. Examples of amines include tetradecylamine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctacedyl amine and methylbehenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine, the alkyl groups of which are derived from hydrogenated tallow fat composed of approximately 4% C_{14}, 31% C_{16}, and 59% C_{18}.

Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include ethylenediamine tetraacetic acid, and carboxylic acids based on cyclic skeletons, e.g., cyclohexane-1,2-dicarboxylic acid,

cyclohexene-1,2-dicarboxylic acid, cyclopentane-1,2-dicarboxylic acid and naphthalene dicarboxylic acid, and 1,4-dicarboxylic acids including dialkyl spirobislactones. Generally, these acids have about 5 to 13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids e.g., phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid and its anhydride are particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US Patent No. 4,147,520, for example. Suitable amines may be those described above.

Other examples are condensates, for example, those described in EP-A-327427.

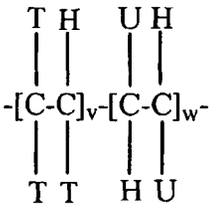
(D) Compounds containing a cyclic ring system carrying at least two substituents of the general formula below on the ring system

$$-A-NR^{15}R^{16}$$

where A is a linear or branched chain aliphatic hydrocarbylene group optionally interrupted by one or more hetero atoms, and R^{15} and R^{16} are the same or different and each is independently a hydrocarbyl group containing 9 to 40 atoms optionally interrupted by one or more hetero atoms, the substituents being the same or different and the compound optionally being in the form of a salt thereof. Advantageously, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group. Such compounds are described in WO 93/04148 and WO 94/07842.

(E) Hydrocarbon polymers.

Examples of suitable hydrocarbon polymers are those of the general formula



wherein

T = H or R^{17} wherein
R^{17} = C_1 to C_{40} hydrocarbyl, and
U = H, T, or aryl

and v and w represent mole fractions, v being within the range of from 1.0 to 0.0, w being in the range of from 0.0 to 1.0. Examples of hydrocarbon polymers are disclosed in WO 91/11488.

Preferred copolymers are ethylene α-olefin copolymers, having a number average molecular weight of at least 30,000. Preferably the α-olefin has at most 28 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g., up to 10% by weight, of other copolymerizable monomers, for example, olefins other than α-olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

The number average molecular weight of the ethylene α-olefin copolymer is, as indicated above, preferably at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120, 000.

Advantageously, the copolymer has a molar ethylene content between 50 and 85 per cent. More advantageously, the ethylene content is within the range of from 57 to 80%, and preferably it is in the range from 58 to 73%; more preferably from 62 to 71%, and most preferably 65 to 70%.

Preferred ethylene-α-olefin copolymers are ethylenepropylene copolymers with a molar ethylene content of from 62 to 71% and a number average molecular weight in the range 60,000 to 120,000; especially preferred copolymers are ethylene-propylene copolymers with an ethylene content of from 62 to 71% and a molecular weight from 80,000 to 100,000.

The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

Other suitable hydrocarbon polymers include a low molecular weight ethylene- α-olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate α-olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent, although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

(F) Polyoxyalkylene compounds.

Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two, C_{10} to C_{30} linear alkyl groups and a polyoxyalkylene glycol group of molecular weight up to 5,000, preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form the subject of EP-A-0061895. Other such additives are described in United States Patent No. 4,491,455.

The preferred esters, ethers or ester/ethers are those of the general formula

$$R^{18}\text{-O(D) -O-}R^{19}$$

where R^{18} and R^{19} may be the same or different and represent

(a) n-alkyl-
(b) n-alkyl-CO-
(c) n-alkyl-O-CO$(CH_2)_x$- or
(d) n-alkyl-O-CO$(CH_2)_x$-CO-

x being, for example, 1 to 30, the alkyl group being linear and containing from 10 to 30 carbon atoms, and D representing the polyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as a polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be present but it is preferred that the glycol is substantially linear. D may also contain nitrogen.

Examples of suitable glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of from 100 to 5,000, preferably from 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use a C_{18}-C_{24} fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is preferred that a major amount of the dialkyl compound be present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Other examples of polyoxyalkylene compounds are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and the esterified alkoxylated amines described in EP-A-117108 and EP-A-326356.

(G) Hydrocarbylated aromatics.

These materials are condensates comprising aromatic and hydrocarbyl parts. The aromatic part is conveniently an aromatic hydrocarbon which may be unsubstituted or substituted with, for example, non-hydrocarbon substituents. Such aromatic hydrocarbon preferably contains a maximum of these substituent groups and/or three condensed rings, and is preferably naphthalene. The hydrocarbyl part is a hydrogen and carbon containing part connected to the rest of the molecule by a carbon atom. It my be saturated or unsaturated, and straight or branched, and may contain one or more hetero-atoms provided they do not substantially affect the hydrocarbyl nature of the part. Preferably, the hydrocarbyl part is an alkyl part, conveniently having more than 8 carbon atoms. The molecular weight of such condensates may, for example, be in the range of 2,000 to 200,000 such as 2,000 to 20,000, preferably 2,000 to 8,000.

Examples are known in the art, primarily as lube oil pour depressants and as dewaxing aids as mentioned hereinbefore, they may, for example, be made by condensing a halogenated wax with an aromatic hydrocarbon. More specifically, the condensation may be a Friedel-Crafts condensation where the halogenated wax contains 15 to 60, e.g., 16 to 50, carbon atoms, has a melting point of about 200 to 400˚C and has been chlorinated to 5 to 25 wt.% chlorine, e.g., 10 to 18 wt. Another way of making similar condensates may be from olefins and the aromatic hydrocarbons.

(H) Alkyl Phenol Formaldehyde Condensates
Suitable alkyl phenol formaldehyde condensates are disclosed in EP 0 311 452 and EP 0 851 776.
The alkyl phenol formaldehyde condensate may be obtainable by the condensation reaction between:

(i) at least one aldehyde or ketone or reactive equivalent thereof, and
(ii) at least one compound comprising one or more aromatic moieties bearing at least one substituent of the formula $-XR^1$ and at least one further substituent $-R^2$, wherein:

X represents oxygen or sulphur,
R^1 represents hydrogen or a moiety bearing at least one hydrocarbyl group, and
R^2 represents a hydrocarbyl group, linear or branched, preferably containing from 4 to 40 carbon atoms, more preferably containing from 8 to 30 carbon atoms and most preferably containing from 8 to 18 carbon atoms.

The alkyl phenol formaldehyde condensate may be present in the fuel oil in an amount ranging from 5 to 5,000 ppm, preferably 10 to 1,000 ppm and most preferably from 20 to 500 ppm.

EXAMPLES

[0035] The invention will now be particularly described, by way of example only, as follows.

EXAMPLE 1

Additives

[0036] The following additives were used:

Polymer 1: an ethylene/vinyl acetate copolymer having a vinyl acetate concentration of about 38.1 wt.% (16.7% mole), a number average molecular weight of about 2,470 and containing about 7.6 alkyl branches per 100 methylene units

Polymer 2: an ethylene/vinyl acetate copolymer having a vinyl acetate concentration of about 15 wt.% (5mole%), a number average molecular weight of about 6,500 and containing about 8 alkyl branches per 100 methylene units

Polymer 3: a polymer of this invention having about 40 wt.% (17.5 mole%) vinyl acetate, a number average molecular weight of about 3,700 and containing about 6 alkyl branches per 100 methylene units

Co-additive: a comb polymer, di-n-dodecyl fumarate/vinyl-acetate.

Test

[0037] Polymers 1, 2, 3 and the co-additive were dissolved in samples of the same rapeseed methyl ester fuel and the Cold Filter Plugging Point (CFPP) test measured by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp 173-285. The CFPP is a measure of filterability. The results are in the table below.

TABLE

Additive	Additive components			Co-additive	Total treat rate	CFPP, ˚C
	Polymer 1	Polymer 2	Polymer 3			
	ppm Ai	ppm Ai	ppm Ai	ppm Ai	ppm Ai	
Base fuel	0	0	0	0	0	-16
A	1920	0	0	80	2000	-20
B	1440	480	0	80	2000	-18

(continued)

Additive	Additive components			Co-additive	Total treat rate	CFPP, ˚C
	Polymer 1	Polymer 2	Polymer 3			
	ppm Ai	ppm Ai	ppm Ai	ppm Ai	ppm Ai	
C	1782	137	0	80	2000	-19
Example A	0	0	1920	80	2000	-24
Example B	0	480	1440	80	2000	-24
Example C	0	137	1782	80	2000	-26
Note: "ppm Ai" refers to the active ingredient of the cold flow additive in ppm by weight, i.e., without regard to any amount of carrier solvent.						

[0038] The examples of the invention are Example A, Example B and Example C, each of which include the polymer of this invention, Polymer 3, which exhibits superior performance in the CFPP test.

Claims

1. A composition comprising a major proportion of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, or its mixtures with petroleum-based oils, wherein such mixtures comprise 95-5wt% of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof and 5-95wt% of petroleum-based oils, in admixture with a minor proportion of an ethylene-vinyl ester copolymer cold flow additive having 17-25 mole% vinyl ester units and containing 5-8 alkyl branches per 100 backbone methylenes, and having an Mn molecular weight in the range of 3,000 to 5,000 as measured by GPC using polystyrene standards.

2. The composition of claim 1, wherein the composition further comprises one or more of the following:

   (a) another ethylene-unsaturated ester copolymer;
   (b) a comb polymer;
   (c) polar nitrogen compounds;
   (d) a compound containing a cyclic ring system;
   (e) a hydrocarbon polymer;
   (f) a polyoxyalkylene compound;
   (g) a hydrocarbylated-aromatic pour point depressant; or
   (h) alkyl phenol formaldehyde condensates.

3. The composition of any one of the preceding claims, wherein the vinyl ester is vinyl acetate having 17-19 mole% vinyl acetate.

4. The composition of any one of the preceding claims, wherein said major proportion of oil is a biofuel selected from the group comprising methyl esters of rapeseed oil, cottonseed oil, soyabean oil, sunflower oil, olive oil or palm oil.

5. The composition of any one of the preceding claims, wherein the composition includes 1 to 10,000 ppm, preferably 10 to 5,000 ppm, of cold flow additive (active ingredient) by weight per weight of oil.

6. Use of an ethylene-vinyl ester copolymer cold flow additive having 17 - 25 mole% vinyl ester units and containing 5 -8 alkyl branches per 100 backbone methylenes, and having an Mn molecular weight in the range of 3,000 to 5,000 as measured by GPC using polystyrene standards, to improve low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, or its mixtures with petroleum-based oils, wherein such mixtures comprise 95-5wt% of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof and 5-95wt% of petroleum-based oils

7. A method of improving low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, or its mixtures with petroleum-based oils, wherein such mixtures comprise 95-5wt% of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof and

5-95wt% of petroleum-based oils, the method including the step of adding an ethylene-vinyl ester copolymer cold flow additive having 17 - 25 mole% vinyl ester units and containing 5-8 alkyl branches per 100 backbone methylenes, and having an Mn molecular weight in the range of 3,000 to 5,000 as measured by GPC using polystyrene standards, to the oil.

Patentansprüche

1. Zusammensetzung, die einen größeren Anteil an Öl umfasst, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, oder seine Mischungen mit Ölen auf Erdölbasis, wobei solche Mischungen 95 - 5 Gew.-% eines Öls, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, und 5 - 95 Gew.-% Öle auf Erdölbasis umfassen, in Mischung mit einem geringeren Anteil eines Kaltfließverbesserer-Additivs aus Ethylen/Vinylester-Copolymer, das 17 - 25 Mol.-% Vinylestereinheiten aufweist und 5 bis 8 Alkylverzweigungen pro 100 Methyleneinheiten des Grundgerüsts enthält und ein Molekulargewicht (Zahlenmittel, M_n) im Bereich von 3000 bis 5000 aufweist, gemessen mittels GPC unter Verwendung von Polystyrolstandards.

2. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung ferner eines oder mehrere der Folgenden umfasst:

   (a) ein weiteres Ethylen/ungesättigtes Ester-Copolymer,
   (b) ein Kammpolymer,
   (c) polare Stickstoffverbindungen,
   (d) eine Verbindung, die ein cyclisches Ringsystem enthält,
   (e) ein Kohlenwasserstoffpolymer,
   (f) eine Polyoxyalkylen-Verbindung,
   (g) ein mit Kohlenwasserstoff substituiertes aromatisches Stockpunkt-Senkungsmittel, oder
   (h) Alkylphenolformaldehyd-Kondensate.

3. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei der Vinylester Vinylacetat mit 17 bis 19 Mol.-% Vinylacetat ist.

4. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei der größere Anteil des Öls ein Biobrennstofföl ist, das ausgewählt ist aus der Gruppe bestehend aus Methylestern von Rapsöl, Bauwollsamenöl, Sojabohnenöl, Sonnenblumenöl, Olivenöl oder Palmöl.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, wobei die Zusammensetzung 1 bis 10.000 Gew.-ppm, vorzugsweise 10 bis 5000 Gew.-ppm Kaltfließadditiv (aktiver Bestandteil), bezogen auf das Gewicht des Öls, aufweist.

6. Verwendung eines Kaltfließadditivs aus Ethylen/Vinylester-Copolymer, das 17 bis 25 Mol.-% Vinylestereinheiten aufweist und 5 bis 8 Alkylverzweigungen pro 100 Methyleneinheiten des Grundgerüsts enthält und ein Molekulargewicht (Zahlenmittel, M_n) im Bereich von 3000 bis 5000, wie mittels GPC unter Verwendung von Polystyrolstandards gemessen, aufweist, zur Verbesserung der Tieftemperatureigenschaften eines Öls, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, oder seiner Mischungen mit Ölen auf Erdölbasis, wobei solche Mischungen 95 bis 5 Gew.-% eines Öls, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, und 5 bis 95 Gew.-% Ölen auf Erdölbasis umfassen.

7. Verfahren zum Verbessern der Tieftemperatureigenschaften eines Öls, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, oder seinen Mischungen mit Ölen auf Erdölbasis, wobei solche Mischungen 95 bis 5 Gew.-% Öl, das aus Methylestern tierischen oder pflanzlichen Materials oder beidem oder Derivaten davon erhalten wird, und 5 bis 95 Gew.-% Öle auf Erdölbasis umfassen, wobei das Verfahren den Schritt einschließt, dass ein Kaltfließadditiv aus Ethylen/Vinylester-Copolymer, das 17 bis 25 Mol.-% Vinylestereinheiten aufweist und 5 bis 8 Alkylverzweigungen pro 100 Methyleneinheiten des Grundgerüsts enthält und ein Molekulargewicht (Zahlenmittel, M_n) im Bereich von 3000 bis 5000, wie mittels GPC unter Verwendung von Polystyrolstandards gemessen, aufweist, dem Öl zugesetzt wird.

Revendications

1. Composition comprenant une proportion dominante d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances ou de leurs dérivés, ou de ses mélanges avec des huiles dérivées du pétrole, dans laquelle ces mélanges comprennent 95 à 5 % en poids d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances ou de leurs dérivés et 5 à 95 % en poids d'huiles dérivées du pétrole, en mélange avec une petite proportion d'un copolymère éthylène-ester vinylique servant d'additif d'écoulement à froid comprenant 17 à 25 % en moles de motifs ester vinylique et contenant 5 à 8 ramifications alkyle pour 100 groupes méthylène de squelette, et ayant un poids moléculaire Mn dans l'intervalle de 3000 à 5000 de la manière mesurée par CPG en utilisant des échantillons de polystyrène de référence.

2. Composition suivant la revendication 1, ladite composition comprenant en outre un ou plusieurs des agents suivants :

   (a) un autre copolymère éthylène-ester insaturé ;
   (b) un polymère en peigne ;
   (c) des composés azotés polaires ;
   (d) un composé contenant un système de noyau cyclique ;
   (e) un polymère hydrocarboné ;
   (f) un composé de polyoxyalkylène ;
   (g) un composé aromatique hydrocarbylé servant d'agent abaissant le point d'écoulement ; ou
   (h) des produits de condensation alkylphénol-formaldéhyde.

3. Composition suivant l'une quelconque des revendications précédentes, dans laquelle l'ester vinylique est l'acétate de vinyle comprenant 17 à 19 % en moles d'acétate de vinyle.

4. Composition suivant l'une quelconque des revendications précédentes, dans laquelle ladite proportion dominante d'une huile est un biocarburant choisi dans le groupe comprenant des esters méthyliques d'huile de colza, d'huile de graines de cotonnier, d'huile de soja, d'huile de tournesol, d'huile d'olive ou d'huile de palme.

5. Composition suivant l'une quelconque des revendications précédentes, ladite composition comprenant 1 à 10 000 ppm, de préférence 10 à 5000 ppm, d'additif d'écoulement à froid (ingrédient actif) en poids par poids d'huile.

6. Utilisation d'un copolymère éthylène-ester vinylique servant d'additif d'écoulement à froid comprenant 17 à 25 % en moles de motifs ester vinylique et contenant 5 à 8 ramifications alkyle pour 100 groupes méthylène de squelette, et ayant un poids moléculaire Mn dans l'intervalle de 3000 à 5000, de la manière mesurée par CPG en utilisant des échantillons de polystyrène de référence, pour améliorer les propriétés à basses températures d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances, ou de leurs dérivés, ou de ses mélanges avec des huiles dérivées du pétrole, dans laquelle ces mélanges comprennent 95 à 5 % en poids d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances, ou de leurs dérivés, et 5 à 95 % en poids d'huiles dérivées du pétrole.

7. Procédé pour améliorer les propriétés à basse température d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances, ou de leurs dérivés, ou de ses mélanges avec des huiles dérivées du pétrole, dans lequel ces mélanges comprennent 95 à 5 % en poids d'une huile obtenue à partir d'esters méthyliques d'une substance animale ou végétale ou de ces deux substances, ou de leurs dérivés, et 5 à 95 % en poids d'huiles dérivées du pétrole, le procédé comprenant l'étape d'addition d'un copolymère éthylène-ester vinylique servant d'additif d'écoulement à froid comprenant 17 à 25 % en moles de motifs ester vinylique et contenant 5 à 8 ramifications alkyle pour 100 groupes méthylène de squelette, et ayant un poids moléculaire Mn dans l'intervalle de 3000 à 5000, de la manière mesurée par CPG en utilisant des échantillons de polystyrène de référence, à l'huile.

REFERENCES CITED IN THE DESCRIPTION

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