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(54) **OIL COMPOSITIONS**

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(57) **ABSTRACT**

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, in admixture with an ethylene-vinyl ester copolymer cold flow additive having at least 17 mole % vinyl ester units and containing 5 or more alkyl branches per 100 backbone methylenes. The copolymer improves the low temperature properties of the oil.

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### OIL COMPOSITIONS

[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 known 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:



[0007] 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.

[0008] 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  $-5^\circ\text{C}$ ., 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.

[0009] 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 U.S. Pat. No. 3,048,479; GB-A-1,263,152; U.S. Pat. No. 3,961,916; U.S. Pat. No. 4,211,534; EP-A-153,176 and EP-A-153,177.

[0010] 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.

[0011] 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.

[0012] 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.

[0013] EP0629231 B1 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 EP0629231 B1 are ethylene unsaturated ester copolymer flow improvers. Polymer A of EP0629231 B1 at page 11 has about 16 mole % vinyl acetate.

[0014] 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.

[0015] The present invention comprises a major proportion of an oil obtained from methyl esters of animal or vegetable oils, or both, or derivatives thereof, or their mixtures with petroleum-based oils in admixture with a minor proportion of an ethylene-vinyl ester copolymer flow improver having a polymethylene backbone divided into segments by oxyhydrocarbon chains, the polymer having a vinyl ester content of at least 17, preferably 17-25, more preferably 17-19, mole % and the number of short-chain alkyl branches, measured as the number of alkyls per 100 backbone methylenes should be greater than 5, preferably from 6 to 8. The esters are those of monocarboxylic acids having 2 to 30, preferably 2 to 10 carbon atoms.

[0016] The following copolymers are preferred: ethylene-vinyl acetate, ethylene-vinyl propionate, ethylene-vinyl hexanoate, ethylene-vinyl 2-ethylhexanoate, or ethylene-vinyl octanoate copolymer. The Mn molecular weight of the copolymers will be in the range of 1,000 to 10,000, preferably 2,000 to 6,000, more preferably 3,000 to 5,000, as measured by GPC using polystyrene standards.

[0017] They may also be in the form of mixture of two copolymers such as those described in U.S. Pat. No. 3,961,916. 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.

[0018] 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.

[0019] The polymers of this invention may be used in combination with conventional cold flow additives which may comprise one or more of the following:

- [0020] (a) another ethylene-unsaturated ester copolymer;
- [0021] (b) a comb polymer;
- [0022] (c) polar nitrogen compounds;
- [0023] (d) a compound containing a cyclic ring system;
- [0024] (e) a hydrocarbon polymer;
- [0025] (f) a polyoxyalkylene compound;
- [0026] (g) a hydrocarbylated-aromatic pour point depressant; or
- [0027] (h) alkyl phenol formaldehyde condensates.

[0028] The features of this invention will now be discussed in further detail.

[0029] Oils

[0030] Examples of oils derived from animal or vegetable material are rapeseed oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor 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 known 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.

[0031] 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.

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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 ( $\text{CO} + \text{H}_2$ ) 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.

[0036] 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.

[0037] 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.

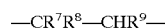
[0038] A concentrate comprising the additive dissolved or dispersed in carrier liquid (e.g. in solution) is convenient as

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.

[0039] 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.

[0040] The conventional cold flow additives for use in combination with the polymers of the invention are defined in (A)-(H) below.

[0041] (A) Other Ethylene-Unsaturated Ester Copolymers, More Especially One Having, in Addition to Units Derived from Ethylene, Units of the Formula



[0042] 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  $C_6$ , 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  $-COOR^{10}$ .

[0043] 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.

[0044] Preferably, the copolymers contain from 0.3 up to 15 mole %, preferably from 3.5 up to 15 mole % of the vinyl ester.

[0045] They may also be in the form of mixtures of two copolymers such as those described in U.S. Pat. No. 3,961, 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.

[0046] 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.

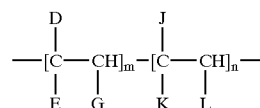
[0047] (B) Comb Polymers.

[0048] 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. Platè and V. P. Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

[0049] 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.

[0050] 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 percent of the units of which have, side chains containing at least 6, and preferably at least 10, atoms.

[0051] As examples of preferred comb polymers there may be mentioned those of the general formula



[0052] wherein

[0053]  $D=R^{11}$ ,  $COOR^{11}$ ,  $OCOR^{11}$ ,  $R^{12}COOR^{11}$ , or  $OR^{11}$ ,

[0054]  $E=H$ ,  $CH_3$ ,  $D$ , or  $R^{12}$ ,

[0055]  $G=H$  or  $D$

[0056]  $J=H$ ,  $R^{12}$ ,  $R^{12}COOR^{11}$ , or an aryl or heterocyclic group,

[0057]  $K=H$ ,  $COOR^{12}$ ,  $OCOR^{12}$ ,  $OR^{12}$  or  $COOH$ ,

[0058]  $L=H$ ,  $R^{12}$ ,  $COOR^{12}$ ,  $OCOR^{12}$ ,  $COOH$ , or aryl,

[0059]  $R^{11} \geq C_{10}$  hydrocarbyl,

[0060]  $R^{12} \geq C_1$  hydrocarbyl or hydrocarbylene,

[0061] 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.

[0062]  $R^{11}$  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.

[0063] The comb polymer may contain units derived from other monomers if desired or required.

[0064] These comb polymers may be copolymers of maleic anhydride or fumaric or itaconic acids and another ethylenically unsaturated monomer, e.g., an  $\alpha$ -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.

[0065] 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-methylpentadecan-1-ol or 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols.

[0066] 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.

[0067] 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.

[0068] 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.

[0069] Other suitable comb polymers are the polymers and copolymers of  $\alpha$ -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  $\alpha$ -olefin, the  $\alpha$ -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.

[0070] (C) Polar Nitrogen Compounds.

[0071] 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:

[0072] 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.

[0073] Ester/amides may be used, containing 30 to 300, preferably 50 to 150, total carbon atoms. These nitrogen compounds are described in U.S. Pat. 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.

[0074] 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 dioctadecyl 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%  $C_{18}$ .

[0075] 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 spirobis lactones. 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.

[0076] 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 U.S. Pat. No. 4,147,520, for example. Suitable amines may be those described above.

[0077] Other examples are condensates, for example, those described in EP-A-327427.

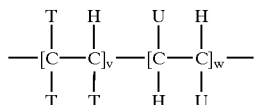
[0078] (D) Compounds Containing a Cyclic Ring System Carrying at Least Two Substituents of the General Formula Below on the Ring System



[0079] 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.

[0080] (E) Hydrocarbon Polymers.

[0081] Examples of suitable hydrocarbon polymers are those of the general formula



[0082] wherein

[0083]  $T=H$  or  $R^{17}$  wherein

[0084]  $R^{17}=C_1$  to  $C_{40}$  hydrocarbyl, and

[0085]  $U=H, T$ , or aryl

[0086] 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.

[0087] Examples of hydrocarbon polymers are disclosed in WO 91/11488.

[0088] Preferred copolymers are ethylene  $\alpha$ -olefin copolymers, having a number average molecular weight of at least 30,000. Preferably the  $\alpha$ -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  $\alpha$ -olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

[0089] The number average molecular weight of the ethylene  $\alpha$ -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.

[0090] Advantageously, the copolymer has a molar ethylene content between 50 and 85 percent. 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%.

[0091] Preferred ethylene- $\alpha$ -olefin copolymers are ethylene-propylene 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.

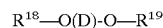
[0092] The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

[0093] Other suitable hydrocarbon polymers include a low molecular weight ethylene- $\alpha$ -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  $\alpha$ -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar percent, although for ethylene-propylene copolymers up to 86 molar percent by weight ethylene may be employed with advantage.

[0094] (F) Polyoxyalkylene Compounds.

[0095] 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 U.S. Pat. No. 4,491,455.

[0096] The preferred esters, ethers or ester/ethers are those of the general formula



[0097] where  $R^{18}$  and  $R^{19}$  may be the same or different and represent

[0098] (a) n-alkyl-

[0099] (b) n-alkyl-CO—

[0100] (c) n-alkyl-O—CO(CH<sub>2</sub>)<sub>x</sub>— or

[0101] (d) n-alkyl-O—CO(CH<sub>2</sub>)<sub>x</sub>—CO—

[0102] x being, for example, 1 to 30, the alkyl group being linear and containing from 10 to 30 carbon atoms, and D representing the polyoxyalkylene 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.

[0103] 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<sub>18</sub>-C<sub>24</sub> fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

[0104] 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.

[0105] 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.

[0106] (G) Hydrocarbylated Aromatics.

[0107] 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.

[0108] 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 may 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.

[0109] 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.

[0110] (H) Alkyl Phenol Formaldehyde Condensates

[0111] Suitable alkyl phenol formaldehyde condensates are disclosed in EP 0 311 452 and EP0 851 776.

[0112] The alkyl phenol formaldehyde condensate may be obtainable by the condensation reaction between:

[0113] (i) at least one aldehyde or ketone or reactive equivalent thereof, and

[0114] (ii) at least one compound comprising one or more aromatic moieties bearing at least one substituent of the formula —XR<sup>1</sup> and at least one further substituent —R<sup>2</sup>, wherein:

[0115] X represents oxygen or sulphur,

[0116] R<sup>1</sup> represents hydrogen or a moiety bearing at least one hydrocarbyl group, and

[0117] R<sup>2</sup> 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.

[0118] 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

[0119] The invention will now be particularly described, by way of example only, as follows.

##### Example 1

[0120] Additives

[0121] The following additives were used:

[0122] 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

[0123] Polymer 2: an ethylene/vinyl acetate copolymer having a vinyl acetate concentration of about 15 wt. % (5 mole %), a number average molecular weight of about 6,500 and containing about 8 alkyl branches per 100 methylene units

[0124] 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

[0125] Co-additive: a comb polymer, di-n-dodecyl fumarate/vinyl-acetate.

[0126] Test

[0127] 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				Total	
	Polymer 1 ppm Ai	Polymer 2 ppm Ai	Polymer 3 ppm Ai	Co-additive ppm Ai	treat rate ppm Ai	CFPP, ° C.
Base fuel	0	0	0	0	0	-16
A	1920	0	0	80	2000	-20
B	1440	480	0	80	2000	-18
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.

[0128] 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.

1. A composition comprising an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, and an ethylene-vinyl ester copolymer cold flow additive having at least 17 mole % vinyl ester units and containing 5 or more alkyl branches per 100 backbone methylenes.

2. The composition of claim 1, which 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; and
- (h) alkyl phenol formaldehyde condensates.

3. The composition of claim 1, in which the ethylene-vinyl ester copolymer has 17-25 mole % vinyl ester.

4. The composition of claim 1, in which the ethylene-vinyl ester copolymer has 6-8 alkyl branches per 100 backbone methylenes.

5. The composition of claim 1, in which the ethylene-vinyl ester copolymer is an ethylene-vinyl acetate copolymer having 17-19 mole % vinyl acetate.

6. The composition of claim 1, in which the major proportion of the oil is a biofuel selected from the group comprising methyl esters of rapeseed oil, cottonseed oil, soyabean oil, sunflower oil, olive oil and palm oil.

7. The composition of claim 1, which includes 1 to 10,000 ppm of cold flow additive by weight per weight of oil.

8. The composition of claim 1, which further comprises a petroleum based oil.

9. A method of using an ethylene-vinyl ester copolymer cold flow additive having at least 17 mole % vinyl ester units and containing 5 or more alkyl branches per 100 backbone methylenes, to improve low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof.

10. An additive concentrate for blending with an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, which additive concentrate comprises an ethylene-vinyl ester copolymer cold flow additive having at least 17 mole % vinyl ester units and containing 5 or more alkyl branches per 100 backbone methylenes.

11. A method of improving low temperature properties of an oil obtained from methyl esters of animal or vegetable material or both or derivatives thereof, which method comprises adding to the oil an ethylene-vinyl ester copolymer cold flow additive having at least 17 mole % vinyl ester units and containing 5 or more alkyl branches per 100 backbone methylenes.

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