



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(54) Title: ADDITIVES FOR OILS</p> <p>(57) Abstract</p> <p>One or more additives are used to modify the wax crystal growth properties of oils derived from animal or vegetable material.</p>		

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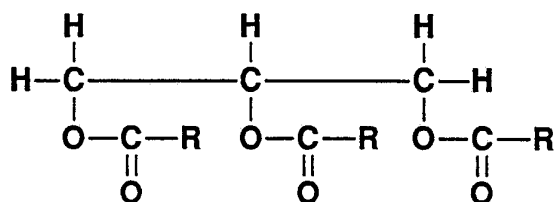
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## Additives for Oils

This invention relates to the use of wax crystal modifying additives in oils obtained from animal or vegetable material or both, or derivatives thereof.

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Oils obtained from animal or vegetable material are mainly metabolites comprising triglycerides of monocarboxylic acids, e.g. acids containing 10-25 carbon atoms and of the form:



10

where R is an aliphatic radical of 10-25 carbon atoms which may be saturated or unsaturated.

15 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.

20 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.

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

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:

30



where R<sup>1</sup> contains 5 to 23 carbon atoms, being a substantially linear saturated or unsaturated aliphatic radical and R<sup>2</sup> contains 1 to 12 carbon atoms, being a linear or branched, saturated or unsaturated, aliphatic radical. Such fuel

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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.

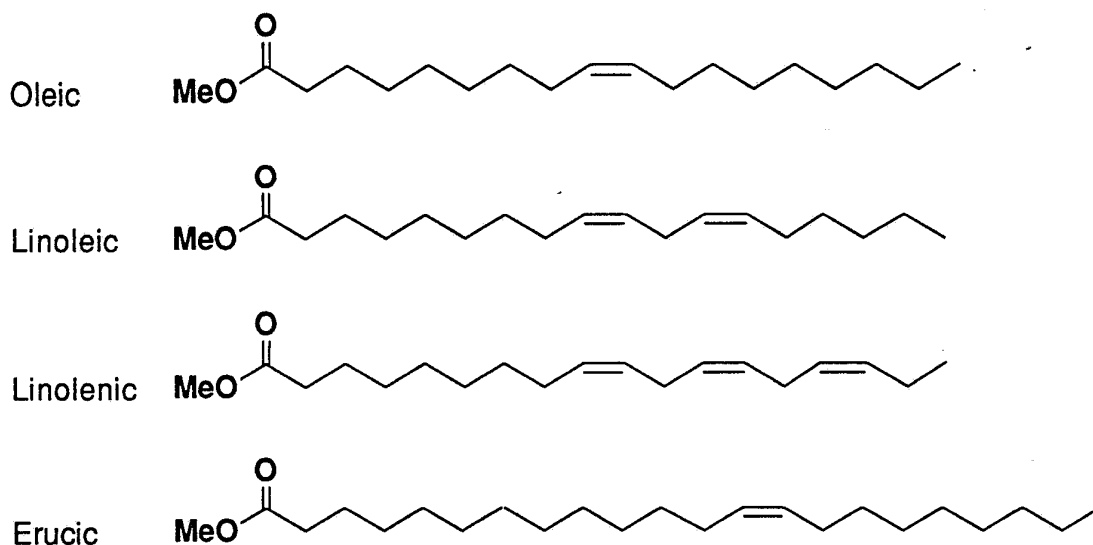
However the usefulness of such fatty acid ester compositions as diesel fuels is limited by their low temperature properties. DE-A-4,040,317 discloses that at temperatures below  $-5^{\circ}\text{C}$ , such fuels may solidify in supply lines due to inadequate filterability, and describes a process for 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.

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; UK-A-1,263,152; US-A-3,961,916; US-A-4,211,534; EP-A-153,176 and EP-A-153,177. They are sometimes referred to as "Cold Flow Additives". "Chemicals in the Oil Industry", a collection of papers edited by P H Ogden, Esq. which documents the proceedings of a Symposium organised by the Royal Society of Chemistry and held at the University of Manchester on 22-23 March 1983, describes on page 112 how certain alkylated regions of the molecular structure of such additives are believed to resemble the linear, saturated hydrocarbon chains of the heavier n-alkane molecules (paraffin wax) naturally present as minor constituents of these oils. Furthermore, by virtue of these structural similarities, such additives are believed to interfere in some way with the crystallisation of said n-alkanes into plate-like crystals, as they precipitate out of solution in the oil at low temperatures. The additives thus modify the size and shape of wax crystals and reduce the cohesive forces between the crystals and between the wax and the oil, in such a manner as to permit the oil to remain fluid at a lower temperature and to pass through coarse filters.

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 illustrated below.

Major rapeseed oil methyl ester components:



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.

This preponderance of ethylenically-unsaturated fatty acid esters provides such oils with crystallisation behaviour 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.

Surprisingly, it has now been discovered that certain additives effective as wax crystal modifying additives in mineral oils and derivatives thereof are also effective as wax crystal modifying additives in oils derived from animal or

vegetable material, despite their apparent lack of structural similarity towards ethylenically-unsaturated hydrocarbon chains.

In a first aspect therefore, the invention is a composition comprising a major proportion of an oil consisting essentially of an oil that is derived from animal or vegetable material, in admixture with a minor proportion of mineral oil cold flow additive, provided that said composition does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms.

In a preferred embodiment of the first aspect therefore, the invention is a composition comprising a major proportion of an oil consisting essentially of an oil that is derived from animal or vegetable material, in admixture with a minor proportion of an additive comprising one or more of the following:

- (i) a comb polymer
- (ii) a polyoxyalkylene ester, ester/ether or a mixture thereof
- (iii) an ethylene/unsaturated ester copolymer
- (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor
- (v) a hydrocarbon polymer, and
- (vi) sulphur carboxy compounds
- (vii) a hydrocarbylated-aromatic pour point depressant

provided that said composition does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms.

In a second aspect, the invention is the use of a mineral oil cold flow additive, provided that said additive does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms, for modifying the wax crystal growth properties of an oil that is derived from animal or vegetable material.

In a preferred embodiment of the second aspect, the invention is the use of an additive comprising one or more of the following:

- (i) a comb polymer,

- (ii) a polyoxyalkylene ester, ether, ester/ether or a mixture thereof,
- (iii) an ethylene/unsaturated ester copolymer,
- (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor,
- (v) a hydrocarbon polymer, and
- (vi) sulphur carboxy compounds.
- (vii) a hydrocarbylated-aromatic pour point depressant

provided that said additive does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms, for modifying the wax crystal growth properties of an oil that is derived from animal or vegetable material.

In a third aspect, the invention is a method of modifying the wax crystal growth properties of an oil consisting essentially of an oil that is derived from animal or vegetable material, comprising admixture with an additive as defined in the second aspect above.

The features of the invention will now be discussed in further detail.

## OILS

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.

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 50 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.

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.

Particularly preferred are oils according to this invention capable of being utilised 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. It has recently been reported that mixtures of a rapeseed ester, for example, rapeseed oil methyl ester (RME), with petroleum distillate fuels in ratios of, for example, 10:90 by volume are likely to be commercially available in the near future.

Thus, a biofuel is an oil obtained from vegetable or animal material, or both, or a derivative thereof, capable of being utilised as a fuel.

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.



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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, preferably 25 to 500 ppm, more preferably 100 to 200 ppm.

The additive or additives should be soluble in the oil to the extent of at least 1000 ppm by weight per weight of oil at ambient temperature. However, at least some of the additive may come out of solution near the cloud point of the oil in order to modify the wax crystals that form.

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.

A concentrate comprising the additive 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.

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.

## ADDITIVES

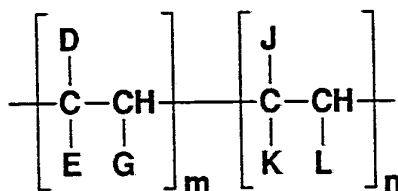
Preferred additives in accordance with the various aspects of this invention are described below.

### (i) Comb Polymers

Comb polymers are polymers in which 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).

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

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



- where
- D = R<sup>11</sup>, COOR<sup>11</sup>, OCOR<sup>11</sup>, R<sup>12</sup>COOR<sup>11</sup> or OR<sup>11</sup>
  - E = H, CH<sub>3</sub>, D or R<sup>12</sup>
  - G = H or D
  - J = H, R<sup>12</sup>, R<sup>12</sup>COOR<sup>11</sup>, or an aryl or heterocyclic group
  - K = H, COOR<sup>12</sup>, OCOR<sup>12</sup>, OR<sup>12</sup> or COOH
  - L = H, R<sup>12</sup>, COOR<sup>12</sup>, OCOR<sup>12</sup> or aryl
  - R<sup>11</sup> ≥ C<sub>10</sub> hydrocarbyl
  - R<sup>12</sup> ≥ C<sub>1</sub> hydrocarbyl

and m and n represent mole ratios, m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R<sup>11</sup> advantageously represents a

hydrocarbyl group with from 10 to 30 carbon atoms, and R<sup>12</sup> advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

The comb polymer may contain units derived from other monomers if desired or required. It is within the scope of the invention to include two or more different comb copolymers.

These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an  $\alpha$ -olefin or an unsaturated ester, for example, vinyl acetate. 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 copolymer 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, n-dodecan-1-ol, n-tetradecan-1-ol, n-hexadecan-1-ol, and n-octadecan-1-ol. The alcohols may also include up to one methyl branch per chain, for example, 1-methylpentadecan-1-ol, 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<sup>12</sup> 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<sup>12</sup> refers to the straight chain backbone segment of the alcohol.

These comb polymers may especially be fumarate or itaconate polymers and copolymers such as for example those described in European Patent Applications 153 176, 153 177 and 225 688, 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<sub>14</sub>/C<sub>16</sub> 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

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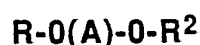
alcohols, which are preferably straight chain alcohols. When the mixture is used it is advantageously a 1:1 by weight mixture of normal C<sub>14</sub> and C<sub>16</sub> alcohols. Furthermore, mixtures of the C<sub>14</sub> ester with the mixed C<sub>14</sub>/C<sub>16</sub> ester may advantageously be used. In such mixtures, the ratio of C<sub>14</sub> to C<sub>14</sub>/C<sub>16</sub> 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 fumarate comb polymers may, for example, have a number average molecular weight in the range of 1,000 to 100,000, preferably 1,000 to 30,000, as measured by Vapour Phase Osmometry (VPO).

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.

#### (ii) Polyoxyalkylene Compounds

Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two C<sub>10</sub> to C<sub>30</sub> linear saturated 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 European Patent Publication 0 061 895 A2. Other such additives are described in United States Patent 4 491 455.

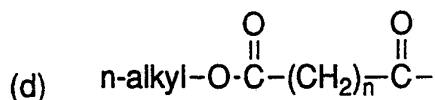
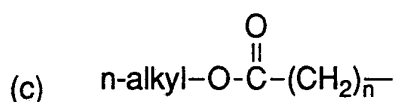
The preferred esters, ethers or ester/ethers which may be used may be structurally depicted by the formula



where R and R<sup>2</sup> are the same or different and may be

(a) n-alkyl

(b) n-alkyl-C $\begin{matrix} \text{O} \\ \parallel \end{matrix}$



n being, for example, 1 to 30, the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A 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. A may also contain nitrogen.

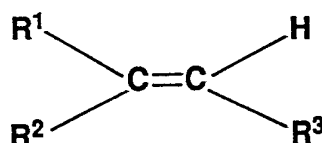
Examples of suitable glycols are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols 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.

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 important for additive performance that a major amount of the dialkyl compound is 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 (both Sanyo), and the esterified alkoxyated amines described in EP-A-117,108 and EP-A-326,356 (both Nippon Oil and Fats).

(iii) **Ethylene/Unsaturated Ester Copolymers**

Ethylene copolymer flow improvers have a polymethylene backbone divided into segments by oxyhydrocarbon side chains, i.e. ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers copolymerisable with ethylene to form the copolymers include unsaturated mono and diesters of the general formula:



wherein R<sup>1</sup> represents hydrogen or a methyl group;  
R<sup>2</sup> represents a -OOCR<sup>4</sup> or -COOR<sup>4</sup> group wherein R<sup>4</sup> represents hydrogen or a C<sub>1</sub> to C<sub>28</sub>, preferably C<sub>1</sub> to C<sub>16</sub>, more preferably a C<sub>1</sub> to C<sub>8</sub>, straight or branched chain alkyl group, provided that R<sup>4</sup> does not represent hydrogen when R<sup>2</sup> represents -COOR<sup>4</sup>; and  
R<sup>3</sup> is hydrogen or -COOR<sup>4</sup>.

The monomer, when R<sup>2</sup> and R<sup>3</sup> are hydrogen and R<sup>1</sup> is -OOCR<sup>4</sup>, includes vinyl alcohol esters of C<sub>1</sub> to C<sub>29</sub>, preferably C<sub>1</sub> to C<sub>5</sub>, monocarboxylic acids, and preferably C<sub>2</sub> to C<sub>29</sub>, more preferably C<sub>1</sub> to C<sub>5</sub> monocarboxylic acids, most preferably C<sub>2</sub> to C<sub>5</sub> monocarboxylic acids. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate and vinyl propionate being preferred. Preferably, the copolymers contain from 5 to 40 wt% of the vinyl ester, more preferably from 10 to 35 wt% vinyl ester [change to molar]. They may also be in the form of mixtures of two copolymers such as those described in US Patent 3,961,916. Preferably, number average molecular weight, as measured by vapour phase osmometry, of the copolymer is 1,000 to 10,000, more preferably 1,000 to 5,000. 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 isobutylene or diisobutylene.

Such copolymers may also be made by transesterification, or by hydrolysis and re-esterification, of an ethylene unsaturated ester copolymer to give a different ethylene unsaturated ester copolymer. For example, ethylene vinyl hexanoate

and ethylene vinyl octanoate copolymers may be made in this way, e.g. from an ethylene vinyl acetate copolymer.

**(iv) Polar Organic, Nitrogen-containing Compounds**

The oil-soluble polar nitrogen compound is either ionic or non-ionic and is capable of acting as a wax crystal growth inhibitor in fuels. It comprises for example one or more of the compounds (a) to (c) as follows:

- (a) 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 1 to 4 carboxylic acid groups or its anhydride.

Ester/amides may be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US Patent 4 211 534. Suitable amines are usually long chain C<sub>12</sub>-C<sub>40</sub> primary, secondary, tertiary or quaternary amines or mixtures thereof but shorter chain amines may be used provided the resulting nitrogen compound is oil soluble and therefore normally contains about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C<sub>8</sub> to C<sub>40</sub>, preferably C<sub>14</sub> to C<sub>24</sub>, alkyl segment.

Suitable amines include primary, secondary, tertiary or quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, and hydrogenated tallow amine. Examples of secondary amines include dioctadecyl amine and methyl-behenyl amine. Amine mixtures are also suitable such as those derived from natural materials. A preferred amine is a secondary hydrogenated tallow amine of the formula HNR<sup>1</sup>R<sup>2</sup> wherein R<sup>1</sup> and R<sup>2</sup> are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C<sub>14</sub>, 31% C<sub>16</sub>, 59% C<sub>18</sub>.

Examples of suitable carboxylic acids and their anhydrides for preparing the nitrogen compounds include 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 lactone. Generally, these acids have about 5-13 carbon

atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is 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-A-4 147 520, for example. Suitable amines may be those described above.

Other examples are condensates such as described in EP-A-327,423.

- (b) A chemical compound comprising or including a cyclic ring system, the compound carrying at least two substituents of the general formula (I) below on the ring system



where A is an aliphatic hydrocarbyl group that is optionally interrupted by one or more hetero atoms and that is straight chain or branched, and R<sup>1</sup> and R<sup>2</sup> are the same or different and each is independently a hydrocarbyl group containing 9 to 40 carbon 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.

Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

As used in this specification the term "hydrocarbyl" refers to a group having a carbon atom directly attached to the rest of the molecule and having a hydrocarbon or predominantly hydrocarbon character. Examples include hydrocarbon groups, including aliphatic (e.g. alkyl or alkenyl), alicyclic (e.g. cycloalkyl or cycloalkenyl), aromatic, and alicyclic-



substituted aromatic, and aromatic-substituted aliphatic and alicyclic groups. Aliphatic groups are advantageously saturated. These groups may contain non-hydrocarbon substituents provided their presence does not alter the predominantly hydrocarbon character of the group. Examples include keto, halo, hydroxy, nitro, cyano, alkoxy and acyl. If the hydrocarbyl group is substituted, a single (mono) substituent is preferred.

Examples of substituted hydrocarbyl groups include 2-hydroxyethyl, 3-hydroxypropyl, 4-hydroxybutyl, 2-ketopropyl, ethoxyethyl, and propoxypropyl. The groups may also or alternatively contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include, for example, nitrogen, sulphur, and, preferably, oxygen.

The cyclic ring system may include homocyclic, heterocyclic, or fused polycyclic assemblies, or a system where two or more such cyclic assemblies are joined to one another and in which the cyclic assemblies may be the same or different. Where there are two or more such cyclic assemblies, the substituents of the general formula (I) may be on the same or different assemblies, preferably on the same assembly. Preferably, the or each cyclic assembly is aromatic, more preferably a benzene ring. Most preferably, the cyclic ring system is a single benzene ring when it is preferred that the substituents are in the ortho or meta positions, which benzene ring may be optionally further substituted.

The ring atoms in the cyclic assembly or assemblies are preferably carbon atoms but may for example include one or more ring N, S or O atom, in which case or cases the compound is a heterocyclic compound.

Examples of such polycyclic assemblies include:

- (i) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;
- (ii) condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene oxide;

- (iii) rings joined "end-on" such as diphenyl;
- (iv) heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine;
- (v) non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene),  $\alpha$ -pinene, cardinene, and bornylene; and
- (vi) three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

Each hydrocarbyl group constituting R<sup>1</sup> and R<sup>2</sup> in the invention (Formula I) may for example be an alkyl or alkylene group or a mono- or poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with only two substituents of the general formula (I) and that A is a methylene group.

Examples of salts of the chemical compounds are the acetate and the hydrochloride.

The compounds may conveniently be made by reducing the corresponding amide which may be made by reacting a secondary amine with the appropriate acid chloride; and

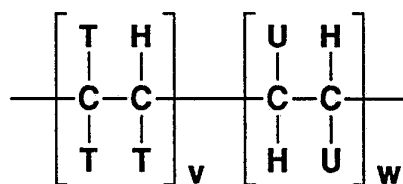
- (c) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

Specific examples include polymers such as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561; and also esters of telemer acid and alkanoloamines such as described in US-A-4,639,256; a long chain epoxide/amine reaction product which may optionally be further reacted with a polycarboxylic acid; and the reaction product of an

amine containing a branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

(v) **Hydrocarbon Polymers**

Examples are those represented by the following general formula



where T = H or R<sup>1</sup>  
 U = H, T or aryl  
 R<sup>1</sup> = C<sub>1</sub>-C<sub>30</sub> hydrocarbyl

and v and w represent mole ratios, v being within the range 1.0 to 0.0, w being within the range 0.0 to 1.0.

These polymers may be made directly from ethylenically unsaturated monomers or indirectly by hydrogenating the polymer made from monomers such as isoprene and butadiene.

Preferred hydrocarbon polymers are copolymers of ethylene and at least one  $\alpha$ -olefin, having a number average molecular weight of at least 30,000. Preferably the  $\alpha$ -olefin has at most 20 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. It is within the scope of the invention to include two or more different ethylene- $\alpha$ -olefin copolymers of this type.

The number average molecular weight of the ethylene- $\alpha$ -olefin copolymer is, as indicated above, 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- $\alpha$ -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.

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

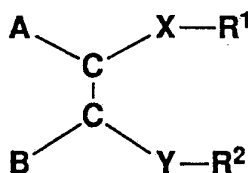
The additive composition may also comprise a further ethylene- $\alpha$ -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate  $\alpha$ -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

Examples of hydrocarbon polymers are described in WO-A-9 111 488.

#### (vi) Sulphur Carboxy Compounds

Examples are those described in EP-A-0,261,957 which describes the use of compounds of the general formula

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in which  $-\text{Y-R}^2$  is  $\text{SO}_3^{(-)(+)}\text{NR}_3^3\text{R}^2$ ,  $-\text{SO}_3^{(-)(+)}\text{HNR}_2^3\text{R}^2$ ,

$-\text{SO}_3^{(-)(+)}\text{H}_2\text{NR}_3^3\text{R}^2$ ,  $-\text{SO}_3^{(-)(+)}\text{H}_3\text{NR}^2$ ,

$-\text{SO}_2\text{NR}_3^3\text{R}^2$  or  $-\text{SO}_3\text{R}^2$ ;

$-\text{X-R}^1$  is  $-\text{Y-R}^2$  or  $-\text{CONR}_3^3\text{R}^1$ ,

$-\text{CO}_2^{(-)(+)}\text{NR}_3^3\text{R}^1$ ,  $-\text{CO}_2^{(-)(+)}\text{HNR}_2^3\text{R}^1$ ,

$-\text{R}^4\text{-COOR}_1$ ,  $-\text{NR}_3^3\text{COR}_1$ ,

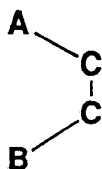
$-\text{R}^4\text{OR}_1$ ,  $-\text{R}^4\text{OCOR}_1$ ,  $-\text{R}^4, \text{R}^1$ ,

$-\text{N}(\text{COR}^3)\text{R}^1$  or  $\text{Z}^{(-)(+)}\text{NR}_3^3\text{R}^1$ ;

$-\text{Z}^{(-)}$  is  $\text{SO}_3^{(-)}$  or  $-\text{CO}_2^{(-)}$ ;

$\text{R}^1$  and  $\text{R}^2$  are alkyl, alkoxyalkyl or polyalkoxyalkyl containing at least 10 carbon atoms in the main chain;

$\text{R}^3$  is hydrocarbyl and each  $\text{R}^3$  may be the same or different and  $\text{R}^4$  is absent or is  $\text{C}_1$  to  $\text{C}_5$  alkylene and in



the carbon-carbon (C-C) bond is either a) ethylenically unsaturated when A and B may be alkyl, alkenyl or substituted hydrocarbyl groups or b) part of a cyclic structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic, it is preferred that  $\text{X-R}^1$  and  $\text{Y-R}^2$  between them contain at least three alkyl, alkoxyalkyl or polyalkoxyalkyl groups.

#### (vii) 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 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.

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.

Multicomponent additive systems may be used and the ratios of additives to be used will depend on the fuel to be treated.

## **EXAMPLES**

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

### **EXAMPLE 1**

#### **Additives**

The following additives were used:

- A: an ethylene/vinyl acetate copolymer having a vinyl acetate concentration of about 37 wt% and a number average molecular weight of about 2,700.

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- B: a 3:1 (wt:wt) mixture of additive A above and an ethylene/vinyl acetate copolymer having a vinyl acetate concentration of about 13.5 wt% and a number average molecular weight of about 5,000.
- C: a mixture containing the same compounds as B but where the wt:wt ratio is 13:1.

Number average molecular weights are as measured by Vapour Phase Osmometry (VPO).

### Test

Additives A, B and C were each dissolved in samples of the same rapeseed methyl ester fuel and the Cold Filter Plugging Point (CFPP) 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 show in the table below.

Additive	CFPP (°C) Treat Rate (ppm; ai)	
	500	1000
A	-14	-16
B	-13	-14
C	-15	-18

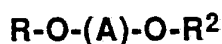
In comparison, the CFPP of the untreated fuel was -9°C. It is therefore seen that additives A, B and C each improved the filterability of the fuel as measured by the CFPP test.

**Claims:**

1. A composition comprising a major proportion of an oil consisting essentially of an oil that is derived from animal or vegetable material, in admixture with a minor proportion of a mineral oil cold flow additive, provided that said composition does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms.
  
2. A composition comprising a major proportion of an oil consisting essentially of an oil that is derived from animal or vegetable material, in admixture with a minor proportion of an additive comprising one or more of the following:
  - (i) a comb polymer
  - (ii) a polyoxyalkylene ester, ester/ether or a mixture thereof
  - (iii) an ethylene/unsaturated ester copolymer
  - (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor
  - (v) a hydrocarbon polymer, and
  - (vi) sulphur carboxy compounds
  - (vii) a hydrocarbylated-aromatic pour point depressant

provided that said composition does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms.

3. The composition of claim 2 wherein said polyoxyalkylene ester, ester/ether or mixture thereof is defined by the formula

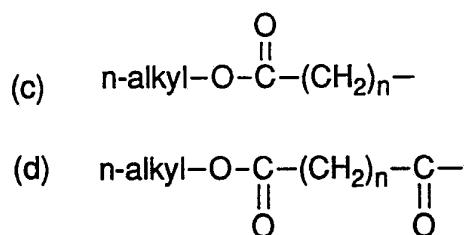


where R and R<sup>2</sup> are the same or different and may be

- (a) n-alkyl

- (b) n-alkyl-C $\begin{matrix} \text{O} \\ \parallel \end{matrix}$





where the alkyl group is linear and saturated and contains 10 to 30 carbon atoms, and

A represents a polyoxyalkylene segment of molecular weight 100-5,000 in which the alkylene group has 1-4 carbon atoms.

4. The composition of claim 2 or claim 3 wherein said polar, organic, nitrogen-containing wax crystal growth inhibitor is prepared from a hydrocarbyl acid having 1 to 4 carboxylic acid groups or its anhydride, and preferably from a benzene dicarboxylic acid or its anhydride.
5. The use of a mineral oil cold flow additive provided that said additive does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms, for modifying the wax crystal growth properties of an oil consisting essentially of an oil that is derived from animal or vegetable material.
6. The use of an additive comprising one or more of the following
  - (i) a comb polymer
  - (ii) a polyoxyalkylene ester, ester/ether or a mixture thereof
  - (iii) an ethylene/unsaturated ester copolymer
  - (iv) a polar, organic, nitrogen-containing wax crystal growth inhibitor
  - (v) a hydrocarbon polymer, and
  - (vi) sulphur carboxy compounds
  - (vii) a hydrocarbylated-aromatic pour point depressant

provided that said additive does not comprise mixtures of polymeric esters or copolymers of esters of acrylic and/or methacrylic acid derived from alcohols possessing 1 to 22 carbon atoms, for modifying the wax

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crystal growth properties of an oil consisting essentially of an oil that is derived from animal or vegetable material.

7. The composition or use of any preceding claim wherein said oil is a biofuel.
8. The composition or use of any preceding claim wherein said biofuel is a vegetable oil or derivative thereof.
9. The composition or use of claim 8 wherein said biofuel is selected from the group comprising rapeseed oil, cottonseed oil, soyabean oil, sunflower oil, olive oil, palm oil, or alkyl ester derivatives thereof.
10. The composition or use of claim 8 wherein said biofuel is rapeseed oil methyl ester.
11. The composition or use of any preceding claim wherein said biofuel comprises a mixture of vegetable oils, and/or a mixture of derivatives thereof.
12. The composition or use of any preceding claim wherein said additive comprises an ethylene/vinyl ester copolymer, or mixture of copolymers thereof.
13. A method of modifying the wax crystal growth properties of an oil consisting essentially of an oil that is derived from animal or vegetable material, comprising admixture with an additive as defined in claim 4 or claim 5.
14. A method of modifying the wax crystal growth properties of a biofuel, comprising admixture with an additive as defined in claim 4 or claim 5.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/EP 93/00471

## A. CLASSIFICATION OF SUBJECT MATTER

IPC5: C10L 1/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CLAIMS/US PATENTS, CA

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB, A, 2090613 (INSTITUT FRANCAIS DU PETROLE), 14 July 1982 (14.07.82), claim 1 --	1
A	GB, A, 2099449 (W.E. ERNER), 8 December 1982 (08.12.82), claims 6,14 --	1
P,A	WO, A1, 9211345 (HENKEL KOMMANDITGESELLSCHAFT AUF AKTIEN ET AL.), 9 July 1992 (09.07.92), claims 1, 9 -- -----	1

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&amp;" document member of the same patent family


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12 May 1993

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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

31/03/93

International application No.  
PCT/EP 93/00471

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2090613	14/07/82	DE-A, C- 3150988	05/08/82
		FR-A, B- 2497222	02/07/82
		OA-A- 6976	31/07/83
		DE-A, C- 3149170	29/07/82
		DE-A, C- 3150989	05/08/82
		FR-A, B- 2498622	30/07/82
		GB-A, B- 2090611	14/07/82
		GB-A, B- 2090612	14/07/82
		OA-A- 6975	31/07/83
		OA-A- 6982	31/08/83
		GB-A- 2099449	08/12/82
WO-A1- 9211345	09/07/92	DE-A- 4040317	25/06/92