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(54) Additive concentrate

(57) An additive concentrate for incorporation into wax containing fuel oil to improve its low temperature flow properties comprises an oil-soluble polar nitrogen compound, and a solvent comprising an alkanol and an aromatic hydrocarbon to improve the stability of the concentrate.

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Description

This invention relates to an additive concentrate for incorporation into wax containing fuel oil compositions, in particular to improve low temperature flow properties.

Fuel oils, whether derived from petroleum or from vegetable sources, contain components that at low temperature tend to precipitate as large crystals or spherulites of wax in such a way as to form a gel structure which causes the fuel to lose its ability to flow. The lowest temperature at which the fuel will still flow is known as the pour point.

As the temperature of the fuel falls and approaches the pour point, difficulties arise in transporting the fuel through lines and pumps. Further, the wax crystals tend to plug fuel lines, screens, and filters at temperatures above the pour point. These problems are well recognised in the art, and various additives have been proposed, many of which are in commercial use, for depressing the pour point of fuel oils. Similarly, other additives have been proposed and are in commercial use for reducing the size and changing the shape of the wax crystals that do form. Smaller size crystals are desirable since they are less likely to clog a filter. The wax from a diesel fuel, which is primarily an alkane wax, crystallises as platelets; certain additives, usually referred to as cold flow improvers, inhibit this, causing the wax to adopt an acicular habit, the resulting needles being more likely to pass through a filter than are platelets.

A further problem encountered at temperatures low enough for wax to form in a fuel is the settlement of the wax to the lower region of any storage vessel. This has two effects; one in the vessel itself where the settled layer of wax may block an outlet at the lower end, and the second in subsequent use of the fuel. The composition of the wax-rich portion of fuel will differ from that of the remainder, and will have poorer low temperature properties than that of the homogeneous fuel from which it is derived.

There are various additives available, usually referred to as wax anti-settling additives, which change the nature of the wax formed, so that it remains suspended in the fuel, achieving a dispersion of waxy material throughout the depth of the fuel in the vessel, with a greater or lesser degree of uniformity depending on the effectiveness of the additive on the fuel.

Although the way in which cold flow improvers and wax anti-settling additives function is not completely understood, there is evidence that their effectiveness depends to a significant extent on matching of the alkanes in the fuel to alkyl or alkylene chains in the additive, the growth of the alkane wax crystals being affected, for example, by the cocrystallization of an alkyl chain of similar length in an additive.

EP-A-104,015 describe an additive concentrate for incorporation into wax containing petroleum fuel oil compositions to improve low temperature flow properties comprising an oil solution containing:

(a) 3% to 90% wt of a C_{30}-C_{300} oil-soluble nitrogen compound wax crystal growth inhibitor having at least one straight C_8-C_{40} alkyl chain and partial esters, and

(b) at least one mole per mole of (a) of an organic acid capable of nitrogen bonding with (a) to improve the solubility of (a) in the oil.

Said specification states that (b), e.g. benzoic acid, improves the fluidity of the additive concentrate; thus, in the absence of (b), (a) tends to crystallise out of the concentrate at ambient temperature because of its low solubility rendering the concentrate difficult to use.

However, the concentrates described in EP-A-104,105 have an instability problem that gives rise to precipitation of insoluble material which can block filters in use of the concentrate.

US-A-4,210,424 describes additive formulations containing high average molecular weight n-paraffinic, isoparaffinic and cycloparaffinic waxes of from 300 to 750 along with oil soluble ethylene backbone distillate flow improving polymer and oil soluble nitrogen compounds in amounts ranging from 10 to 50 wt % package or concentrate, the balance being solvent and/or diluent, which can be usefully stabilised with from 1 to 10 weight percent of an auxiliary compatibility additive which may be a C_8 to C_{18} alkanol. Such concentrates may be highly viscous or even solid at room temperature. The specification describes the practice of further diluting these packages to a fluid form, which is more easily incorporated into the distillate fuel. The dilution with large amounts of heavy aromatic naphtha is said to often lead to phase separation, hence the need for auxiliary compatibility additive, and also leads to dilute packages which therefore require the additive user to handle larger volumes of material.

There exists a continuing need for solvents which provide homogeneous additive concentrates, especially at relatively low dilutions.

There also exists the need for concentrates which retain sufficient fluidity and homogeneity at low tempreatures over substantial storage periods, such conditions being experienced under field conditions, particularly during winter seasons.

In a first aspect therefore, this invention provides the use in admixture with an additive comprising 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, of a solvent comprising:

(i) at least one aliphatic or alicyclic alkanol solvent having at least 4 carbon atoms, and

(ii) at least one aromatic hydrocarbon, and

(iii) wherein the ratio of (i) : (ii) is in the range of 10:1 to 1:2

to form a homogeneous additive concentrate for incorporation into a wax-containing fuel oil composition.

The solvents defined under this first aspect are effective even at relatively low dilutions.

In a second aspect, this invention provides the use, in admixture with an additive comprising an oil-soluble polar nitrogen compound carrying one or more substituents of the forrmula NR^1 where R^1 represents a hydrocarbyl group containing 8 to 40 carbon atoms, of a solvent comprising:

(i) at least one aliphatic or alicyclic alkanol solvent having at least 4 carbon atoms, and

(ii) at least one aromatic hydrocarbon selected from benzene, or benzene substituted with one or more alkyl groups having 1 to 4 carbon atoms, or a mixture thereof

to form a homogeneous additive concentrate for incorporation into a wax-containing fuel oil composition.

The solvents defined under this second aspect provide homogeneity in low temperature conditions.

The features of the invention will now be discussed in further detail as follows:

The Polor nitrogen compound

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 carbon 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 dicarboxylic acids such as phthalic acid, isophthalic acid, and terephthalic acid. Phthalic acid or its anhydride is particularly preferred. The particularly preferred compound is the amide-amine salt formed by reacting 1 molar portion of phthalic anhydride with 2 molar portions'of dihydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

Other examples are long chain alkyl or alkylene substituted dicarboxylic acid derivatives such as amine salts of monoamides of substituted succinic acids, examples of which are known in the art and described in US-A-4 147 520, for example. Suitable amines may be those described above.

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

(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), a-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 polyalkoxyalkyl 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 mono-carboxylic acid polyester such as described in US-A4,631,071.

The Solvent

(i) The alkanol may, for example, have 4 to 10 carbon atoms, such as 4 to 16 carbon atoms. Preferably it is an aliphatic alkanol having from 8 to 16 carbon atoms, more preferably it has 8 to 12 carbon atoms. The alkanol may be straight chain or branched, for example having one branch per molecule. Examples may include isodecanol and, 2-ethylhexanol.

(ii) In accordance with the first aspect of the invention, the solvent additionally comprises at least one aromatic hydrocarbon solvent, such as benzene, benzene substituted with one or more alkyl groups having from 1 to 4 carbon atoms such as xylenes, or mixtures thereof. The weight:weight ratio of alkanol to aromatic hydrocarbon may for example be in the range of 6:1 to 2:1, preferably 4:1 to 3:1.

Particularly preferred under both aspects of the invention as aromatic hydrocarbon are mixtures of o-, p- and m-xylenes, misitylene and high boiling point aromatics.

Other Components

The additive may comprise one or more additional components for improving the low temperature flow properties of fuel oils such as ethylene copolymers, comb polymers, linear compounds, linear hydrocarbon polymers, sulphur carboxy components, and hydrocarbylated aromatic compounds. Such components are known in the art; ethylene copolymers and comb polymers are preferred and will be described in more detail as follows:

Ethylene copolymer flow improvers e.g. ethylene unsaturated ester copolymer flow improvers, have a polymethylene backbone divided into segments by hydrocarbyl side chains interrupted by one or more oxygen atoms and/or carbonyl groups.

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_{16}, more preferably C_1 to C_9, straight or branched chain alkyl group; and R^7 represents hydrogen or a $-COOR^8$ or $-OOCR^8$ group.

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 such as ethylene - acrylates (eg. ethylene -2-ethylhexylacrylate), but the ester is preferably one of an unsaturated alcohol with a saturated carboxylic acid such as described in GB-A-1,263,152. An ethylene-vinyl ester copolymer is advantageous; an ethylene-vinyl acetate, ethylene vinyl propionate, ethylene-vinyl hexanoate, ethylene 2-ethylhexanoate, or ethylene-vinyl octanoate copolymer is preferred. Preferably, the copolymers contain from 1 to 25 such as less than 25, e.g. 1 to 20, mole % of the vinyl ester, more preferably from 3 to 15 mole % vinyl ester. They may also be in the form of mixtures of two copolymers such as those described in US-A-3,961,916 and EP-A-113,581. 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 or another ester giving rise to different units of the above formula and wherein the above-mentioned mole %'s of ester relate to total ester.

Also, the copolymers may include small proportions of chain transfer agents and/or molecular weight modifiers (eg acetaldehyde or propionaldehyde) that may be used in the polymerisation process to make the copolymer.

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

The copolymers may, for example, have 15 or fewer, preferably 10 or fewer, more preferably 6 or fewer, most preferably 2 to 5, methyl terminating side branches per 100 methylene groups, as measured by nuclear magnetic resonance, other than methyl groups on a comonomer ester and other than terminal methyl groups.

The copolymers may have a polydispersity of 1 to 6 preferably 2 to 4, polydispersity being the ratio of weight average molecular wright to number average molecular wright both as measured by Gel Permeation Chromatography using polystyrene standards.

Comb polymers 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).

Generally, comb polymers consist of molecules in which long chain branches such as hydrocarbyl branches, optionally interrupted with one or more oxygen atoms and/or carbonyl groups, having from 6 to 30 such as 10 to 30, carbon atoms, are 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. Generally, comb polymers are distinguished by having a minimum molar proportion of units containing such long chain branches.

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 such as at least 8, and preferably at least 10, atoms, selected from for example carbon, nitrogen and oxygen, in a linear chain or a chain containing a small amount of branching such as a single methyl branch.

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

$$-\left(\mathrm{CDE}-\mathrm{CHG}\right)_m-\left(\mathrm{CJK}-\mathrm{CHL}\right)_n-$$

where

D represents R^{11}, $COOR^{11}$, $OCOR^{11}$, $R^{12}COOR^{11}$ or OR^{11};
E represents H, D or R^{12};
G represents H or D;
J represents H, R^{12}, $R^{12}COOR^{11}$, or a substituted or unsubstituted aryl or heterocyclic group;
K represents H, $COOR^{12}$, $OCOR^{12}$, OR^{12} or COOH;
L represents H, R^{12}, $COOR^{12}$, $OCOR^{12}$ or substituted or unsubstituted aryl;
R^{11} representing a hydrocarbyl group having 10 or more carbon atoms, and
R^{12} representing a hydrocarbyl group being divalent in the $^{12}COOR^{11}$group and otherwise being monovalent,

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, preferably 10 to 24, more preferably 10 to 18. Preferably, R^{11} is a linear or slightly branched alkyl group and R^{12} advantageously represents a hydrocarbyl group with from 1 to 30 carbon atoms when monovalent, preferably with 6 or greater, more preferably 10 or greater, preferably up to 24, more preferably up to 18 carbon atoms. Preferably, $R^{12,}$ when monovalent, is a linear or slightly branched alkyl group. When R^{12} is divalent, it is preferably a methylene or ethylene group. By "slightly branched" is meant having a single methyl branch.

The comb polymer may contain units derived from other monomers if desired or required, examples being CO, vinyl acetate and ethylene. It is within the scope of the invention to include two or more different comb copolymers.

The comb polymers may, for example, 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 as described in EP-A-214,786. 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, 1-octadecene, and styrene. Other examples of comb polymer include methacrylates and acrylates..

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 as described in EP-A-213,879. The alcohol may be a mixture of normal and single methyl branched alcohols. It is preferred to use pure alcohols rather than alcohol mixtures such as may be commerically available; if mixtures are used the number of carbon atoms in the alkyl group is taken to be the average number of carbon atoms in the alkyl groups of the alcohol mixture; if alcohols that contain a branch at the 1 or 2 positions are used the number of carbon atoms in the alkyl group is taken to be the number in the straight chain backbone segment of the alkyl group of the alcohol.

The 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, 156 577 and 225 688, and WO 91/16407.

Particularly preferred fumarate comb polymers are copolymers of alkyl fumarates and vinyl acetate, in which the alkyl groups have from 12 to 20 carbon atoms, more especially polymers in which the alkyl groups have 14 carbon atoms or in which the alkyl groups are a mixture of C_{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 50,000, as measured by Vapour Phase Osmometry (VPO).

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 as described in EP-A-282,342; 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 such as copolymers of ethylene and at least one α-olefin, preferably the α-olefin having at most 20 carbon atoms, examples being n-octene-1, iso octene-1, n-decene-1 and n-dodecene-1, n-tetradecene-1 and n-hexadecene-1 (for example, as described in WO9319106. Preferably, the number average molecular weight measured by Gel Permeation Chromatography against polystyrene standards of such a copolymer is for example, up to 30,000 or up to 40,000. The hydrocarbon copolymers may be prepared by methods known in the art, for example using a Ziegler type catalyst. Such hydrocarbon polymers may for example have an isotacticity of 75% or greater.

Proportions

In accordance with the first aspect of the invention, the concentrate may contain up to 80% for example 35 to 75% preferably 55-75 % by wt of additive in the solvent.

In accordance with the second aspect of the invention the concentrate, which may be incorporated into bulk fuel oil by methods known in the art, may contain from 3 to 75 wt%, preferably 3 to 60 wt%, more preferably 10 to 45 wt%, of additive in the solvent. Other co-additives may be incorporated into bulk fuel oil in the concentrate or separately from the concentrate.

Fuel Oil

The concentrates of the invention are, as indicated, for addition to fuel oil in particular to improve the cold flow properties thereof.

The fuel oil may be e.g. a hydrocarbon fuel such as a petroleum-based fuel oil for example kerosene or distillate fuel oil, suitably a middle distillate fuel oil, i.e. a fuel oil obtained in refining crude oil as the fraction between the lighter kerosene and jet fuels fraction and the heavier fuel oil fraction. Such distillate fuel oils generally boil within the range of about 100°C to about 500°C, e.g. 150° to about 400°C, for example, those having a relatively high Final Boiling Point of above 360°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 fuels, diesel fuels, heating oils 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.

Heating oils may be made of a blend of virgin distillate, e.g. gas oil, naphtha, etc and cracked distillates, e.g. catalytic cycle shock. A representative specification for a diesel fuel includes a minimum flash point of 38°C and a 90% distillation point between 282 and 380°C (see ASTM Designations D-396 and D-975).

Also, the fuel oil may be an animal or vegetable oil.

The fuel oil may also contain other additives such as stabilisers, dispersants, antioxidants, corrosion inhibitors and/or demulsifiers.

The concentration of the additive in the oil may for example in the range of 1 to 5,000 ppm of additive (active ingredient) by weight per weight of fuel, for example 10 to 5,000 ppm such as 10 to 2000 ppm (active ingredient) by weight per weight of fuel, preferably 25 to 500 ppm, more preferably 100 to 200 ppm.

Examples

The invention will now be particularly described as follows:

Components

A a N,N-dialkylammonium salt of 2-N^1,N^1-diakyl-amidobenzoate being the reaction product of reacting one mole of phthalic anhydride with two moles of dihydrogenated tallow amine to form a half amide/half amine salt (53% wt)

B isodecanol (37.6% wt)

C 'Solvesso' (trade mark) 150 aromatic solvent (9.4% wt)

D an ethylene-vinyl acetate copolymer of number average molecular weight 5000 as measured by GPC (Gel Permeation Chromatography) and containing 13.5% by weight of vinyl acetate.

E an ethylene-vinyl acetate copolymer of number average molecular weight 3,500 as measured by GPC and containing 27% by weight of vinyl acetate.

F a fumarate ester vinyl acetate copolymer of number average molecular weight of about 20,000 as measured by GPC, the fumarate ester containing linear alkyl groups of 12-14 carbon atoms

G heavy aromatic naphtha

H a fumarate ester-vinyl acetate copolymer of number average molecular weight of about 20,000 as measured by GPC, the fumarate ester containing linear alkyl groups of 14-15 carbon atoms.

Formulations

Components A, B and C were admixed in the above indicated proportions to give an initial concentrate which was then admixed with three or more of components D-H to give final concentrates (I-III) having the proportions tabulated below.

	Formulation		
	I	II	III
Initial Concentrate	34.0	75.5	56.6
D	8.0	-	-
E	25.6	-	37.5
F	22.5	-	-
G	9.9	7.8	5.9
H	-	16.7	-

All figures represent proportions by weight; a dash indicates that the component was not present.

Tests

(i) Samples of each of the initial concentrate and concentrates I, II and III were stored for 4 weeks in ovens maintained at 40, 50 and 60°C respectively. After the test, all samples were observed to be clear and homogeneous with the exception of formulation I which was hazy but homogeneous.
(ii) Samples of each of the concentrates I, II and III that had been diluted in the ratio of 1:3, one set with a aromatic solvent having an average carbon number of 9 and another set with a heavy aromatic naphtha, were each stored at 0, 5, 10°C and at ambient temperature for about 2 weeks. The appearance of each sample was observed at the end of the test and recorded as follows:

- C9 Aromatics Diluted

	Temperature			
Formulation	0°C	5°C	10°C	Room
I	clear	faintly hazy	faintly hazy	clear
II	hazy	clear	clear	clear
III	clear	clear	clear	clear

- heavy aromatic naphtha diluted

	Temperature			
Formulation	0°C	5°C	10°C	Room
I	hazy	slightly haze	slightly haze	clear
II	hard gel	trace of precipitate	clear	clear
III	hard gel	clear	clear	clear

Note: The hazy samples were all homogeneous.

Thus, the concentrates I, II and III were stable at 40-60°C and exhibited good stability at low temperatures when further diluted.

Claims

1. The use, in admixture with an additive comprising 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, of a solvent comprising:

   (i) at least one aliphatic or alicyclic alkanol solvent having at least 4 carbon atoms, and

   (ii) at least one aromatic hydrocarbon, and

   (iii) wherein the ratio of (i) : (ii) is in the range of 10:1 1 to 1:2,

   to form a homogeneous additive concentrate for incorporation into a wax-containing fuel oil composition.

2. The use of claim 1, wherein the additive concentrate improves the low temperature flow properties of the fuel oil composition, upon incorporation therein.

3. The use of claim 1 or claim 2 wherein the nitrogen compound is 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) being of formula NR^1R^2 where R^1 is defined as in claim 1 and R^2 represents hydrogen or R^1, where R^1 and R^2 may be the same or different, said substitutent(s) constituting part of the amine salt and/or amide groups of the compound.

4. The use of claim 3 wherein the nitrogen compound has 30 to 300 carbon atoms, has at least one straight alkyl group of 8 to 40 carbon atoms, and is the alkyl ammonium salt and/or amide of an aromatic or cycloaliphatic polycarboxylic acid or anhydride thereof or the amide/amine salt of a partial ester of said acid.

5. The use of claim 4 wherein the acid is a benzene dicarboxylic acid.

6. The use of any of the preceding claims wherein the alkanol is an aliphatic alkanol having from 8 to 16 carbon atoms, preferably a branched alkanol having from 8 to 12 carbon atoms.

7. The use of claim 6 wherein the alkanol is isodecanol or 2-ethylhexanol.

8. The use of any of the preceding claim wherein the concentrate contains 10 to 50 % by weight of additive.

9. The use of any of the preceding claims wherein the additive additionally comprises one or more components selected from ethylene copolymers and comb polymers. for improving the low temperature flow properties of fuel oils

10. The use, in admixture with an additive comprising 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, of a

solvent comprising:

(i) at least one aliphatic or alicyclic alkanol solvent having at least 4 carbon atoms, and

(ii) at least one aromatic hydrocarbon selected from benzene, or benzene substituted with one or more alkyl groups having 1 to 4 carbon atoms, or a mixture thereof, and (iii) wherein the ratio of (i) : (ii) is in the range of 10:1 to 1:2,

to form a homogeneous additive concentrate for incorporation into a wax-containing fuel oil composition.