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(54) **FUEL OIL COMPOSITIONS**  
**KRAFTÖLZUSAMMENSETZUNGEN**  
**COMPOSITIONS DE FUEL-OIL**

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(56) References cited:  
**EP-A- 0 398 101** **WO-A-94/17159**

**Description**

**[0001]** This invention relates to fuel oils, and to the use of additives to improve the characteristics of fuel oils, more especially of diesel fuel and kerosene.

5 **[0002]** Environmental concerns have led to a need for fuels with reduced sulphur content, especially diesel fuel and kerosene. However, the refining processes that produce fuels with low sulphur contents also result in a product of lower viscosity and a lower content of other components in the fuel that contribute to its lubricity, for example, polycyclic aromatics and polar compounds. Furthermore, sulphur-containing compounds in general are regarded as providing anti-wear properties and a result of the reduction in their proportions, together with the reduction in proportions of other  
10 components providing lubricity, has been an increase in reported failures of fuel pumps in diesel engines using low-sulphur fuels, the failure being caused by wear in, for example, cam plates, rollers, spindles and drive shafts.

**[0003]** This problem may be expected to become worse in future because, in order to meet stricter requirements on exhaust emissions generally, high pressure fuel pumps, including in-line, rotary and unit injector systems, are being introduced, these being expected to have more stringent lubricity requirements than present equipment, at the same  
15 time as lower sulphur levels in fuels become more widely required.

**[0004]** At present, a typical sulphur content in a diesel fuel is about 0.25% by weight. In Europe maximum sulphur levels are being reduced to 0.20%, and are expected to be reduced to 0.05%; in Sweden grades of fuel with levels below 0.005% (Class 2) and 0.001% (Class 1) are already being introduced. A fuel oil composition with a sulphur level below 0.20% by weight is referred to herein as a low-sulphur fuel.

20 **[0005]** The present invention is based on the observation that a cold flow improver enhances the lubricity of a low-sulphur fuel.

**[0006]** In a first aspect of the invention, there is provided the use of a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formula  $>NR^{13}$ , where  $R^{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver to enhance the lubricity of a fuel oil composition having a sulphur content of at most 0.05% by weight, such that the composition has a wear scar diameter, as measured by the HFRR test at 60°C, of at most 450  $\mu\text{m}$ .

**[0007]** In a second aspect of the invention, there is provided a process for the manufacture of a petroleum based fuel oil of enhanced lubricity, which comprises refining a crude oil to produce a fuel oil of low sulphur content, and blending a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formula  $>NR^{13}$ , where  $R^{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver with the refined product to provide a fuel oil composition with a sulphur content of at most 0.05% by weight, and having a lubricity such as to give a wear scar diameter, as measured by the HFRR test (as hereinafter defined) at 60°C of at most 450  $\mu\text{m}$ , preferably at most 380  $\mu\text{m}$ , more preferably at most 350  $\mu\text{m}$ .

35 **[0008]** Advantageously, the petroleum-based fuel oil is a middle distillate fuel oil.

**[0009]** In a third aspect of the invention, there is provided a composition comprising a major proportion of a petroleum-based fuel oil and a minor proportion of a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formulae  $>NR^{13}$ , where  $R^{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver, the composition having a sulphur content of at most 0.05% by weight, and a lubricity such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 450  $\mu\text{m}$ .

**[0010]** Advantageously, the petroleum-based fuel is a middle distillate fuel oil.

45 **[0011]** Advantageously, the composition resulting from the use of the first aspect, and the composition of the third aspect of the invention have a lubricity as defined with reference to the second aspect.

**[0012]** As used herein, the term "cold flow improver" refers to any additive which will lower the vehicle operability temperature relative to untreated base fuel, as evidenced, for example by lowering the pour point, the cloud point, the wax appearance temperature, the cold filter plugging point (hereinafter CFPP) or the Low Temperature Flow Test (LTFT) temperature of a fuel, or will reduce the extent of wax settlement in a fuel, especially a middle distillate fuel.

50 **[0013]** As used herein, the term "middle distillate" refers to fuel oils obtainable in refining crude oil as the fraction from the lighter, kerosene or jet fuel, fraction to the heavy fuel oil fraction. The fuel oils may also comprise atmospheric or vacuum distillate, cracked gas oil or a blend, in any proportions, of straight run and thermally and/or catalytically cracked distillate. Examples include kerosene, jet fuel, diesel fuel, heating oil, visbroken gas oil, light cycle oil, vacuum gas oil, light fuel oil and fuel oil. Such middle distillate fuel oils usually boil over a temperature range, generally within the range of 100°C to 500°C, as measured according to ASTM D86, more especially between 150°C and 400°C.

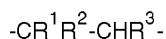
55 **[0014]** It is within the scope of the invention to include as a component of the composition a vegetable-based fuel oil, or "biofuel", for example a rapeseed methyl ester or vegetable oil.

[0015] The HFRR, or High Frequency Reciprocating Rig, test is that described according to CEC F-06-T-94 and ISO TC22/SC7/WG6N180.

[0016] The CFPP test is defined in "Journal of the Institute of Petroleum", 52 (1966) pp 173 to 185.

[0017] The cold flow improvers usable in the present invention will now be described in further detail.

[0018] An ethylene-unsaturated ester copolymer, more especially one having, in addition to units derived from ethylene, units of the formula



wherein R<sup>1</sup> represents hydrogen or methyl, R<sup>2</sup> represents COOR<sup>4</sup>, wherein R<sup>4</sup> represents an alkyl group having from 1 to 9 carbon atoms, which is straight chain or, if it contains 3 or more carbon atoms, branched, or R<sup>2</sup> represents OOCR<sup>5</sup>, wherein R<sup>5</sup> represents R<sup>4</sup> or H, and R<sup>3</sup> represents H or COOR<sup>4</sup>.

[0019] 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 a saturated alcohol and an unsaturated carboxylic acid, but preferably the ester is 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 copolymer contains from 5 to 40wt% of the vinyl ester, more preferably from 10 to 35wt% vinyl ester. A mixture of two copolymers, for example as described in US Patent No. 3,961,916, may be used. The number average molecular weight of the copolymer, as measured by vapour phase osmometry, is advantageously 1,000 to 10,000, preferably 1,000 to 5,000. If desired, the copolymer may contain units derived from additional comonomers, e.g. a terpolymer, tetrapolymer or a higher polymer, for example where the additional comonomer is isobutylene or disobutylene.

[0020] The copolymers may be made by direct polymerization of comonomers, or 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.

Polar nitrogen compounds.

[0021] Such compounds, as indicated above, are oil-soluble polar nitrogen compounds carrying one or more, preferably two or more, substituents of the formula >NR<sup>13</sup>, where R<sup>13</sup> represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom. R<sup>13</sup> preferably represents an aliphatic hydrocarbyl group containing 12 to 24 carbon atoms. The oil soluble polar nitrogen compound is generally one capable of acting as a wax crystal growth inhibitor in fuels.

[0022] Preferably, the hydrocarbyl group is linear or slightly linear, i.e. it may have one short length (1-4 carbon atoms) hydrocarbyl branch. When the substituent is amino, it may carry more than one said hydrocarbyl group, which may be the same or different.

[0023] 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.

[0024] 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.

[0025] More especially, the or each amino or imino substituent is bonded to a moiety via an intermediate linking group such as -CO-, -CO<sub>2</sub>(<sup>-</sup>), -SO<sub>3</sub>(<sup>-</sup>) or hydrocarbylene. Where the linking group is anionic, the substituent is part of a cationic group, as in an amine salt group.

[0026] When the polar nitrogen compound carries more than one amino or imino substituent, the linking groups for each substituent may be the same or different.

[0027] Suitable amino substituents are long chain C<sub>12</sub>-C<sub>40</sub>, preferably C<sub>12</sub>-C<sub>24</sub>, alkyl primary, secondary, tertiary or quaternary amino substituents.

[0028] Preferably, the amino substituent is a dialkylamino substituent, which, as indicated above, may be in the form of an amine salt thereof; tertiary and quaternary amines can form only amine salts. Said alkyl groups may be the same

or different.

**[0029]** Examples of amino substituents include dodecylamino, tetradecylamino, cocoamino, and hydrogenated tallow amino. Examples of secondary amino substituents include dioctadecylamino and methylbehenylamino. Mixtures of amino substituents may be present such as those derived from naturally occurring amines. A preferred amino substituent is the secondary hydrogenated tallow amino substituent, the alkyl groups of which are derived from hydrogenated tallow fat and are typically composed of approximately 4% C<sub>14</sub>, 31% C<sub>16</sub> and 59% C<sub>18</sub> n-alkyl groups by weight.

**[0030]** Suitable imino substituents are long chain C<sub>12</sub>-C<sub>40</sub>, preferably C<sub>12</sub>-C<sub>24</sub>, alkyl substituents.

**[0031]** Said moiety may be monomeric (cyclic or non-cyclic) or polymeric. When non-cyclic, it may be obtained from a cyclic precursor such as an anhydride or a spirobis lactone.

**[0032]** 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 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.

**[0033]** 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

**[0034]**

(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, benzothiofene, carbazole and thiodiphenylamine;

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

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

**[0035]** Examples of polar nitrogen compounds are described below:

**[0036]** (i) an amine salt and/or amide of a mono- or poly-carboxylic acid, e.g. having 1 to 4 carboxylic acid groups. It may be made, for example, by reacting at least one molar proportion of a hydrocarbyl substituted amine with a molar proportion of the acid or its anhydride.

**[0037]** When an amide is formed, the linking group is -CO-, and when an amine salt is formed, the linking group is -CO<sub>2</sub><sup>(-)</sup>.

**[0038]** The moiety may be cyclic or non-cyclic. Examples of cyclic moieties are those where the acid is cyclohexane 1,2-dicarboxylic acid; cyclopentane 1,2-dicarboxylic acid; and naphthalene dicarboxylic acid. Generally, such acids have 5 to 13 carbon atoms in the cyclic moiety. Preferred such cyclic acids are benzene dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid, and benzene tetracarboxylic acids such as pyromellitic acid, phthalic acid being particularly preferred. US-A-4,211,534 and EP-A-272,889 describes polar nitrogen compounds containing such moieties.

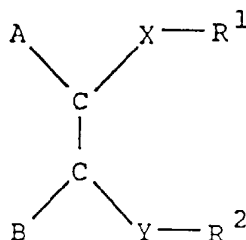
**[0039]** Examples of non-cyclic moieties are those when the acid is a long chain alkyl or alkylene substituted dicarboxylic acid such as succinic acid, as described in US-A-4,147,520 for example.

**[0040]** Other examples of non-cyclic moieties are those where the acid is a nitrogen-containing acid such as ethylene diamine tetracetic acid and nitriloacetic acid, as described in DE-A-3,916,366 (equivalent to CA-A-2,017,126) (BASF).

**[0041]** Further examples are the moieties obtained where a dialkyl spirobis lactone is reacted with an amine as described in EP-A-413,279 (Hoechst).

**[0042]** (ii) EP-A-0,261,957 describes polar nitrogen compounds according to the present description of the general formula

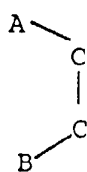
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10 in which -Y-R<sup>2</sup> is SO<sub>3</sub><sup>(-)(+)</sup>NR<sub>3</sub><sup>3</sup>R<sup>2</sup>, -SO<sub>3</sub><sup>(-)(+)</sup>HNR<sub>2</sub><sup>3</sup>R<sup>2</sup>, -SO<sub>3</sub><sup>(-)(+)</sup>H<sub>2</sub>NR<sup>3</sup>R<sup>2</sup>, -SO<sub>3</sub><sup>(-)(+)</sup>H<sub>3</sub>NR<sup>2</sup>, -SO<sub>2</sub>NR<sup>3</sup>R<sup>2</sup> or -SO<sub>3</sub>R<sup>2</sup>; and -X-R<sup>1</sup> is -Y-R<sup>2</sup> or -CONR<sup>3</sup>R<sup>1</sup>, -CO<sub>2</sub><sup>(-)(+)</sup>NR<sub>3</sub><sup>3</sup>R<sup>1</sup>, -CO<sub>2</sub><sup>(-)(+)</sup>HNR<sub>2</sub><sup>3</sup>R<sup>1</sup>, -R<sup>4</sup>-COOR<sub>1</sub>, -NR<sup>3</sup>COR<sup>1</sup>, -R<sup>4</sup>OR<sup>1</sup>, -R<sup>4</sup>OCOR<sup>1</sup>, -R<sup>4</sup>, R<sup>1</sup>, -N(COR<sup>3</sup>)R<sup>1</sup> or Z<sup>(-)(+)</sup>NR<sub>3</sub><sup>3</sup>R<sup>1</sup>; -Z<sup>(-)</sup> is SO<sub>3</sub><sup>(-)</sup> or -CO<sub>2</sub><sup>(-)</sup>;

15 [0043] R<sup>1</sup> and R<sup>2</sup> are alkyl, alkoxyalkyl or polyalkoxyalkyl containing at least 10 carbon atoms in the main chain;

[0044] R<sup>3</sup> is hydrocarbyl and each R<sup>3</sup> may be the same or different and R<sup>4</sup> is absent or is C<sub>1</sub> to C<sub>5</sub> alkylene and in

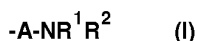


25 the carbon-carbon (C-C) bond is either a) ethylenically unsaturated when A and B may be alkyl, alkenyl or substituted hydrocarbyl groups or b) part of a cyclic structure which may be aromatic, polynuclear aromatic or cyclo-aliphatic, it is preferred that X-R<sup>1</sup> and Y-R<sup>2</sup> between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

[0045] Multicomponent additive systems may be used and the ratios of additives to be used will depend on the fuel to be treated.

30 [0046] (iii) EP-A-0,316,108 describes an amine or diamine salt of (a) a sulphosuccinic acid, b) an ester or diester of a sulphosuccinic acid, c) an amide or a diamide of a sulphosuccinic acid, or d) an ester-amide of a sulphosuccinic acid.

[0047] (iv) WO 9304148 describes 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.

[0048] Preferably, A has from 1 to 20 carbon atoms and is preferably a methylene or polymethylene group.

[0049] Each hydrocarbyl group constituting R<sup>1</sup> and R<sup>2</sup> in the invention (Formula 1) 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.

45 The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

[0050] 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.

[0051] Examples of salts of the chemical compounds are the acetate and the hydrochloride.

50 [0052] 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. WO 9407842 describes other compounds (Mannich bases) in this classification.

[0053] (v) A condensate of long chain primary or secondary amine with a carboxylic acid-containing polymer.

55 [0054] 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 telomer 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 epoxide and a mono-carboxylic acid polyester such as described in US-A4,631,071.

[0055] EP-0,283,292 describes amide containing polymers and EP-0,343,981 describes amine-salt containing polymers.

[0056] It should be noted that the polar nitrogen compounds may contain other functionality such as ester functionality.

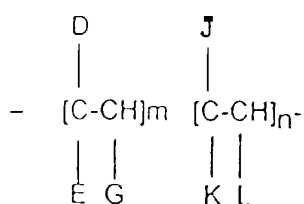
[0057] Other classes of flow improvers, especially middle distillate flow improvers, are suitable for use in the present invention. Among these there may be mentioned:

5 [0058] A comb polymer. Such polymers are polymers in which branches containing hydrocarbyl groups are pendant from a polymer backbone, and are discussed in "Comb-Like Polymers. Structure and Properties", N. A. Plate and V P Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

10 [0059] Generally, comb polymers have one or more long chain hydrocarbyl branches, e.g., oxyhydrocarbyl branches, normally having from 10 to 30 carbon atoms, pendant from a polymer backbone, said branches being bonded directly or indirectly to the backbone. Examples of indirect bonding include bonding via interposed atoms or groups, which bonding can include covalent and/or electrovalent bonding such as in a salt.

[0060] 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 carbon atoms.

15 [0061] As examples of preferred comb polymers there may be mentioned those of the general formula



wherein

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 or hydrocarbylene,

and m and n represent mole fractions, m being finite and preferably within the range of from 1.0 to 0.4, n being less than 1 and preferably in the range of from 0 to 0.6. R<sup>11</sup> advantageously represents a hydrocarbyl group with from 10 to 30 carbon atoms, while R<sup>12</sup> advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms.

[0062] The comb polymer may contain units derived from other monomers if desired or required.

45 [0063] These comb polymers may be copolymers of maleic anhydride or fumaric or itaconic acids and another ethylenically unsaturated monomer, e.g., an α-olefin, including styrene, or an unsaturated ester, for example, vinyl acetate or homopolymer of fumaric or itaconic acids. It is preferred but not essential that equimolar amounts of the comonomers be used although molar proportions in the range of 2 to 1 and 1 to 2 are suitable. Examples of olefins that may be copolymerized with e.g., maleic anhydride, include 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene.

50 [0064] The acid or anhydride group of the comb polymer may be esterified by any suitable technique and although preferred it is not essential that the maleic anhydride or fumaric acid be at least 50% esterified. Examples of alcohols which may be used include n-decan-1-ol, 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 or 2-methyltridecan-1-ol. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than the commercially available alcohol mixtures but if mixtures are used the R<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.

[0065] These comb polymers may especially be fumarate or itaconate polymers and copolymers such for example as those described in EP-A-153176, -153177 and -225688, and WO 91/16407.

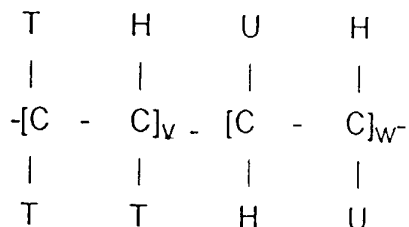
[0066] Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which

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 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 comb polymers are those having a number average molecular weight, as measured by vapour phase osmometry, of 1,000 to 100,000, more especially 1,000 to 30,000.

**[0067]** Other suitable comb polymers are the polymers and copolymers of  $\alpha$ -olefins and esterified copolymers of styrene and maleic anhydride, and esterified copolymers of styrene and fumaric acid; mixtures of two or more comb polymers may be used in accordance with the invention and, as indicated above, such use may be advantageous. Other examples of comb polymers are hydrocarbon polymers, e.g., copolymers of ethylene and at least one  $\alpha$ -olefin, the  $\alpha$ -olefin preferably having at most 20 carbon atoms, examples being n-decene-1 and n-dodecene-1. Preferably, the number average molecular weight of such a copolymer is at least 30,000 measured by GPC. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst.

A hydrocarbon polymer.

**[0068]** Examples of suitable hydrocarbon polymers are those of the general formula



wherein

T = H or R<sup>21</sup> wherein

R<sup>21</sup> = C<sub>1</sub> to C<sub>40</sub> hydrocarbyl, and

U = H, T, or aryl

and v and w represent mole fractions, v being within the range of from 1.0 to 0.0, w being in the range of from 0.0 to 1.0.

**[0069]** The hydrocarbon polymers may be made directly from monoethylenically unsaturated monomers or indirectly by hydrogenating polymers from polyunsaturated monomers, e.g., isoprene and butadiene.

**[0070]** Examples of hydrocarbon polymers are disclosed in WO 91/11488.

**[0071]** Preferred copolymers are ethylene  $\alpha$ -olefin copolymers, having a number average molecular weight of at least 30,000. Preferably the  $\alpha$ -olefin has at most 28 carbon atoms. Examples of such olefins are propylene, 1-butene, isobutene, n-octene-1, isooctene-1, n-decene-1, and n-dodecene-1. The copolymer may also comprise small amounts, e.g. up to 10% by weight, of other copolymerizable monomers, for example olefins other than  $\alpha$ -olefins, and non-conjugated dienes. The preferred copolymer is an ethylene-propylene copolymer.

**[0072]** The number average molecular weight of the ethylene  $\alpha$ -olefin copolymer is, as indicated above, preferably at least 30,000, as measured by gel permeation chromatography (GPC) relative to polystyrene standards, advantageously at least 60,000 and preferably at least 80,000. Functionally no upper limit arises but difficulties of mixing result from increased viscosity at molecular weights above about 150,000, and preferred molecular weight ranges are from 60,000 and 80,000 to 120,000.

**[0073]** 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%.

**[0074]** 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.

**[0075]** The copolymers may be prepared by any of the methods known in the art, for example using a Ziegler type catalyst. The polymers should be substantially amorphous, since highly crystalline polymers are relatively insoluble in fuel oil at low temperatures.

5 **[0076]** Other suitable hydrocarbon polymers include a low molecular weight ethylene- $\alpha$ -olefin copolymer, advantageously with a number average molecular weight of at most 7500, advantageously from 1,000 to 6,000, and preferably from 2,000 to 5,000, as measured by vapour phase osmometry. Appropriate  $\alpha$ -olefins are as given above, or styrene, with propylene again being preferred. Advantageously the ethylene content is from 60 to 77 molar per cent, although for ethylene-propylene copolymers up to 86 molar per cent by weight ethylene may be employed with advantage.

10 Linear, eg polyoxyalkylene compounds.

**[0077]** Such compounds comprise a compound in which at least one substantially linear alkyl group having 10 to 30 carbon atoms is connected via an optional linking group that may be branched to a non-polymeric residue, such as an 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, sulphur and/or nitrogen atoms. The linking group may be polymeric.

15 **[0078]** By "substantially linear" is meant that the alkyl group is preferably straight chain, but that straight chain alkyl groups having a small degree of branching such as in the form of a single methyl group branch may be used.

**[0079]** Preferably, the compound has at 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 the linking group between any two such alkyl groups in the compound.

20 **[0080]** The oxygen atom or atoms, if present, are preferably directly interposed between carbon atoms in the chain and may, for example, be provided in the linking group, if present, 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.

**[0081]** As indicated the chain or chains include carbon, oxygen, sulphur and/or nitrogen atoms.

25 **[0082]** 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 ether 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.

30 **[0083]** Examples include 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 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.

35 **[0084]** The preferred esters, ethers or ester/ethers which may be used may comprise compounds in which one or more groups (such as 2, 3 or 4 groups) of formula -OR<sup>25</sup> are bonded to a residue E, where E may for example represent A (alkylene)<sub>q</sub>, where A represents C or N or is absent, q represents an integer from 1 to 4, and the alkylene group has from one to four carbon atoms, A (alkylene)<sub>q</sub> for example being N(CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>; C(CH<sub>2</sub>)<sub>4</sub>; or (CH<sub>2</sub>)<sub>2</sub>; and R<sup>25</sup> may independently be

(a) n-alkyl-

(b) n-alkyl-CO-

45 (c) n-alkyl-OCO-(CH<sub>2</sub>)<sub>n</sub>-

(d) n-alkyl-OCO-(CH<sub>2</sub>)<sub>n</sub>CO-

n being, for example, 1 to 34, the alkyl group being linear and containing from 10 to 30 carbon atoms. For example, they may be represented by the formula R<sup>23</sup>OBOR<sup>24</sup>, R<sup>23</sup> and R<sup>24</sup> each being defined as for R<sup>25</sup> above, 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.

50 **[0085]** 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<sub>18</sub> to C<sub>24</sub> fatty acid, especially behenic acid. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.



[0086] 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.

[0087] 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.

[0088] It is within the scope of the invention to use more than two flow improvers advantageously selected from more than one of the different classes outlined above.

[0089] The flow improver is advantageously employed in a proportion within the range of from 0.001 to 1%, e.g. from 0.01% to 1% advantageously 0.05% to 0.5%, and preferably from 0.075 to 0.25%, by weight, based on the weight of fuel.

[0090] The flow improver may also be used in combination with one or more other co-additives such as known in the art, for example the following: detergents, antioxidants, corrosion inhibitors, dehazers, demulsifiers, antifoaming agents, cetane improvers, cosolvents, package compatibilizers, and other, known, lubricity additives.

EXAMPLES

[0091] The following Examples illustrate the invention:

[0092] In the examples, the HFRR test was employed under the following conditions, wear being measured at 60°C throughout.

LOAD	2N
STROKE	1 mm (0.5 mm AMPLITUDE)
FREQUENCY	50 Hz
TEMPERATURE	60°C
METALLURGY	BALL ANSI 52 100 (hardened bearing tool steel) 645 HV 30 FLAT ANSI 52 100 (bearing tool steel) 180 HV 30
DURATION	75 minutes

[0093] Wear was measured at the end of the test.

[0094] Various additives were tested in Fuels I, II and III.

[0095] Fuel I is a Class 1 diesel fuel commercially available in Sweden. The characteristics of the fuel were as follows:

Specific Gravity:		0.8088
Sulphur:		0.001 wt%
Distillation, °C,	IBP	186
	10%	203
	50%	225
	95%	273

[0096] The HFRR results on the fuel alone were as follows:

WEAR, µm.  
701

(results are mean of two tests)

[0097] Fuel II has the following characteristics

Specific Gravity		0.8184
Sulphur		0.03 wt%
Distillation, °C,	IBP	156
	10%	192
	20%	202
	50%	233
	90%	303
	95%	326

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(continued)

	FBP	355
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5 [0098] The HFRR results on the fuel alone were as follows:

WEAR,  $\mu\text{m}$   
575

(result is the mean of two tests).

10 [0099] Fuel III has the following characteristics:

Specific Gravity		0.8204
Sulphur		0.03 wt%
Distillation, °C,	IBP	161
	10%	197
	20%	208
	50%	239
	90%	301
	95%	314
	FBP	336

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[0100] The HFRR result on the fuel alone was 585  $\mu\text{m}$  (mean of two tests)

[0101] Various additives were used in the numbered Examples, the results and the treat rates, in ppm by weight of active ingredient based on the weight of the fuel, being given in the Tables.

25

Additives used

Example 1

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[0102] A polar nitrogen compound, an N,N-dialkylammonium salt of 2-N'N' dialkylamidobenzoate, the product of reacting one mole of phthalic anhydride and two moles of di(hydrogenated tallow) amine.

Example 2

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[0103] A cold flow improver additive commercially available from BASF as "Keroflux 3243" and believed to contain the reaction product of ethylene diamine tetracetic acid and di(hydrogenated tallow) amine in a mole ratio of 1:4, in combination with an ethylene-vinyl propionate copolymer.

Example 3

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[0104] A cold flow improver additive commercially available from Hoechst as "Dodiflow V/4237" and believed to contain the reaction product of an alkenyl spiro bislactone with one mole of di(hydrogenated tallow) amine and one mole of (hydrogenated tallow) amine.

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Example 4

[0105] An ethylene-vinyl acetate copolymer, vinyl acetate content 13.5%, Mn 5000, measured by gel permeation chromatography (GPC).

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Example 5

[0106] An ethylene-vinyl acetate copolymer, vinyl acetate content 36.5 wt%, Mn 3000 (GPC).

Example 6

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[0107] Ethylene-vinyl acetate copolymer; 29 wt% vinyl acetate, Mn 3400 (GPC).

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### Example 7

[0108] Ethylene-vinyl acetate copolymer; 28 wt% vinyl acetate, Mn 18000 (GPC).

5 Example 8

[0109] 1:3 (wt/wt) blend of Examples 4 and 5.

### Example 9

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[0110] An ethylene-vinyl propionate copolymer, 38 wt% vinyl propionate, Mn approximately 5200 (GPC).

### Example 10

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[0111] A dodecyl fumarate-vinyl acetate (mole ratio 1:1) comb polymer.

### Example 11

[0112] A hexadecyl itaconate comb polymer.

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### Example 12

[0113] An octadecyl itaconate comb polymer.

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### Example 13

[0114] A tetradecyl fumarate~styrene mole ratio 1:1 comb polymer.

### Example 14

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[0115] The reaction product of ethylene diamine tetracetic acid and di(hydrogenated tallow) amine in a mole ratio of 1:4.

### Example 15

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[0116] The reaction product of nitriloacetic acid and di(hydrogenated tallow) amine in a mole ratio of 1:3.

### Example 16

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[0117] The reaction product of one mole of an alkenyl spiro bislactone with one mole of di(hydrogenated tallow) amine and one mole of (hydrogenated tallow) amine.

## RESULTS

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[0118]

(FUEL I)		
Example	Treat Rate, ppm	Wear, $\mu\text{m}$
2	1000	246
9	1000	471
Fuel Alone	-	701

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FUEL II			
Example and (Treat Rate (ppm))			Wear $\mu\text{m}$
(i)	1(60)		480
		4(450)	535
	1(60);	4(495)	340
(ii)	1(60)		480
		9(750)	565
	1(60);	9(700)	305
(iii)	1(60)		480
		2(165)	420
	1(60);	2(165)	300
(iv)	1(60)		480
		2(150)	495
	1(60);	2(150)	315
Fuel Alone			-
			575

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**[0119]** The results show that certain combinations of flow improvers act synergistically in enhancing lubricity, as measured by wear reductions.

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FUEL III	
Example and (Treat Rate (ppm))	Wear ( $\mu\text{m}$ )
1(300)	385
1(144); 4(36)	385
Fuel Alone	585

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**[0120]** The results show that a small quantity of the ethylene-vinyl acetate copolymer of Example 4 enhanced the lubricity of the polar nitrogen compound of Example 1.

**Claims**

40

1. The use of a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formula  $>\text{NR}^{13}$ , where  $\text{R}^{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituents may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver to enhance the lubricity of a fuel oil composition having a sulphur content of at most 0.05% by weight, such that the composition has a lubricity such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 450 $\mu\text{m}$ .

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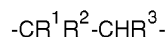
2. A process for the manufacture of a petroleum based fuel oil of enhanced lubricity, which comprises refining a crude oil to produce a fuel oil of low sulphur content, and blending a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formula  $>\text{NR}^{13}$ , where  $\text{R}^{13}$  represents a hydrocarbyl group containing 8 to 40 carbon atoms, which substituents may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver with the refined product to provide a fuel oil composition, said composition having a sulphur content of at most 0.05% by weight and having a lubricity such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 450 $\mu\text{m}$ .

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3. The use or process of claim 1 or claim 2 wherein  $\text{R}^{13}$  represents an aliphatic hydrocarbyl group containing 12 to 24 carbon atoms.

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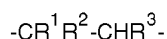
4. The use or process of claim 3 wherein the hydrocarbonyl group is a straight chain alkyl group.
5. The use or process of any of the claims 1 to 4 wherein  $>NR^{13}$  is of formula  $-NR^{13}R^{14}$  where  $R^{14}$  represents hydrogen or  $R^{13}$ , provided that  $R^{13}$  and  $R^{14}$  may be the same or different.
- 5 6. The use or process of any of the preceding claims, wherein the polar nitrogen compound is a wax crystal growth inhibitor.
7. The use or process of any of the preceding claims, wherein the substituent is amino.
- 10 8. The use or process of claim 7, wherein the amino substituent is a  $C_{12}$  to  $C_{40}$  alkyl primary, secondary, tertiary or quaternary amino substituent.
9. The use or process of any of the preceding claims, wherein the polar nitrogen compound is an amine salt and/or amide of a mono- or polycarboxylic acid.
- 15 10. The use or process of claim 9, wherein the acid moiety is cyclic, preferably a benzene dicarboxylic or tetracarboxylic acid.
- 20 11. The use or process of claim 9, wherein the acid moiety is acyclic.
12. The use or process of claim 11, wherein the acid moiety is a long chain alkyl or alkylene substituted dicarboxylic acid.
13. The use or process of claim 11, wherein the acid moiety is a nitrogen-containing acid.
- 25 14. The use or process of claim 13 wherein the acid is ethylene diamine tetraacetic or nitriloacetic acid.
15. The use or process of claim 14 wherein the polar nitrogen compound is the reaction product of ethylene diamine tetraacetic acid and di(hydrogenated tallow) amine in a mole ratio of 1:4.
- 30 16. The use or process of any of the claims 1 to 15 wherein the cold flow improver comprises two or more of said polar nitrogen compounds.
17. The use or process of any of the preceding claims wherein the copolymer is one having, in addition to units derived from ethylene, units of the formula
- 35



40 wherein  $R^1$  represents hydrogen or methyl,  $R^2$  represents  $COOR^4$ , wherein  $R^4$  represents an alkyl group having from 1 to 9 carbon atoms, which is straight chain or, if it contains 3 or more carbon atoms, branched, or  $R^2$  represents  $OOCR^5$ , wherein  $R^5$  represents  $R^4$  or H, and  $R^3$  represents H or  $COOR^4$ .

- 45 18. The use or process of any of the preceding claims wherein the ethylene-unsaturated ester copolymer is an ethylene vinyl ester copolymer.
19. The use or process of claim 18 wherein the copolymer is an ethylene vinyl acetate, ethylene vinyl propionate, ethylene vinyl hexanoate or ethylene vinyl octanoate copolymer.
- 50 20. The use or process of any of the preceding claims wherein a mixture of two copolymers is used.
21. The use or process of any of the preceding claims wherein from 0.001 to 1% by weight of the cold flow improvers based on the weight of the fuel are present.
- 55 22. The use or process of any of the preceding claims wherein the fuel oil is a middle distillate fuel oil.
23. The use or process of any of the preceding claims wherein the lubricity is such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 380  $\mu m$ .

24. A composition comprising a major proportion of a petroleum-based fuel oil and a minor proportion of a cold flow improver comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the formula  $>NR^{13}$ , where  $R^{13}$  represents a hydrocarbonyl group containing 8 to 40 carbon atoms, which substituent or one or more of which substituents may be in the form of a cation derived therefrom, in combination with an ethylene-unsaturated ester copolymer flow improver, the composition having a sulphur content of at most 0.05% by weight and a lubricity such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 450µm.
25. The composition of claim 24 wherein  $R^{13}$  represents an aliphatic hydrocarbonyl group containing 12 to 24 carbon atoms.
26. The composition of claim 25 wherein the hydrocarbonyl group is a straight chain alkyl group.
27. The composition of any of the claims 24 to 26 wherein  $>NR^{13}$  is of formula  $-NR^{13}R^{14}$  where  $R^{14}$  represents hydrogen or  $R^{13}$ , provided that  $R^{13}$  and  $R^{14}$  may be the same or different.
28. The composition of any of claims 24 to 27, wherein the polar nitrogen compound is a wax crystal growth inhibitor.
29. The composition of any of claims 24 to 28, wherein the substituent is amino.
30. The composition of claim 29, wherein the amino substituent is a  $C_{12}$  to  $C_{40}$  alkyl primary, secondary, tertiary or quaternary amino substituent.
31. The composition of any of claims 24 to 30, wherein the polar nitrogen compound is an amine salt and/or amide of a mono- or polycarboxylic acid.
32. The composition of claim 31 wherein the acid moiety is cyclic, preferably a benzene dicarboxylic or tetracarboxylic acid.
33. The composition of claim 31, wherein the acid moiety is acyclic.
34. The composition of claim 33, wherein the acid moiety is a long chain alkyl or alkylene substituted dicarboxylic acid.
35. The composition of claim 33, wherein the acid moiety is a nitrogen-containing acid.
36. The composition of claim 35 wherein the acid is ethylene diamine tetraacetic acid or nitriloacetic acid.
37. The composition of claim 36 wherein the polar nitrogen compound is the reaction product of ethylene diamine tetraacetic acid and di(hydrogenated tallow) amine in a mole ratio of 1:4.
38. The composition of any of the claims 24 to 37 wherein the cold flow improver comprises two or more of said polar nitrogen compounds.
39. The composition of any of the claims 24 to 38 wherein the ethylene-unsaturated ester copolymer is one having, in addition to units derived from ethylene, units of the formula



wherein  $R^1$  represents hydrogen or methyl,  $R^2$  represents  $COOR^4$ , wherein  $R^4$  represents an alkyl group having from 1 to 9 carbon atoms, which is straight chain or, if it contains 3 or more carbon atoms, branched, or  $R^2$  represents  $OOCR^5$ , wherein  $R^5$  represents  $R^4$  or H, and  $R^3$  represents H or  $COOR^4$ .

40. The composition of any of the claims 24 to 39 wherein the ethylene-unsaturated ester copolymer is an ethylene vinyl ester copolymer.
41. The composition of claim 40 wherein the copolymer is an ethylene vinyl acetate, ethylene vinyl propionate, ethylene vinyl hexanoate or ethylene vinyl octanoate copolymer.

42. The composition of any of claims 24 to 41 wherein a mixture of two copolymers is used.
43. The composition of any of claims 24 to 42 wherein 0.001 to 1% by weight of the cold flow improvers based on the weight of fuel are present.
- 5 44. The composition of any of claims 24 to 43 wherein the fuel oil is a middle distillate fuel oil.
45. The composition of any of claims 24 to 44 wherein the lubricity is such as to give a wear scar diameter, as measured by the HFRR test at 60°C, of at most 380µm.
- 10

**Patentansprüche**

- 15 1. Verwendung von Kaltfließverbesserer, der öllösliche polare Stickstoffverbindung, die einen oder mehreren Substituenten mit der Formel >NR<sup>13</sup> trägt, wobei R<sup>13</sup> eine Kohlenwasserstoffgruppe mit 8 bis 40 Kohlenstoffatomen bedeutet, wobei die Substituenten in Form eines daraus abgeleiteten Kations vorliegen können, in Kombination mit einem Ethylen/ungesättigter Ester-Copolymer-Fließverbesserer umfaßt, zur Erhöhung der Schmierfähigkeit von Brennstoffölzusammensetzung mit einem Schwefelgehalt von höchstens 0,05 Gew.%, so daß die Zusammensetzung eine Schmierfähigkeit hat, um einen mit dem HFRR-Test bei 60°C gemessenen Verschleißnarbendurchmesser von höchstens 450 µm zu ergeben.
- 20 2. Verfahren zur Herstellung von Brennstofföl auf Erdölbasis mit erhöhter Schmierfähigkeit, bei dem Rohöl raffiniert wird, um Brennstofföl mit niedrigem Schwefelgehalt herzustellen, und Kaltfließverbessereradditiv, das öllösliche polare Stickstoffverbindung, die einen oder mehrere Substituenten mit der Formel >NR<sup>13</sup> trägt, wobei R<sup>13</sup> eine Kohlenwasserstoffgruppe mit 8 bis 40 Kohlenstoffatomen bedeutet, wobei die Substituenten in Form eines daraus abgeleiteten Kations vorliegen können, in Kombination mit einem Ethylen/ungesättigter Ester-Copolymer-Fließverbesserer umfaßt, mit dem raffinierten Produkt gemischt wird, um eine Brennstoffölzusammensetzung zu ergeben, wobei die Zusammensetzung einen Schwefelgehalt von höchstens 0,05 Gew.% und eine Schmierfähigkeit hat, um einen mit dem HFRR-Test bei 60°C gemessenen Verschleißnarbendurchmesser von höchstens 450 µm zu ergeben.
- 25 3. Verwendung oder Verfahren nach Anspruch 1 oder Anspruch 2, bei der bzw. bei dem R<sup>13</sup> eine aliphatische Kohlenwasserstoffgruppe mit 12 bis 24 Kohlenstoffatomen bedeutet.
- 30 4. Verwendung oder Verfahren nach Anspruch 3, bei der bzw. bei dem die Kohlenwasserstoffgruppe eine geradkettige Alkylgruppe ist.
- 35 5. Verwendung oder Verfahren nach einem der Ansprüche 1 bis 4, bei der bzw. bei dem >NR<sup>13</sup> die Formel -NR<sup>13</sup>R<sup>14</sup> hat, wobei R<sup>14</sup> Wasserstoff oder R<sup>13</sup> bedeutet, mit der Maßgabe, daß R<sup>13</sup> und R<sup>14</sup> gleich oder unterschiedlich sein können.
- 40 6. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem die polare Stickstoffverbindung ein Paraffinkristallwachstumshemmstoff ist.
- 45 7. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem der Substituent Amino ist.
8. Verwendung oder Verfahren nach Anspruch 7, bei der bzw. bei dem der Aminosubstituent ein C<sub>12</sub>- bis C<sub>40</sub>-Alkylprimärer, -sekundärer, -tertiärer oder -quartärer Aminosubstituent ist.
- 50 9. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem die polare Stickstoffverbindung ein Aminsalz und/oder Amid von Mono- oder Polycarbonsäure ist.
- 55 10. Verwendung oder Verfahren nach Anspruch 9, bei der bzw. bei dem der Säureanteil cyclisch ist, vorzugsweise eine Benzoldicarbon- oder -tetracarbonsäure.
11. Verwendung oder Verfahren nach Anspruch 9, bei der bzw. bei dem der Säureanteil acyclisch ist.

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12. Verwendung oder Verfahren nach Anspruch 11, bei der bzw. bei dem der Säureanteil mit langkettigem Alkyl oder Alkylen substituierte Dicarbonsäure ist.

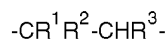
13. Verwendung oder Verfahren nach Anspruch 11, bei der bzw. bei dem der Säureanteil stickstoffhaltige Säure ist.

14. Verwendung oder Verfahren nach Anspruch 13, bei der bzw. bei dem die Säure Ethylendiamintetraessigsäure oder Nitriloessigsäure ist.

15. Verwendung oder Verfahren nach Anspruch 14, bei der bzw. bei dem die polare Stickstoffverbindung das Reaktionsprodukt von Ethylendiamintetraessigsäure und Di(hydriertem Talg)amin in einem Molverhältnis von 1:4 ist.

16. Verwendung oder Verfahren nach einem der Ansprüche 1 bis 15, bei der bzw. bei dem der Kaltfließverbesserer zwei oder mehr der polaren Stickstoffverbindungen umfaßt.

17. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Copolymer zusätzlich zu von Ethylen abgeleiteten Einheiten Einheiten mit der Formel



aufweist, in der R<sup>1</sup> Wasserstoff oder Methyl bedeutet, R<sup>2</sup> COOR<sup>4</sup> bedeutet, wobei R<sup>4</sup> eine Alkylgruppe mit 1 bis 9 Kohlenstoffatomen bedeutet, die geradkettig oder, wenn sie 3 oder mehr Kohlenstoffatome enthält, verzweigt ist, oder R<sup>2</sup> OOCR<sup>5</sup> bedeutet, wobei R<sup>5</sup> R<sup>4</sup> oder H bedeutet und R<sup>3</sup> H oder COOR<sup>4</sup> bedeutet.

18. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem das Ethylen/ungesättigter Ester-Copolymer ein Ethylen/Vinylester-Copolymer ist.

19. Verwendung oder Verfahren nach Anspruch 18, bei der bzw. bei dem das Copolymer ein Ethylen/Vinylacetat-, Ethylen/Vinylpropionat-, Ethylen/Vinylhexanoat- oder Ethylen/Vinyloctanoat-Copolymer ist.

20. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem eine Mischung aus zwei Copolymeren verwendet wird.

21. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem 0,001 bis 1 Gew. % der Kaltfließverbesserer vorhanden sind, bezogen auf das Gewicht des Brennstoffs.

22. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem das Brennstofföl ein Mitteldestillatbrennstofföl ist.

23. Verwendung oder Verfahren nach einem der vorhergehenden Ansprüche, bei der bzw. bei dem die Schmierfähigkeit so ist, daß sie einen gemäß dem HFRR-Test bei 60°C gemessenen Verschleißnarbendurchmesser von höchstens 380 µm ergibt.

24. Zusammensetzung, die einen größeren Anteil Brennstofföl auf Erdölbasis und einen geringeren Anteil Kaltfließverbesserer umfaßt, der öllösliche polare Stickstoffverbindung, die einen oder mehreren Substituenten mit der Formel >NR<sup>13</sup> trägt, wobei R<sup>13</sup> eine Kohlenwasserstoffgruppe mit 8 bis 40 Kohlenstoffatomen bedeutet, wobei der Substituent oder einer oder mehrere der Substituenten in Form eines daraus abgeleiteten Kations vorliegen können, in Kombination mit einem Ethylen/ungesättigter Ester-Copolymer-Fließverbesserer umfaßt, wobei die Zusammensetzung einen Schwefelgehalt von höchstens 0,05 Gew.% und eine Schmierfähigkeit hat, um einen mit dem HFRR-Test bei 60°C gemessenen Verschleißnarbendurchmesser von höchstens 450 µm zu ergeben.

25. Zusammensetzung nach Anspruch 24, bei der R<sup>13</sup> eine aliphatische Kohlenwasserstoffgruppe mit 12 bis 24 Kohlenstoffatomen bedeutet.

26. Zusammensetzung nach Anspruch 25, bei der die Kohlenwasserstoffgruppe eine geradkettige Alkylgruppe ist.

27. Zusammensetzung nach einem der Ansprüche 24 bis 26, bei der >NR<sup>13</sup> die Formel -NR<sup>13</sup>R<sup>14</sup> hat, wobei R<sup>14</sup> Wasserstoff oder R<sup>13</sup> bedeutet, mit der Maßgabe, daß R<sup>13</sup> und R<sup>14</sup> gleich oder unterschiedlich sein können.



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28. Zusammensetzung nach einem der Ansprüche 24 bis 27, bei der die polare Stickstoffverbindung ein Paraffinkristallwachstumshemmstoff ist.
29. Zusammensetzung nach einem der Ansprüche 24 bis 28, bei der der Substituent Amino ist.
- 5 30. Zusammensetzung nach Anspruch 29, bei der der Aminosubstituent ein C<sub>12</sub>- bis C<sub>40</sub>-Alkyl-primärer, -sekundärer, -tertiärer oder -quartärer Aminosubstituent ist.
- 10 31. Zusammensetzung nach einem der Ansprüche 24 bis 30, bei der die polare Stickstoffverbindung ein Aminsalz und/oder Amid von Mono- oder Polycarbonsäure ist.
32. Zusammensetzung nach Anspruch 31, bei der der Säureanteil cyclisch ist, vorzugsweise eine Benzoldicarbon- oder -tetracarbonsäure.
- 15 33. Zusammensetzung nach Anspruch 31, bei der der Säureanteil acyclisch ist.
34. Zusammensetzung nach Anspruch 33, bei der der Säureanteil mit langkettigem Alkyl oder Alkylen substituierte Dicarbonsäure ist.
- 20 35. Zusammensetzung nach Anspruch 33, bei der der Säureanteil stickstoffhaltige Säure ist.
36. Zusammensetzung nach Anspruch 35, bei der die Säure Ethylendiamintetraessigsäure oder Nitriloessigsäure ist.
- 25 37. Zusammensetzung nach Anspruch 36, bei der die polare Stickstoffverbindung das Reaktionsprodukt von Ethylendiamintetraessigsäure und Di(hydriertem Talg)amin in einem Molverhältnis von 1:4 ist.
38. Zusammensetzung nach einem der Ansprüche 24 bis 37, bei der der Kaltfließverbesserer zwei oder mehr der polaren Stickstoffverbindungen umfaßt.
- 30 39. Zusammensetzung nach einem der Ansprüche 24 bis 38, bei der das Copolymer zusätzlich zu von Ethylen abgeleiteten Einheiten Einheiten mit der Formel
- $$-CR^1R^2-CHR^3-$$
- 35 aufweist, in der R<sup>1</sup> Wasserstoff oder Methyl bedeutet, R<sup>2</sup> COOR<sup>4</sup> bedeutet, wobei R<sup>4</sup> eine Alkylgruppe mit 1 bis 9 Kohlenstoffatomen bedeutet, die geradkettig oder, wenn sie 3 oder mehr Kohlenstoffatome enthält, verzweigt ist, oder R<sup>2</sup> OOCR<sup>5</sup> bedeutet, wobei R<sup>5</sup> R<sup>4</sup> oder H bedeutet und R<sup>3</sup> H oder COOR<sup>4</sup> bedeutet.
- 40 40. Zusammensetzung nach einem der Ansprüche 24 bis 39, bei der das Ethylen/ungesättigter Ester-Copolymer ein Ethylen/Vinylester-Copolymer ist.
41. Zusammensetzung nach Anspruch 40, bei der das Copolymer ein Ethylen/Vinylacetat-, Ethylen/Vinylpropionat-, Ethylen/Vinylhexanoat- oder Ethylen/Vinyloctanoat-Copolymer ist.
- 45 42. Zusammensetzung nach einem der Ansprüche 24 bis 41, bei der eine Mischung aus zwei Copolymeren verwendet wird.
- 50 43. Zusammensetzung nach einem der Ansprüche 24 bis 42, bei der 0,001 bis 1 Gew.% der Kaltfließverbesserer vorhanden sind, bezogen auf das Gewicht des Brennstoffs.
44. Zusammensetzung nach einem der Ansprüche 24 bis 43, bei der das Brennstofföl ein Mitteldestillatbrennstofföl ist.
- 55 45. Zusammensetzung nach einem der Ansprüche 24 bis 44, bei der die Schmierfähigkeit so ist, daß sie einen mit dem HFRR-Test bei 60°C gemessenen Verschleißnarbendurchmesser von höchstens 380 µm ergibt.

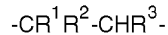
## Revendications

- 5 1. Utilisation d'un agent améliorant l'écoulement à froid, comprenant un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule  $>NR^{13}$ , dans laquelle  $R^{13}$  représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, substituants qui peuvent être sous forme d'un cation qui en est dérivé, en association avec un agent améliorant l'écoulement consistant en un copolymère éthylène-ester insaturé pour accroître le pouvoir lubrifiant d'une composition de fuel-oil ayant une teneur en soufre d'au plus 0,05 % en poids, de telle sorte que la composition ait un pouvoir lubrifiant permettant d'obtenir un diamètre de cicatrice d'usure, mesuré par l'essai HFRR à 60°C, d'au plus 450  $\mu\text{m}$ .
- 10 2. Procédé pour la production d'un fuel-oil dérivé du pétrole, présentant un pouvoir lubrifiant accru, qui comprend le raffinage d'un pétrole brut pour produire un fuel-oil à basse teneur en soufre, et le mélange d'un agent améliorant l'écoulement à froid comprenant un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule  $>NR^{13}$ , dans laquelle  $R^{13}$  représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, substituants qui peuvent être sous forme d'un cation qui en est dérivé, en association avec un agent améliorant l'écoulement consistant en un copolymère éthylène-ester insaturé avec le produit raffiné pour produire une composition de fuel-oil, ladite composition ayant une teneur en soufre d'au plus 0,05 % en poids et ayant un pouvoir lubrifiant permettant de parvenir à un diamètre de cicatrice d'usure, mesuré par l'essai HFRR à 60°C, d'au plus 450  $\mu\text{m}$ .
- 15 3. Utilisation ou procédé suivant la revendication 1 ou la revendication 2, dans lequel  $R^{13}$  représente un groupe hydrocarbyle aliphatique contenant 12 à 24 atomes de carbone.
- 20 4. Utilisation ou procédé suivant la revendication 3, dans lequel le groupe hydrocarbyle est un groupe alkyle à chaîne droite.
- 25 5. Utilisation ou procédé suivant l'une quelconque des revendications 1 à 4, dans lequel  $>NR^{13}$  répond à la formule  $-NR^{13}R^{14}$  dans laquelle  $R^{14}$  représente l'hydrogène ou un groupe  $R^{13}$ , sous réserve que  $R^{13}$  et  $R^{14}$  puissent être identiques ou différents.
- 30 6. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le composé azoté polaire est un inhibiteur de croissance des cristaux de cire.
- 35 7. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le substituant est un substituant amino.
- 40 8. Utilisation ou procédé suivant la revendication 7, dans lequel le substituant amino est un substituant (alkyle en  $C_{12}$  à  $C_{40}$ ) amino primaire, secondaire, tertiaire ou quaternaire.
- 45 9. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le composé azoté polaire est un sel d'amine et/ou un amide d'un acide mono- ou polycarboxylique.
10. Utilisation ou procédé suivant la revendication 9, dans lequel le groupement acide est un groupement acide cyclique, de préférence un acide benzène-dicarboxylique ou -tétracarboxylique.
11. Utilisation ou procédé suivant la revendication 9, dans lequel le groupement acide est acyclique.
12. Utilisation ou procédé suivant la revendication 11, dans lequel le groupement acide est un acide dicarboxylique à substituant alkylène ou alkyle à chaîne longue.
- 50 13. Utilisation ou procédé suivant la revendication 11, dans lequel le groupement acide est un acide contenant de l'azote.
- 55 14. Utilisation ou procédé suivant la revendication 13, dans lequel l'acide consiste en l'acide éthylènediaminotétracétique ou nitriloacétique.
15. Utilisation ou procédé suivant la revendication 14, dans lequel le composé azoté polaire est le produit de réaction de l'acide éthylènediaminotétracétique et de la di(sulf hydrogéné)amine en un rapport molaire égal à 1:4.

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16. Utilisation ou procédé suivant l'une quelconque des revendications 1 à 15, dans lequel l'agent améliorant l'écoulement à froid comprend deux ou plus de deux de tels composés azotés polaires.

5 17. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le copolymère est un copolymère ayant, en plus de motifs dérivés de l'éthylène, des motifs de formule



10 dans laquelle R<sup>1</sup> représente l'hydrogène ou un groupe méthyle, R<sup>2</sup> représente un groupe COOR<sup>4</sup>, dans lequel R<sup>4</sup> représente un groupe alkyle ayant 1 à 9 atomes de carbone, qui est à chaîne droite ou, s'il contient 3 ou plus de 3 atomes de carbone, est à chaîne ramifiée, ou R<sup>2</sup> représente un groupe OOCR<sup>5</sup> dans lequel R<sup>5</sup> représente un groupe R<sup>4</sup> ou H, et R<sup>3</sup> représente H ou un groupe COOR<sup>4</sup>.

15 18. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le copolymère éthylène-ester insaturé est un copolymère éthylène-ester vinylique.

19. Utilisation ou procédé suivant la revendication 18, dans lequel le copolymère est un copolymère éthylène-acétate de vinyle, éthylène-propionate de vinyle, éthylène-hexanoate de vinyle ou éthylène-octanoate de vinyle.

20 20. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel un mélange de deux copolymères est utilisé.

25 21. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel une quantité de 0,001 à 1 % en poids des agents améliorant l'écoulement à froid, sur la base du poids du combustible, est présente.

22. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le fuel-oil est un fuel-oil distillé moyen.

30 23. Utilisation ou procédé suivant l'une quelconque des revendications précédentes, dans lequel le pouvoir lubrifiant est tel qu'il permet d'obtenir un diamètre de cicatrice d'usure, mesuré par l'essai HFRR à 60°C, d'au plus 380 µm.

35 24. Composition comprenant une proportion dominante d'un fuel-oil dérivé du pétrole et une petite proportion d'un agent améliorant l'écoulement à froid comprenant un composé azoté polaire, soluble dans l'huile, portant un ou plusieurs substituants de formule >NR<sup>13</sup>, dans laquelle R<sup>13</sup> représente un groupe hydrocarbyle contenant 8 à 40 atomes de carbone, ce substituant ou bien le ou les substituants pouvant être sous forme d'un cation qui en est dérivé, en association avec un agent améliorant l'écoulement consistant en un copolymère éthylène-ester insaturé, la composition ayant une teneur en soufre d'au plus 0,05 % en poids et un pouvoir lubrifiant permettant d'obtenir un diamètre de cicatrice d'usure, mesuré par l'essai HFRR à 60°C, d'au plus 450 µm.

40 25. Composition suivant la revendication 24, dans laquelle R<sup>13</sup> représente un groupe hydrocarbyle aliphatique contenant 12 à 24 atomes de carbone.

45 26. Composition suivant la revendication 25, dans laquelle le groupe hydrocarbyle est un groupe alkyle à chaîne droite.

27. Composition suivant l'une quelconque des revendications 24 à 26, dans laquelle >NR<sup>13</sup> répond à la formule -NR<sup>13</sup>R<sup>14</sup> dans laquelle R<sup>14</sup> représente l'hydrogène ou un groupe R<sup>13</sup>, sous réserve que R<sup>13</sup> et R<sup>14</sup> puissent être identiques ou différents.

50 28. Composition suivant l'une quelconque des revendications 24 à 27, dans laquelle le composé azoté polaire est un inhibiteur de croissance des cristaux de cire.

29. Composition suivant l'une quelconque des revendications 24 à 28, dans laquelle le substituant est un substituant amino.

55 30. Composition suivant la revendication 29, dans laquelle le substituant amino est un substituant (alkyle en C<sub>12</sub> à C<sub>40</sub>) amino primaire, secondaire, tertiaire ou quaternaire.

31. Composition suivant l'une quelconque des revendications 24 à 30, dans laquelle le composé azoté polaire est un sel d'amine et/ou un amide d'un acide mono- ou polycarboxylique.

5 32. Composition suivant la revendication 31, dans laquelle le groupement acide est un groupement acide cyclique, de préférence l'acide benzène-dicarboxylique ou -tétracarboxylique.

33. Composition suivant la revendication 31, dans laquelle le groupement acide est acyclique.

10 34. Composition suivant la revendication 33, dans laquelle le groupement acide est un acide dicarboxylique à substituant alkyle ou alkylène à chaîne longue.

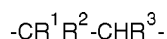
35. Composition suivant la revendication 33, dans laquelle le groupement acide est un acide contenant de l'azote.

15 36. Composition suivant la revendication 35, dans laquelle l'acide consiste en l'acide éthylènediaminetétraacétique ou l'acide nitriloacétique.

37. Composition suivant la revendication 36, dans laquelle le composé azoté polaire est le produit de réaction de l'acide éthylènediaminetétraacétique et de la di(sulf hydrogéné)amine en un rapport molaire égal à 1:4.

20 38. Composition suivant l'une quelconque des revendications 24 à 37, dans laquelle l'agent améliorant l'écoulement à froid comprend deux ou plus de deux de tels composés azotés polaires.

25 39. Composition suivant l'une quelconque des revendications 24 à 38, dans laquelle le copolymère éthylène-ester insaturé est un copolymère ayant, en plus de motifs dérivés de l'éthylène, des motifs de formule



30 dans laquelle R<sup>1</sup> représente l'hydrogène ou un groupe méthyle, R<sup>2</sup> représente un groupe COOR<sup>4</sup>, dans lequel R<sup>4</sup> représente un groupe alkyle ayant 1 à 9 atomes de carbone, qui est à chaîne droite ou, s'il contient 3 ou plus de 3 atomes de carbone, est à chaîne ramifiée, ou bien R<sup>2</sup> représente un groupe OOCR<sup>5</sup>, dans lequel R<sup>5</sup> représente un groupe R<sup>4</sup> ou H, et R<sup>3</sup> représente H ou un groupe COOR<sup>4</sup>.

35 40. Composition suivant l'une quelconque des revendications 24 à 39, dans laquelle le copolymère éthylène-ester insaturé est un copolymère éthylène-ester vinylique.

41. Composition suivant la revendication 40, dans laquelle le copolymère est un copolymère éthylène-acétate de vinyle, éthylène-propionate de vinyle, éthylène-hexanoate de vinyle ou éthylène-octanoate de vinyle.

40 42. Composition suivant l'une quelconque des revendications 24 à 41, dans laquelle un mélange de deux copolymères est utilisé.

45 43. Composition suivant l'une quelconque des revendications 24 à 42, dans laquelle une quantité de 0,001 à 1 % en poids des agents améliorant l'écoulement à froid, sur la base du poids du combustible, est présente.

44. Composition suivant l'une quelconque des revendications 24 à 43, dans laquelle le fuel-oil est un fuel-oil distillé moyen.

50 45. Composition suivant l'une quelconque des revendications 24 à 44, dans laquelle le pouvoir lubrifiant est tel qu'il permette d'obtenir un diamètre de cicatrice d'usure, mesuré par l'essai HFRR à 60°C, d'au plus 380 µm.

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