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(54) **Use of additives in fuel compositions**

Verwendung von Zusatzstoffen in Treibstoffzusammensetzungen

Utilisation de compositions d'additifs dans un combustible

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Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description

[0001] This application is a divisional of European application No. 94 924 280.4 published as EP 0 721 492 A.

[0002] This invention relates to the use of additives for improving the cold flow properties of fuel oil, for example distillate petroleum fuel such as middle distillate fuel oil boiling within the range of 110°C to 500°C.

[0003] When fuel oils are subjected to low ambient temperatures, wax may separate out from the fuel and impair the flow properties of the oil. For example, middle distillate fuels contain wax which precipitates at low temperatures to form large waxy crystals which tend to plug the small pore openings of fuel filters. This problem is particularly acute when the fuel is a diesel fuel because the nominal apertures in the fuel filter of diesel engines are typically of diameter between about 5 and 50 microns. Additives are known in the art for overcoming the above problem and are called Flow Improvers.

[0004] Such additives may act as wax crystal modifiers when blended with waxy mineral oil by modifying the shape and size of crystals of the wax therein and reducing the adhesive forces between the crystals and between the wax and the oil to permit the oil to remain fluid at a lower temperature than in the absence of the additive.

[0005] Many additives are described in the art for improving the cold-flow properties of oils, for example in the form of oil-soluble addition products or condensates that may be polymeric or monomeric and as described, for example, in US-A-3,048,479; GB-A-1,263,152; US-A-3,961,961; and EP-A-0,261,957. Some of the above additives have been and are used commercially as Cold Flow Improvers.

[0006] The art also describes Cold Flow Improvers as being usable in combination with other additives. For example, GB- A-1,112,808 describes ethylene-vinyl acetate copolymers in combination with rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye-stabilisers, haze inhibitors, and anti-static additives.

[0007] DE-A-2 156 425 relates to middle distillate fuel oils comprising a flow-improving system containing certain pour point depressant polymers in combination with non-nitrogen-containing, oil-soluble, auxiliary, flow-improving compounds. The second component of the flow-improving system may be, inter alia, an ester.

[0008] In this invention, it has surprisingly been found that the cold flow properties of Cold Flow Improvers such as the above-described may be further enhanced by using co-additives not hitherto known in the art to exhibit cold flow improving properties.

[0009] Thus, a first aspect of the invention is the use of a co-additive selected from component (A) which comprises an oil-soluble lubricity additive comprising an ester of a dicarboxylic acid and a polyhydroxy alcohol wherein the acid has from 2 to 50 carbon atoms, the alcohol has one or more carbon atoms and is a trihydric alcohol or a diol of the formula $R^2(OH)_y$ wherein R^2 represents an unsubstituted polymethylene group having 1 to 10 carbon atoms and y represents an integer and is the number of hydroxy groups; and wherein the ester is composed only of carbon hydrogen and oxygen and has one or more free hydroxy groups;
said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver, and being to enhance the cold flow properties of the composition.

[0010] The enhancement of the cold flow performance of component (B) by component (A) according to this invention can be applied to the blending of additives into a fuel oil. Thus, a second aspect of the invention is a process for blending additives with a fuel oil comprising

(i) injecting component (B) as defined above into the fuel oil;

(ii) injecting component (A) as defined above into the fuel oil;

(iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii); and

(iv) adjusting the relative rate of injection of components (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.

[0011] In the second aspect of this invention, the fuel oil is preferably in the form of a flowing stream wherein step (i) takes places at a first station and step (ii) takes place at a second station, though the first and second stations may be co-terminous and injection be via a common injector. The process can be automated so that a sensor can carry out step (iii), e.g. by measuring the cold filter plugging point (CFPP), and the information fed via a controller to control injection of one or both of components (B) and (A).

[0012] The invention surprisingly enables less of component (B) to be used to achieve a desired cold flow improvement performance.

[0013] The features of the invention will now be discussed in further detail.
Specifications referred to hereinafter are incorporated herein by reference.

[0014] 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.

[0015] 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.

[0016] The acid, alcohol and ester characterising the lubricity additive will now be discussed in further detail as follows.

(i) Acid

The acid from which the ester is derived may be an aliphatic, saturated or unsaturated, straight or branched chain dicarboxylic acid having from 2 to 50 carbon atoms. For example, the acid may be generalised in the formula

$$R'(COOH)_2$$

where R' represents a substituted or unsubstituted polymethylene group having from 2 to 50 carbon atoms the -COOH groups optionally being substituent on different carbon atoms from one another.

(ii) Alcohol

The alcohol from which the ester is derived is a polyhydroxy alcohol being a diol, or trihydric alcohol of the formula

$$R^2(OH)_y$$

where y represents an integer and R^2 represents an unsubstituted polymethylene group having 1 to 10 carbon atoms, the -OH groups optionally being substituent on different carbon atoms from one another.

The polyhydric alcohol preferably has 2 to 5, carbon atoms in the molecule, such as glycerol.

(iii) The Esters

The esters may be used alone or as mixtures of one or more esters and are composed only of carbon, hydrogen and oxygen and have one or more free hydroxy groups. Preferably the ester has a molecular weight of 200 or greater, or has at least 10 carbon atoms, or has both.

Examples of esters of polyhydric alcohols that may be used are those where all of the hydroxy groups are esterified, those where not all of the hydroxy groups are esterified, and mixtures thereof. Specific examples are esters prepared from trihydric alcohols and one or more of the above-mentioned saturated or unsaturated dicarboxylic acids, such as glycerol diesters, e.g. glycerol dioleate. Such polyhydric esters may be prepared by esterification as described in the art and/or may be commercially available.

[0017] Examples are described in WO-PCT/EP 94/00148.

COMPONENT (B)

[0018] Ethylene copolymer flow improvers, e.g. ethylene/unsaturated ester copolymer flow improvers have a polymethylene backbone divided into segments by oxyhydrocarbon side chains.

[0019] More especially, the copolymer may comprise an ethylene copolymer having, in addition to units derived from ethylene, units of the formula

$$-CR^5R^6-CHR^7-$$

wherein R^6 represents hydrogen or a methyl group;

R^5 represents a -$OOCR^8$ or -$COOR^8$ group wherein R^8 represents hydrogen or a C_1 to C_{28}, preferably C_1 to C_9, straight or branched chain alkyl group, provided that R^8 does not represent hydrogen when R^5 represents -$COOR^8$; and R^7 is hydrogen or -$COOR^8$.

[0020] 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, but the ester is preferably one of an unsaturated alcohol with a saturated carboxylic acid. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene vinyl propionate, ethylene-vinyl hexanoate, or ethylene-vinyl octanoate copolymer is preferred. Preferably, the copolymers contain from 1 to 25, e.g. 1 to 20 mole % of the vinyl ester, more preferably from 3 to 17 mole % vinyl ester. 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.

[0021] The copolymers may be made by direct polymerisation of comonomers. 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.

[0022] Component (B) may be used with co-components such as one or more of the following:

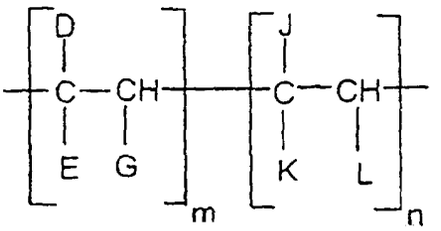
Comb Polymers

[0023] Comb polymers 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).

[0024] Generally, comb polymers have one or more long chain branches such as hydrocarbyl branches, such as oxyhydrocarbyl branches, having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branch or 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.

[0025] Advantageously, the comb polymer is a homopolymer having, or a copolymer 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, selected from for example carbon, nitrogen and oxygen, in a linear chain.

[0026] As examples of preferred comb polymers there may be mentioned those containing units of the general formula



where

D = R^{11}, $COOR^{11}$, $OCOR^{11}$, $R^{12}COOR^{11}$ or OR^{11}
E = H, CH_3, D or R^{12}
G = HorD
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}, $COOR^{12}$, $OCOR^{12}$ or aryl
$R^{11} \geq$ C_{10} hydrocarbyl
$R^{12} \geq$ C_1 hydrocarbyl

and m and n represent mole ratios, their sum being 1 and m being finite and being up to and including 1 and n being from zero to less than 1, preferably m being within the range of from 1.0 to 0.4, n being in the range of from 0 to 0.6. R^{11} advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, and R^{12} advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

[0027] 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.

[0028] These comb polymers may be copolymers of maleic anhydride or fumaric acid and another ethylenically unsaturated monomer, e.g. an α-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.

[0029] 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^{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.

[0030] 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.

[0031] 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 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).

[0032] 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.

[0033] Other examples of comb polymers are hydrocarbon polymers such as copolymers of ethylene and at least one α-olefin, preferably the α-olefin 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. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

Linear Group Compounds

[0034] Such compounds comprise a compound in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected to a non-polymeric organic residue to provide at least one linear chain of atoms that includes the carbon atoms of said alkyl groups and one or more non-terminal oxygen atoms.

[0035] By "substantially linear" is meant that the alkyl group is preferably straight chain, but that essentially straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group may be used.

[0036] Preferably, the compound has a least two of said alkyl groups when the linear chain may include the carbon atoms of more than one of said alkyl groups. When the compound has at least three of said alkyl groups, there may be more than one of such linear chains, which chains may overlap. The linear chain or chains may provide part of a linking group between any two such alkyl groups in the compound.

[0037] The oxygen atom or atoms are preferably directly interposed between carbon atoms in the chain and may, for example, be provided in the form of a mono- or poly-oxyalkylene group, said oxyalkylene group preferably having 2 to 4 carbon atoms, examples being oxyethylene and oxypropylene.

[0038] As indicated the chain or chains include carbon and oxygen atoms. They may also include other hetero-atoms such as nitrogen atoms.

[0039] The compound may be an ester where the alkyl groups are connected to the remainder of the compound as -O-CO n alkyl, or -CO-O n alkyl groups, in the former the alkyl groups being derived from an acid and the remainder of the compound being derived from a polyhydric alcohol and in the latter the alkyl groups being derived from an alcohol and the remainder of the compound being derived from a polycarboxylic acid. Also, the compound may be an ester where the alkyl groups are connected to the remainder of the compound as —O—n—alkyl groups. The compound may be both an ester and an ether or it may contain different ester groups.

[0040] Examples include polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those con-

taining 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 alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms, as described in EP-A-61 895 and in U.S. Patent No. 4,491,455.

[0041] The preferred esters, ethers or ester/ethers which may be used may be structurally depicted by the formula

$$R^{23}OBOR^{24}$$

where R^{23} and R^{24} are the same or different and may be

(a) n-alkyl-
(b) n-alkyl-CO-
(c) n-alkyl-OCO-(CH_2)n-
(d) n-alkyl-OCO-$(CH_2)_n$CO-

n being, for example, 1 to 34, the alkyl group being linear and containing from 10 to 30 carbon atoms, and B representing the polyalkylene segment of the glycol in which the alkylene group has from 1 to 4 carbon atoms, for example, 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 tolerated but it is preferred that the glycol should be substantially linear. B may also contain nitrogen.

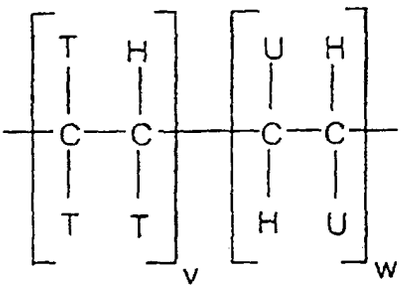
[0042] Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10 to 30 carbon atoms are useful for reacting with the glycols to form the ester additives, it being preferred to use C_{18} to C_{24} fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

[0043] Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred when the petroleum based component is a narrow boiling distillate, when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for active 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.

[0044] Examples of other compounds in this general category are those described in Japanese Patent Publication Nos. 2-51477 and 3-34790, and EP-A-117,108 and EP-A-326,356, and cyclic esterified ethoxylates such as described EP-A-356,256.

Hydrocarbon Polymers

[0045] Examples are those represented by the following general formula



where

T = H or R^1
U = H, T or aryl
R^1 = C_{1-30} 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.

[0046] These polymers may be made directly from ethylenically unsaturated monomers or indirectly by hydrogenating

the polymer made from monomers such as isoprene and butadiene.

[0047] Preferred hydrocarbon polymers are copolymers of ethylene and at least one α-olefin, having a number average molecular weight of at least 30,000. Preferably the α-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 α-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-α-olefin copolymers of this type.

[0048] The number average molecular weight of the ethylene-α-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.

[0049] 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%.

[0050] Preferred ethylene-α-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.

[0051] 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.

[0052] The additive composition may also comprise a further 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.

[0053] Examples of hydrocarbon polymers are described in WO-A-9 111 488.

Polar Compounds

[0054] Such compounds comprise an oil-soluble polar nitrogen compound carrying one or more, preferably two or more, substituents of the formula $=NR^1$, where R^1 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 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 (i) to (iii) as follows:

(i) 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, the substituent (s) of formula $=NR^1$ being of the formula $-NR^1R^2$ where R^1 is defined as above and R^2 represents hydrogen or R^1, provided that R^1 and R^2 may be the same of 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 4 211 534. Suitable amines are usually long chain C_{12}-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 and therefore normally contains 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 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 dioctacedyl 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^1R^2 wherein R^1 and R^2 are alkyl groups derived from hydrogenated tallow fat composed of approximately 4% C_{14}, 31 % C_{16}, 59% C_{18}.

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 spirobislactone. Generally, these acids have about 5-13 carbon atoms in the cyclic moiety. Preferred acids useful in the present invention are benzene dicar-

boxylic 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.

(ii) 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

$$-A-NR^1R^2 \qquad (I)$$

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^1 and R^2 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

(a) condensed benzene structures such as naphthalene, anthracene, phenanthrene, and pyrene;

(b) condensed ring structures where none of or not all of the rings are benzene such as azulene, indene, hydroindene, fluorene, and diphenylene oxides:

(c) rings joined "end-on" such as diphenyl;

(d) heterocyclic compounds such as quinoline, indole, 2:3 dihydroindole, benzofuran, coumarin, isocoumarin, benzothiophen, carbazole and thiodiphenylamine;

(e) non-aromatic or partially saturated ring systems such as decalin (i.e. decahydronaphthalene), α-pinene, cardinene, and bornylene; and

(f) three-dimensional structures such as norbornene, bicycloheptane (i.e. norbornane), bicyclooctane, and bicyclooctene.

Each hydrocarbyl group constituting R^1 and R^2 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

(iii) 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; and the reaction product of an amine containing a branched carboxylic acid ester, an episode and a monocarboxylic acid polyester such as described in US-A4,631,071.

Sulphur Carboxy Compounds

[0055] Examples are those described in EP-A-0,261,957.

FUEL OIL

[0056] The fuel oil is suitably a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of about 110°C to about 500°C, e.g. 150° to about 400°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or 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 fuel, diesel fuels, heating oil and heavy fuel oils. The heating oil may be a straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt%, of vacuum gas oil or cracked gas oils or of both.

[0057] The fuel oil may be animal, vegetable or mineral oil and may also be synthetic. It may also contain additives other than those mentioned hereinbefore.

[0058] The concentration of the additive combination in the oil may for example be in the range of 1 to 5,000 ppm of additive (active ingredient) by weight per weight of fuel, 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.

[0059] The additive should be soluble in the oil to the extent of at least 1000 ppm by 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.

[0060] Concentrates 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 and heater oil; aromatic hydrocarbon containing aromatic fractions (e.g. Solvesso (trade name)); and paraffinic hydrocarbons such as hexane, pentane and isoparaffins, and includes mixtures of the above. The carrier liquid must, of course, be selected having regard to its compatibility with the additive and with the fuel.

[0061] The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If others 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. Examples of other additives include antioxidants, corrosion inhibitors, dehazers, metal deactivators, cosolvents, package compatibilisers, reodorants, antistatic additives (conductivity improvers), biocides, dyes, smoke reducers, catalyst life enhancers, power boosters, additives for fuel economy, demulsifiers, and spray modifiers.

EXAMPLES

[0062] The following examples illustrate the invention.

Additives

[0063] The following additives were used, identified by their preceding reference codes:

B2: an ethylene-vinyl acetate copolymer of number average molecular weight 5,000 as measured by GPC and

containing about 13.5% by weight of vinyl acetate.

A5: an ester obtained by reacting dilinoleic acid (a C_{36} dimer acid) with ethylene glycol and neutralising acid groups with methanol, as described in US-A-3,287,273.

Fuel

[0064] The following fuel was used, characterised as follows:

IBP	207
10%	236
20%	248
50%	281
70%	305
90%	343
FBP	374
CP	2
CFPP	-4
SFPP	0

KEY

[0065]

- All figures are in °C
- Distillation characteristics are measured according to ASTM D-86 (IBP and FBP are initial and final boiling points respectively)
- CP is Cloud Point measured according to IP 219/82
- CFPP is Cold Filter Plugging Point and SFPP is Simulated Filter Plugging Point (see below under "TESTS" for further details)

Tests

[0066] Additives were dissolved in the fuels and the following tests performed on fuel treated with additives to measure the following in order to assess the effectiveness of the additives tested as filterability improvers in distillate fuels.

Simulated Filter Plugging Point (SFPP)

[0067] The test was carried out by the procedure substantially as described in EP-A-0,403,097 and is a variation of the CFPP test.

The Cold Filter Plugging Point Test (or CFPP Test)

[0068] The test which is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285, is designed to correlate with the cold flow of a middle distillate in automotive diesels.

[0069] In brief, a sample of the oil to be tested (40 ml) is cooled in a bath which is maintained at about -34°C to give non-linear cooling at about 1°C/min. Periodically (at each one degree centigrade starting from above the cloud point), the cooled oil tested for its ability to flow through a fine screen in a prescribed time period using a test device which is a pipette to whose lower end is attached an inverted funnel which is positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area defined by a 12 millimetre diameter. The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml of oil. After each successful passage, the oil is returned immediately to the CFPP tube. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds, the temperature at which failure occurs being reported as the CFPP temperature.

Results

KEY

[0070]

- ΔSFPP and ΔCFPP represent the difference between the SFPP (or CFPP) of the base fuel and that of the treated fuel
- The figures under the component codes are treat rates of active ingredient in parts per million per weight of fuel
- * represent results for additive combination of the invention
- a dash means that no readings were taken

B2	A5	ΔCFPP	ΔSFPP
60		3	0
100		1.5	0
		0.5	1
	100	3.5	0
60	40	7	3*

[0071] The results show that substituting part of the 'B' component with an 'A' component either enhances or does not deleteriously effect the filterability of the fuel. Also, they show that a filterability target can be met by the inventive combinations using less of the 'B' component, noting that the 'A' component itself provides advantageous properties.

[0072] The additive combinations of the invention may also be effective in reducing the tendency of wax in the fuel to settle (i.e. they may be wax anti-settling additives) and may exhibit activity in slow cooling tests such as the Extended Programmed Cooling Test (XPCT) which is known in the art.

Claims

1. The use of a co-additive (A) which comprises an oil soluble lubricity additive comprising an ester of a dicarboxylic acid and a polyhydroxyalcohol wherein the acid has from 2 to 50 carbon atoms, the alcohol has one or more carbon atoms and is a trihydric alcohol or a diol of the formula $R^2(OH)_y$ wherein R^2 represents an unsubstituted polymethylene group having 1 to 10 carbon atoms and y represents an integer and is the number of hydroxy groups; and wherein the ester is composed only of carbon, hydrogen and oxygen and has one or more free hydroxy groups; said use being in a composition comprising a major proportion of a fuel oil and a minor proportion of component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver, and being to enhance the cold flow properties of the composition.

2. The use of claim 1 wherein the lubricity additive comprises the ester of an aliphatic, saturated or unsaturated, straight or branched chain dicarboxylic acid.

3. The use of any of the preceding claims wherein the lubricity additive comprises the ester of a dicarboxylic acid of the formula:

$$R'(COOH)_2$$

wherein R' represents a substituted or unsubstituted polymethylene group having from 2 to 50 carbon atoms.

4. The use of any of the preceding claims wherein the lubricity additive comprises the ester of a trihydric alcohol.

5. The use of claim 4 wherein the trihydric alcohol is glycerol.

6. The use of any of claims 1 to 3 wherein the lubricity additive comprises the ester of a diol.

7. The use of claim 6 wherein the lubricity additive comprises the ester obtained by reacting dilinoleic acid with eth-

ylene glycol and neutralising acid groups with methanol.

8. The use of any of the preceding claims wherein the lubricity additive comprises an ester having a molecular weight of 200 or greater.

9. The use of any of the preceding claims wherein component (B) comprises an ethylene/unsaturated ester copolymer.

10. The use of claim 9 wherein the unsaturated ester is of an unsaturated alcohol with a saturated carboxylic acid.

11. The use of any of the preceding claims additionally comprising, as a co-additive, an oil-soluble polar nitrogen compound carrying one or more substituents of the formula

$$-NR^1-,$$

where R^1 represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents is optionally in the form of a cation derived thereform.

12. The use of any of the preceding claims wherein the fuel oil is a middle distillate fuel oil.

13. The use of the preceding claims wherein the total concentration of components (A) and (B) in the fuel oil is in the range 25 to 500ppm of active ingredient by weight per weight of fuel oil.

14. A fuel oil composition comprising a major proportion of a fuel oil and a combination of:

a component (A) which comprises an oil soluble lubricity additive, comprising an ester of a dicarboxylic acid and a polyhydroxyalcohol wherein the acid has from 2 to 50 carbon atoms, the alcohol has one or more carbon atoms and is a trihydric alcohol or a diol of the formula $R^2(OH)_y$ wherein R^2 represents an unsubstituted polymethylene group having 1 to 10 carbon atoms and y represents an integer and is the number of hydroxy groups; and wherein the ester is composed only of carbon, hydrogen and oxygen and has one or more free hydroxy groups; and a component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver; and
optionally other additives.

15. An additive concentrate containing:

a component (A) which comprises an oil soluble lubricity additive, comprising an ester of dicarboxylic acid and a polyhydroxyalcohol wherein the acid has from 2 to 50 carbon atoms, the alcohol has one or more carbon atoms and is a trihydric alcohol or a diol of the formula $R^2(OH)_y$ wherein R^2 represents an unsubstituted polymethylene group having 1 to 10 carbon atoms and y represents an integer and is the number of hydroxy groups; and wherein the ester is composed only of carbon, hydrogen and oxygen and has one or more free hydroxy groups; and a component (B) which comprises a cold flow improver additive comprising a copolymeric ethylene flow improver; and
optionally other additives.

16. The composition of claim 14 or claim 15 wherein the lubricity additive comprises the ester of an aliphatic, saturated or unsaturated, straight or branched chain dicarboxylic acid.

17. The composition of any of claims 14 to 16 wherein the lubricity additive comprises the ester of a dicarboxylic acid of the formula

$$R'(COOH)_2$$

wherein R' represents a substituted or unsubstituted polymethylene group having 2 to 50 carbon atoms.

18. The composition of any of claims 14 to 17 wherein the lubricity additive comprises the ester of a trihydric alcohol.

19. The composition of claim 18 wherein the trihydric alcohol is glycerol.

20. The composition of any of claims 14 to 17 wherein the lubricity additive comprises the ester of a diol.

21. The composition of claim 20 wherein the lubricity additive comprises the ester obtained by reacting dilinoleic acid with ethylene glycol and neutralising acid groups with methanol.

22. The composition of any of claims 14 to 21 wherein the lubricity additive comprises an ester having a molecular weight of 200 or greater.

23. The composition of any of claims 14 to 22 wherein component (B) comprises an ethylene/unsaturated ester copolymer.

24. The composition of claim 23 wherein the unsaturated ester is of an unsaturated alcohol with a saturated carboxylic acid.

25. The composition of any of claims 14 to 24 additionally comprising, as a co-additive, an oil-soluble polar nitrogen compound carrying one or more substituents of the formula

$$- NR^1 -,$$

where R^1 represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents is optionally in the form of a cation derived therefrom.

26. The composition of claim 14, or any of claims 16 to 25 when dependent on claim 14, wherein the fuel oil is a middle distillate fuel oil.

27. The composition of claim 14, or of any of claims 16 to 26 when dependent on claim 14, wherein the total concentration of components (A) and (B) in the fuel oil is in the range 25 to 500 ppm of active ingredient by weight per weight of fuel oil.

28. A process for blending additives with a fuel oil comprising:

(i) injecting component (B) as defined in claim 1 into the fuel oil;
(ii) injecting component (A) as defined in claim 1 into the fuel oil;
(iii) measuring the cold flow properties of the fuel oil after the injections of steps (i) and (ii): and
(iv) adjusting the relative rates of injection component (B) and (A) and thereby their relative proportions to take account of the results of step (iii) and to provide desired cold flow properties in the fuel oil.

29. The process of claim 28 wherein the fuel oil comprises a flowing steam thereof, step (i) taking place at a first station and step (ii) taking place at a second station.

30. The process of claim 28 or 29 wherein a sensor carries out step (iii) and information is fed via a controller to control injection of one or both of components (B) and (A).

Patentansprüche

1. Verwendung eines Co-Additivs (A), das ein öllösliches Schmieradditiv umfasst, das einen Ester einer Dicarbonsäure und eines Polyhydroxyalkohols umfasst, bei dem die Säure 2 bis 50 Kohlenstoffatome aufweist, der Alkohol ein oder mehrere Kohlenstoffatome aufweist und ein dreiwertiger Alkohol oder ein Diol der Formel $R^2(OH)_y$ ist, in der R^2 eine unsubstituierte Polymethylengruppe darstellt, die 1 bis 10 Kohlenstoffatome aufweist und y eine ganze Zahl und die Anzahl der Hydroxylgruppen darstellt, und bei dem der Ester nur aus Kohlenstoff, Wasserstoff und Sauerstoff zusammengesetzt ist und eine oder mehrere freie Hydroxygruppen aufweist, wobei die Verwendung in einer Zusammensetzung erfolgt, die einen größeren Anteil eines Brennstofföls und einen kleineren Anteil einer Komponente (B) umfasst, die ein Kaltfließverbessereradditiv umfasst, das einen copolymeren Ethylen-Fließ-verbesserer umfasst und vorhanden ist, um die Kaltfließeigenschaften der Zusammensetzung zu verstärken.

2. Verwendung nach Anspruch 1, bei der das Schmieradditiv den Ester einer aliphatischen, gesättigten oder ungesättigten, geradkettigen oder verzweigtkettigen Dicarbonsäure umfasst.

3. Verwendung nach einem der vorhergehenden Ansprüche, bei dem das Schmieradditiv den Ester einer Dicarbonsäure der Formel:

$$R'(COOH)_2$$

umfasst, in der R' eine substituierte oder unsubstituierte Polymethylengruppe darstellt, die 2 bis 50 Kohlenstoffatome aufweist.

4. Verwendung nach einem der vorhergehenden Ansprüche, bei der das Schmieradditiv den Ester eines dreiwertigen Alkohols umfasst.

5. Verwendung nach Anspruch 4, bei der der dreiwertige Alkohol Glycerin ist.

6. Verwendung nach einem der Ansprüche 1 bis 3, bei der das Schmieradditiv den Ester eines Diols umfasst.

7. Verwendung nach Anspruch 6, bei dem das Schmieradditiv den Ester umfasst, der durch Umsetzung von Dilinolsäure mit Ethylenglykol und Neutralisation der Säuregruppen mit Methanol erhalten wird.

8. Verwendung nach einem der vorhergehenden Ansprüche, bei der das Schmieradditiv einen Ester umfasst, der ein Molekulargewicht von 200 oder größer aufweist.

9. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Komponente (B) ein Ethylen/ungesättigter Ester-Copolymer umfasst.

10. Verwendung nach Anspruch 9, bei der der ungesättigte Ester aus einem ungesättigten Alkohol mit einer gesättigten Carbonsäure ist.

11. Verwendung nach einem der vorhergehenden Ansprüche, die zusätzlich als ein Co-Additiv eine öllösliche, polare Stickstoffverbindung umfasst, die einen oder mehrere Substituenten der Formel

$$-NR^1-$$

trägt, in der R^1 eine Kohlenwasserstoffgruppe darstellt, die 8 bis 40 Kohlenstoffatome enthält, wobei der Substituent oder einer oder mehrere der Substituenten gegebenenfalls in Form eines davon abgeleiteten Kations vorliegt.

12. Verwendung nach einem der vorhergehenden Ansprüche, bei der das Brennstofföl ein Mitteldestillatbrennstofföl ist.

13. Verwendung einer der vorhergehenden Ansprüche, bei der die Gesamtkonzentration der Komponenten (A) und (B) im Brennstofföl im Bereich von 25 bis 500 ppm an wirksamen Bestand teil liegt, bezogen auf das Gewicht, pro Gewicht Brennstofföl.

14. Brennstoffölzusammensetzung, die einen größeren Anteil eines Brennstofföls und eine Kombination:

einer Komponente (A), die ein öllösliches Schmieradditiv umfasst, das einen Ester einer Dicarbonsäure und eines Polyhydroxyalkohols umfasst, bei dem die Säure 2 bis 50 Kohlenstoffatome aufweist, der Alkohol eine oder mehrere Kohlenstoffatome aufweist und ein dreiwertiger Alkohol oder ein Diol der Formel $R^2(OH)_y$ ist, in der R^2 eine unsubstituierte Polymethylengruppe darstellt, die 1 bis 10 Kohlenstoffatome aufweist, und y eine ganze Zahl darstellt und die Anzahl der Hydroxygruppen ist, und bei dem der Ester nur aus Kohlenstoff, Wasserstoff und Sauerstoff zusammengesetzt ist und eine oder mehrere freie Hydroxygruppen aufweist, und einer Komponente (B), die ein Kaltfließverbessereradditiv umfasst, das einen copolymeren Ethylenkaltfließverbesserer umfasst, und

gegebenenfalls anderen Additiven umfasst.

15. Additivkonzentrat, das:

eine Komponente (A), die ein öllösliches Schmieradditiv umfasst, das einen Ester einer Dicarbonsäure und eines Polyhydroxyalkohols umfasst, bei dem die Säure 2 bis 50 Kohlenstoffatome aufweist, der Alkohol ein oder mehrere Kohlenstoffatome aufweist und ein dreiwertiger Alkohol oder ein Diol der Formel $R^2(OH)_y$ ist, bei der R^2 eine unsubstituierte Polymethylengruppe darstellt, die 1 bis 10 Kohlenstoffatome aufweist, und y eine ganze Zahl darstellt und die Anzahl der Hydroxygruppen ist, und bei dem der Ester nur aus Kohlenstoff, Wasserstoff und Sauerstoff zusammengesetzt ist und eine oder mehrere freie Hydroxygruppen aufweist, und eine Komponente (B), die ein Kaltfließverbessereradditiv umfasst, das einen copolymeren Ethylenklatfließverbesserer umfasst, und

gegebenenfalls andere Additive umfasst.

16. Zusammensetzung nach Anspruch 14 oder 15, bei der das Schmieradditiv den Ester einer aliphatischen, gesättigten oder ungesättigten, geradkettigen oder verzweigtkettigen Dicarbonsäure umfasst.

17. Zusammensetzung nach einem der Ansprüche 14 bis 16, bei der das Schmieradditiv den Ester einer Dicarbonsäure der Formel

$$R'(COOH)_2$$

umfasst, in der R' eine substituierte oder unsubstituierte Polymethylengruppe darstellt, die 2 bis 50 Kohlenstoffatome aufweist.

18. Zusammensetzung nach einem der Ansprüche 14 bis 17, bei der das Schmieradditiv den Ester eines dreiwertigen Alkohols umfasst.

19. Zusammensetzung nach Anspruch 18, bei der der dreiwertige Alkohol Glycerin ist.

20. Zusammensetzung nach einem der Ansprüche 14 bis 17, bei der das Schmieradditiv den Ester eines Diols umfasst.

21. Zusammensetzung nach Anspruch 20, bei der das Schmieradditiv den Ester umfasst, der durch Umsetzung von Dilinolsäure mit Ethylenglykol und Neutralisation der Säuregruppen mit Methanol erhalten wird.

22. Zusammensetzung nach einem der Ansprüche 14 bis 21, bei der das Schmieradditiv einen Ester umfasst, der ein Molekulargewicht von 200 oder größer aufweist.

23. Zusammensetzung nach einem der Ansprüche 14 bis 22, bei der die Komponente (B) ein Ethylen/ungesättigter Ester-Copolymer umfasst.

24. Zusammensetzung nach Anspruch 23, bei der der ungesättigte Ester aus einem ungesättigten Alkohol mit einer gesättigten Carbonsäure ist.

25. Zusammensetzung nach einem der Ansprüche 14 bis 24, die zusätzlich als ein Co-Additiv eine öllösliche polare Stickstoffverbindung umfasst, die einen oder mehrere Substituenten der Formel

$$-NR^1-$$

trägt, in der R^1 eine Kohlenwasserstoffgruppe darstellt, die 8 bis 40 Kohlenstoffatome enthält, wobei der Substituent oder einer oder mehrere der Substituenten gegebenenfalls in Form eines davon abgeleiteten Kations vorliegt.

26. Zusammensetzung nach Anspruch 14 oder einem der Ansprüche 16 bis 25, falls abhängig von Anspruch 14, bei der das Brennstofföl ein Mitteldestillatbrennstofföl ist.

27. Zusammensetzung nach Anspruch 14 oder einem der Ansprüche 16 bis 26, falls abhängig von Anspruch 14, bei der die Gesamtkonzentration der Komponenten (A) und (B) im Brennstofföl im Bereich von 25 bis 500 ppm an wirksamen Bestandteil liegt, pro Gewicht des Brennstofföls.

28. Verfahren zur Mischung von Additiven mit einem Brennstofföl, das:

(i) Einspritzen von Komponente (B), die wie in Anspruch 1 definiert ist, in das Brennstofföl;

(ii) Einspritzen von Komponente (A), die wie in Anspruch 1 definiert ist, in das Brennstofföl;

(iii) Vermessen der Kaltfließeigenschaften des Brennstofföls nach dem Einspritzen der Schritte (i) und (ii) und

(iv) Einstellen der relativen Einspritzraten der Komponenten (B) und (A) und dadurch von deren relativen Anteilen umfasst, um die Ergebnisse des Schrittes (iii) zu berücksichtigen und die gewünschten Kaltfließeigenschaften im Brennstofföl bereitzustellen,

29. Verfahren nach Anspruch 28, bei dem das Brennstofföl einen fließenden Dampf desselben umfasst, Schritt (i) in einer ersten Station stattfindet und Schritt (ii) in einer zweiten Station stattfindet.

30. Verfahren nach Anspruch 28 oder 29, bei dem ein Sensor Schritt (iii) durchführt und Information über ein Steuergerät zugeführt wird, um das Einspritzen von einer oder beiden Komponenten (B) und (A) zu regeln.

Revendications

1. Utilisation d'un co-additif (A) qui comprend un additif lubrifiant, soluble dans l'huile, comprenant un ester d'un acide dicarboxylique et d'un alcool polyhydroxylique, dans laquelle l'acide a 2 à 50 atomes de carbone, l'alcool a un ou plusieurs atomes de carbone et est un alcool trihydroxylique ou un diol de formule $R^2(OH)_y$ dans laquelle R^2 représente un groupe polyméthyle non substitué ayant 1 à 10 atomes de carbone et y représente un nombre entier et est le nombre de groupes hydroxy ; et dans laquelle l'ester est constitué seulement de carbone, d'hydrogène et d'oxygène et possède un ou plusieurs groupes hydroxy libres ; ladite utilisation étant l'utilisation dans une composition comprenant une proportion dominante de fuel-oil et une petite proportion du constituant (B) qui comprend un additif améliorant l'écoulement à froid, comprenant un agent améliorant l'écoulement à froid à base d'éthylène copolymère, destiné à améliorer les propriétés d'écoulement à froid de la composition.

2. Utilisation suivant la revendication 1, dans laquelle l'additif lubrifiant comprend l'ester d'un acide dicarboxylique aliphatique à chaîne droite ou ramifiée, saturé ou insaturé.

3. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle l'additif lubrifiant comprend l'ester d'un acide dicarboxylique de formule

$$R'(COOH)_2$$

dans laquelle R' représente un groupe polyméthylène, substitué ou non substitué, ayant 2 à 50 atomes de carbone.

4. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle l'additif lubrifiant comprend l'ester d'un alcool trihydroxylique.

5. Utilisation suivant la revendication 4, dans laquelle l'alcool trihydroxylique est le glycérol.

6. Utilisation suivant l'une quelconque des revendications 1 à 3, dans laquelle l'additif lubrifiant comprend l'ester d'un diol.

7. Utilisation suivant la revendication 6, dans laquelle l'additif lubrifiant comprend l'ester obtenu en faisant réagir de l'acide dilinoléique avec de l'éthylèneglycol et en neutralisant les groupes acides avec du méthanol.

8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle l'additif lubrifiant comprend un

ester ayant un poids moléculaire égal ou supérieur à 200.

9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le constituant (B) comprend un copolymère éthylène/ester insaturé.

10. Utilisation suivant la revendication 9, dans laquelle l'ester insaturé est un ester d'un alcool insaturé avec un acide carboxylique saturé.

11. Utilisation suivant l'une quelconque des revendications précédentes, comprenant en outre, comme co-additif, un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule

$$-NR^1-,$$

dans laquelle R^1 représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, ce substituant ou bien un ou plusieurs de ces substituants étant facultativement sous forme d'un cation qui en est dérivé.

12. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le fuel-oil est fuel-oil distillé moyen.

13. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la concentration totale des constituants (A) et (B) dans le fuel-oil est comprise dans l'intervalle de 25 à 500 ppm d'ingrédient actif en poids par poids de fuel-oil.

14. Composition de fuel-oil comprenant une proportion dominante d'un fuel-oil et une association :

d'un constituant (A) qui comprend un additif lubrifiant, soluble dans l'huile, comprenant un ester d'un acide dicarboxylique et d'un alcool polyhydroxylique, dans laquelle l'acide a 2 à 50 atomes de carbone, l'alcool a un ou plusieurs atomes de carbone et est un alcool trihydroxylique ou diol de formule $R^2(OH)_y$ dans laquelle R^2 représente un groupe polyméthylène non substitué ayant 1 à 10 atomes de carbone et y représente un nombre entier et est le nombre de groupes hydroxy ; et dans lequel l'ester est constitué seulement de carbone, d'hydrogène et d'oxygène et possède un ou plusieurs groupes hydroxy libres ; et
d'un constituant (B) qui comprend un additif améliorant l'écoulement à froid, comprenant un agent améliorant l'écoulement à base d'éthylène copolymère ; et
facultativement, d'autres additifs.

15. Concentré d'additifs contenant :

un constituant (A) qui comprend un additif lubrifiant, soluble dans l'huile, comprenant un ester d'un acide dicarboxylique et d'un alcool polyhydroxylique dans lequel l'acide a 2 à 50 atomes de carbone, l'alcool a un ou plusieurs atomes de carbone et est un alcool trihydroxylique ou un diol de formule $R^2(OH)_y$ dans laquelle R^2 représente un groupe polyméthylène non substitué ayant 1 à 10 atomes de carbone et y représente un nombre entier et est le nombre de groupes hydroxy ; et dans lequel l'ester est constitué seulement de carbone, d'hydrogène et d'oxygène et possède un ou plusieurs groupes hydroxy libres ; et
un constituant (B) qui comprend un additif améliorant l'écoulement à froid, comprenant un agent améliorant l'écoulement à base d'éthylène copolymère ; et
facultativement, d'autres additifs.

16. Composition suivant la revendication 14 ou la revendication 15, dans laquelle l'additif lubrifiant comprend l'ester d'un acide dicarboxylique aliphatique, à chaîne droite ou ramifiée, saturé ou insaturé.

17. Composition suivant l'une quelconque des revendications 14 à 16, dans laquelle l'additif lubrifiant comprend l'ester d'un acide dicarboxylique de formule

$$R'(COOH)_2$$

dans laquelle R' représente un groupe polyméthylène, substitué ou non substitué, ayant 2 à 50 atomes de carbone.

18. Composition suivant l'une quelconque des revendications 14 à 17, dans laquelle l'additif lubrifiant comprend l'ester d'un alcool trihydroxylique.

19. Composition suivant la revendication 18, dans laquelle l'alcool trihydroxylique est le glycérol.

20. Composition suivant l'une quelconque des revendications 14 à 17, dans laquelle l'additif lubrifiant comprend l'ester d'un diol.

21. Composition suivant la revendication 20, dans laquelle l'additif lubrifiant comprend l'ester obtenu en faisant réagir de l'acide dilinoléique avec de l'éthylèneglycol et en neutralisant les groupes acides avec du méthanol.

22. Composition suivant l'une quelconque des revendications 14 à 21, dans laquelle l'additif lubrifiant comprend un ester ayant un poids moléculaire égal ou supérieur à 200.

23. Composition suivant l'une quelconque des revendications 14 à 22, dans laquelle le constituant (B) comprend un copolymère éthylène/ester insaturé.

24. Composition suivant la revendication 23, dans laquelle l'ester insaturé est un ester d'un alcool insaturé avec un acide carboxylique saturé.

25. Composition suivant l'une quelconque des revendications 14 à 24, comprenant en outre, comme coadditif, un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule

$$-NR^1-,$$

dans laquelle R^1 représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, ce substituant ou bien un ou plusieurs de ces substituants étant facultativement sous forme d'un cation qui en est dérivé.

26. Composition suivant la revendication 14, ou suivant l'une quelconque des revendications 16 à 25 lorsqu'elle dépend de la revendication 14, dans laquelle le fuel-oil est un fuel-oil distillé moyen.

27. Composition suivant la revendication 14, ou suivant l'une quelconque des revendications 16 à 26 lorsqu'elle dépend de la revendication 14, dans laquelle la concentration totale des constituants (A) et (B) dans le fuel-oil est comprise dans l'intervalle de 25 à 500 ppm d'ingrédient actif en poids par poids de fuel-oil.

28. Procédé pour mélanger des additifs à un fuel-oil, comprenant les étapes consistant :

(i) à injecter le constituant (B) tel que défini dans la revendication 1 dans le fuel-oil ;
(ii) à injecter le constituant (A) tel que défini dans la revendication 1 dans le fuel-oil ;
(iii) à mesurer les propriétés d'écoulement à froid du fuel-oil après les injections des étapes (i) et (ii) ; et
(iv) à ajuster les vitesses relatives d'injection des constituants (B) et (A) et ainsi leurs proportions relatives pour tenir compte des résultats de l'étape (iii) et pour obtenir les propriétés désirées d'écoulement à froid dans le fuel-oil.

29. Procédé suivant la revendication 28, dans lequel le fuel-oil comprend un courant en écoulement de ce fuel-oil, l'étape (i) s'effectuant à un premier poste et l'étape (ii) s'effectuant à un second poste.

30. Procédé suivant la revendication 28 ou 29, dans lequel un capteur met en oeuvre l'étape (iii) et l'information est transmise par un moyen de commande pour commander l'injection de l'un des ou des deux constituants (B) et (A).