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(57) Abrégé/Abstract:
An additive composition for improving the cold flow properties of crude oils or fuel oils such as middle distillate fuel oils comprises an addition product or condensate cold flow improver additive in combination with a demulsifier.

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(54) Title: ADDITIVES AND FUEL COMPOSITIONS

(57) Abstract

An additive composition for improving the cold flow properties of crude oils or fuel oils such as middle distillate fuel oils comprises an addition product or condensate cold flow improver additive in combination with a demulsifier.

Additives and Fuel Compositions

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

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

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

Many additives are described in the art for improving the cold-flow properties of oils, for example in the form of oil-soluble addition products or condensates that may be polymeric or monomeric and as described, for example, in US-A-3,048,479; UK-A-1,263,152; US-A-3,961,961; and EP-A-0,261,957. Some of the above additives have been and are used commercially as Cold Flow Improvers. However, there is a need to improve performance, particularly over a range of oils.

US-A-3,850,587 describes fuel compositions comprising a middle distillate fuel and a flow improver composition comprising a hydrocarbyl succinic acid or amine salt thereof, an ethylene-vinyl acetate polymer and, optionally, an aromatic monocarboxylic acid. Other additives are described as optionally being present, one type being a demulsifier. However, the demulsifiers are not described as having flow improver properties.

In this invention, it has surprisingly been found that demulsifiers may improve the cold flow properties of oils and also may act synergistically in providing such properties when used in combination with addition products or condensates that themselves have cold flow improving properties. Also, the proportions of demulsifier that are used may be surprisingly small.

A first aspect of the invention is an additive composition comprising:

(i) one or more non-metallic flow improving oil soluble addition products or condensates capable of improving, either jointly or singly, one or more cold flow properties of a crude oil or fuel oil; and

(ii) a non-metallic oil soluble demulsifier, provided that the component (i) is not a combination of a substituted succinic acid derivative and an ethylene-vinyl acetate copolymer.

The composition may be in admixture with a major proportion of a crude oil or a fuel oil, the composition constituting a minor proportion. Further, the composition may be dispersed in a liquid medium compatible with a crude oil or a fuel to form a concentrate.

A second aspect of the invention is the use of an additive composition of the first aspect of the invention for improving the cold flow properties of a crude oil or a fuel oil.

The examples hereinafter show that a demulsifier used in combination with the addition products and/or the condensates gives rise to unexpected improvements in the cold flow properties of oils.

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

DEMULSIFIER

In this specification, a demulsifier is a material that can cause an oil-water emulsion to break down to form discrete, separable oil and water phases, the oil being a crude oil or fuel oil of the invention, for example at a concentration of 0.1 to 2,000 ppm by weight based on the weight of the fuel. It requires a balance

between hydrophilic and hydrophobic properties. Thus, it must be sufficiently hydrophobic to dissolve in the oil of an oil/water emulsion to break the emulsion, and must be sufficiently hydrophilic to prefer the aqueous phase which separates from the oil phase after the emulsion breaks.

The demulsifier may be a surfactant that alters the surface or interfacial tension of the droplets in the disperse phase of the emulsion to make them unstable, e.g. by raising the surface or interfacial energy.

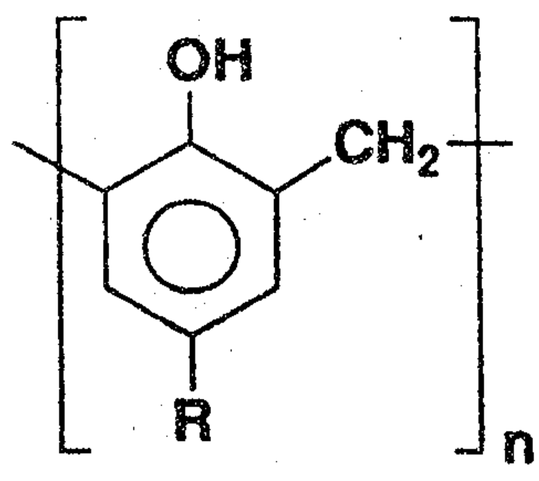
The demulsifiers used in this invention have a hydrophilic part and a hydrophobic part. They may, for example, be divided into two groups as follows:

Group 1 is a condensate comprising a hydrophobic part and one or more oxyalkylated groups comprising the hydrophilic part.

The hydrophobic part is derived from a precursor having one or more groups such as hydroxy groups; amino groups, i.e. primary, secondary, tertiary and quaternary ammonium groups; and halogen groups capable of a condensation reaction to form the oxyalkylated groups.

The oxyalkylated group may, for example, have up to 50 oxyalkyl units per group capable of a condensation reaction, and each such oxyalkylated unit may, for example, have from 2 to 6 carbon atoms and may for example be ethoxy, propoxy, or butoxy. The oxyalkylated units in a particular oxyalkylated group may be the same or different.

One example of demulsifier within Group 1 is a phenolic resin of the general formula below, being a precursor for the hydrophobic part, the hydroxy groups of which have been condensed to form oxyalkylated groups:



where R represents an aliphatic hydrocarbyl group having from 3 to 24 carbon atoms such as 9 or 15, and n represents an integer from 1 to 20 such as 4 to 10. The hydrocarbyl group contains C and H atoms and is bonded to the rest of the molecule by a carbon atom. It may be straight chain or branched, be saturated or unsaturated, or be alicyclic and may contain one or more hetero atoms (e.g. O, S, N) provided that such hetero atoms do not substantially alter the hydrocarbyl nature of the group. Preferably, R is an alkyl group.

Such phenolic resins may be made by the base catalysed oxyalkylation of an alkyl phenol-formaldehyde resin made by acid catalysis. They are described in, for example, US-A-2,499,367; US-A-3,424,565; and US-A-3,752,657.

The number average molecular weight of such oxyalkylated phenolic resins as measured by Gel Permeation Chromatography (GPC) may, for example, be up to 200,000, such as up to 150,000, preferably up to 50,000, more preferably up to 25,000, even more preferably up to 10,000.

Another example of demulsifier within Group 1 is a linear mono or polyhydroxy compound, being a precursor for the hydrophobic part, the hydroxy group(s) of which has or have been condensed to form oxyalkylated groups.

Such linear compounds may be mono or polyhydroxy alcohols such as mono or polyalkylene glycols, e.g. where the alkylene groups have from 1 to 6 carbon atoms, or pentaerythritol, or mono or polycarboxylic acids such as aliphatic fatty acids or adipic acid.

Another example of demulsifier within Group 1 is a diglycidyl ether the epoxide groups of which being ring opened with a hydroxy moiety, e.g. a polyoxyalkylene such as polyethylene glycol or polypropylene glycol to generate, in addition to the oxyalkyl groups, hydroxy groups which themselves can optionally be oxyalkylated to form a branched or cross-linked demulsifier.

Another example of demulsifier within Group 1 is an oxyalkylated amine (primary, secondary, tertiary or quaternary) analogous to the above-mentioned oxyalkylated hydroxy compounds, and oxyalkylated fatty amines reacted with adipic acid.

Examples of demulsifiers are also described in US-A-4,836,829.

Group 2 is a compound having a sulphonate or sulphonic acid group as the hydrophilic part, attached to a hydrophobic part which may, for example, be a long chain alkyl group. Specific examples are alkyl aryl sulphonates.

The demulsifiers used in this invention may also be characterised by their relative solubility numbers, referred to herein as RSN. The RSN can be correlated to the hydrolipophilic balance (HLB), typically between 8 and 11 for demulsifiers. RSN is determined by dissolving 1 g of the demulsifier in 50 ml of acetone and titrating distilled water into the solution until a permanent haze occurs. The number of mls of water added is the RSN. The RSN range of the demulsifiers used in this invention is suitably from about 4 to about 25, preferably to about 20.

Examples of demulsifiers that may be used in this invention are ethylene oxide/propylene oxide copolymers; p-alkylphenolformaldehyde resins of such copolymers and modifications thereof; polyester amines; amineoxyalkylates; oxyalkylates; cyclic-p-alkylphenolformaldehyde resins and complex modifications thereof; cross-linked polyols such as polyol esters, polymeric esters and resins, chain extended polyols, oxyalkylated chain extended polyols, alkoxylated fatty acids, and heteropolyols; amines such as oxyalkylated amines (e.g. ethoxylated amines) and polyester amines; oxyalkylated phenol-formaldehyde resins; sulphonates; sulphosuccinic acid esters; oxyalkylated phenols; poly-alphaolefins; and blocked polyols. The above specified demulsifiers are not necessarily mutually exclusive.

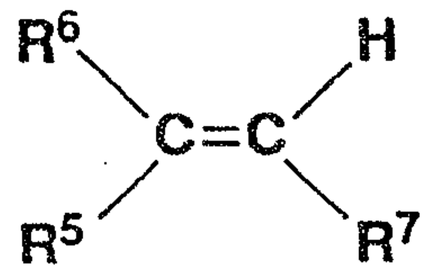
The demulsifiers may be used in this invention singly or as mixtures of more than one demulsifier.

ADDITION PRODUCTS OR CONDENSATES

The addition products are formed by an addition reaction as such and the condensates by a condensation reaction comprising addition of one molecule to another with the elimination of a simple molecule such as water, ammonia or an alcohol. They include materials that are known in the art for improving the cold flow properties of oils. In this specification, reference to such products and condensates includes products and condensates that have been made by a process sequence including an addition or condensation reaction, for example

an addition product or condensate that has been subjected to one or more subsequent processing steps.

Examples of addition products are one or more copolymers of ethylene and an unsaturated monomer of the general formula



wherein R^6 is hydrogen or methyl, R^5 is a $-OOCR^8$ group
wherein R^8 is a hydrogen formate or a C_1 to C_{28}, more usually C_1 to C_{17}, and preferably a C_1 to C_8, straight or branched chain alkyl group; or R^5 is a $-COOR^8$ group
wherein R^8 is as previously described but is not hydrogen
and R^7 is hydrogen or $-COOR^8$ as previously defined, and may include other comonomer(s) to give rise to, for example, terpolymers or tetrapolymers or higher, for example where the other comonomer is an iso-olefin such as di-isobutylene or isobutylene.

The monomer, when R^6 and R^7 are hydrogen and R^5 is $-OOCR^8$, includes vinyl alcohol esters of C_1 to C_{29}, more usually C_1 to C_5, mono-carboxylic acid, and preferably C_2 to C_{29}, more usually C_1 to C_5 mono-carboxylic acid, and preferably C_2 to C_5 mono-carboxylic acid. Examples of vinyl esters which may be copolymerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. It is preferred that these copolymers have a number average molecular weight as measured by vapour phase osometry of 1,000 to 10,000, preferably 1,000 to 5,000.

Examples of condensates are as follows.

An oil-soluble polar nitrogen compound comprising one or more of the compounds (i) to (iii):

(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 their anhydrides, or a condensate 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; and

(iii) a condensate of a long chain primary or secondary amine with a carboxylic acid containing polymer, for example as described in GB-A-2,121,807, FR-A-2,592,387 and DE-A-3,941,561.

In (i), (ii) and (iii) above, the following is to be noted.

(i) 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 containing about 30 to 300 total carbon atoms. The nitrogen compound preferably contains at least one straight chain C_8 to C_{40}, preferably C_{14} to C_{24} alkyl segment.

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 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 where in 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, ethylene diamine tetracarboxylic acid, naphthalene dicarboxylic acid and the like. 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.

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

"Hydrocarbyl" means an organic moiety composed of hydrogen and carbon bonded to the remainder of the molecule by a carbon atom which, unless the context states otherwise, may be aliphatic, including alicyclic; aromatic; or any combination thereof. It may be substituted or unsubstituted alkyl, aryl or aralkyl and may optionally contain unsaturation. Examples where it is substituted are oxy-, halogeno- and hydroxy-hydrocarbyl.

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 oxide;

(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 may for example be an alkyl or alkylene group or a mono- or poly-alkoxyalkyl group. Preferably, each hydrocarbyl group is a straight chain alkyl group. The number of carbon atoms in each hydrocarbyl group is preferably 16 to 40, more preferably 16 to 24.

Also, it is preferred that the cyclic system is substituted with two only 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.

(iii) Esters of telomer acid and alkanoloamines such as described in US-A-4,639,256; the reaction product of an amine containing branched carboxylic acid ester, an epoxide and a mono-carboxylic acid polyester such as described in US-A-4,631,071.

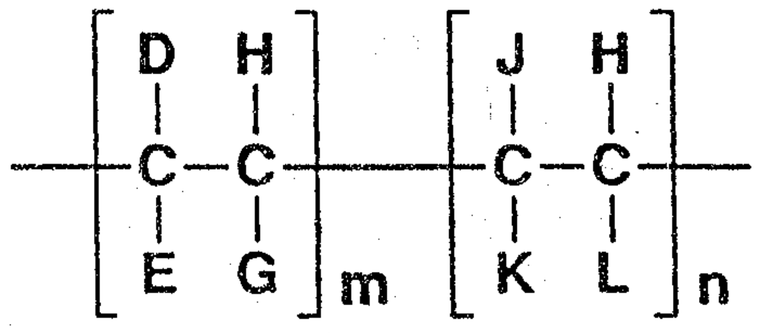
Further examples of condensates are the following, which are co-additives for improving the cold flow properties of distillate fuels. Examples of such co-additives are as follows:

Comb Polymers

Such polymers are discussed in "Comb-Like Polymers. Structure and Properties", N A Platé and V P Shibaev, J. Poly. Sci. Macromolecular Revs., 8, p 117 to 253 (1974).

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

Examples are those having the general formula



where D = R, CO.OR, OCO.R, R^1CO.OR or OR

E = H or CH_3 or D or R^1

G = H, or D

m = 1.0 (homopolymer) to 0.4 (mole ratio)
J = H, R^1, Aryl or Heterocyclic group, or $R^1CO.OR$
K = H, $CO.OR^1$, $OCO.R^1$, OR^1 or CO_2H
L = H, R^1, $CO.OR^1$, $OCO.R^1$, Aryl or CO_2H
n = 0.0 to 0.6 (mole ratio)
$R \geq C_{10}$
$R^1 \geq C_1$

Another monomer may be terpolymerized if necessary.

Examples of suitable comb polymers are fumarate/vinyl acetate copolymers, particularly those described in European Patent Applications 0153176 and 0153177; esterified olefin/maleic anhydride copolymers; polymers and copolymers of alpha olefin/maleic anhydride copolymers; polymers and copolymers of alpha olefins; esterified copolymers of styrene and maleic anhydride or fumaric acid; and polymers of alkyl esters of itaconic acid or citraconic acid such as those where the alkyl groups have from 16 to 18 carbon atoms and the polymer has a number average molecular weight of from 1,000 to 20,000.

Polyoxyalkylene Compounds

Examples are polyoxyalkylene esters, ethers, ester/ethers and mixtures thereof, particularly those containing at least one, preferably at least two C_{10} to C_{30} linear saturated alkyl groups and a polyoxyalkylene glycol group of molecular weight 100 to 5,000 preferably 200 to 5,000, the alkyl group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. These materials form the subject of European Patent Publication 0 061 895 A2. Other such additives are described in United States Patent 4 491 455.

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

$$R\text{-}O(A)\text{-}O\text{-}R^2$$

where R and R^2 are the same or different and may be

(a) n-alkyl

(b) n-alkyl–C(=O)

(c) n-alkyl-O-C(=O)–$(CH_2)_n$–

(d) n-alkyl-O-C(=O)–$(CH_2)_n$-C(=O)–

the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as 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. A may also contain nitrogen.

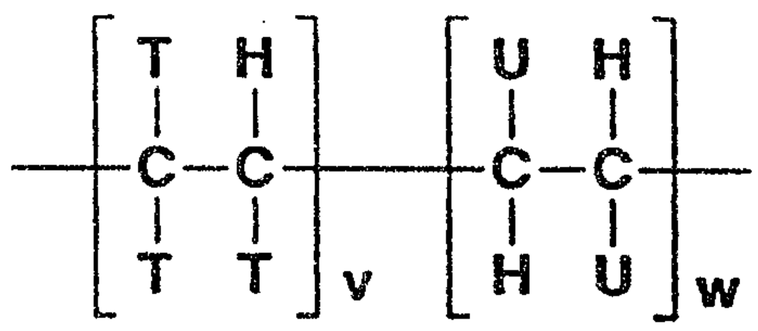
Suitable glycols generally are substantially linear polyethylene glycols (PEG) and polypropylene glycols (PPG) having a molecular weight of about 100 to 5,000, preferably about 200 to 2,000. Esters are preferred and fatty acids containing from 10-30 carbon atoms are useful for reacting with the glycols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

Polyoxyalkylene diesters, diethers, ether/esters and mixtures thereof are suitable as additives, diesters being preferred for use in narrow boiling distillates when minor amounts of monoethers and monoesters (which are often formed in the manufacturing process) may also be present. It is important for additive performance that a major amount of the dialkyl compound is present. In particular, stearic or behenic diesters of polyethylene glycol, polypropylene glycol or polyethylene/polypropylene glycol mixtures are preferred.

Examples of other compounds in this general category are those described in Japanese Patent Publication Nos 2-51477 and 3-34790 (Sanyo), and EP-A-117,108 and EP-A-326,356 (NOF).

Hydrocarbon Polymers

Examples are those represented by the following general formula



where T = H or R^1

U = H, T or Aryl

v = 1.0 to 0.0 (mole ratio)

w = 0.0 to 1.0 (mole ratio)

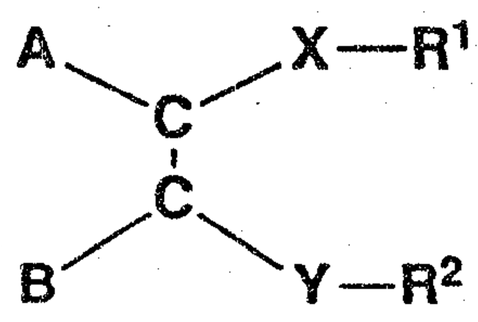
where R^1 is alkyl.

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

A particularly preferred hydrocarbon polymer is a copolymer of ethylene and propylene having an ethylene content preferably between 20 and 60% (w/w) and is commonly made via homogeneous catalysts.

Sulphur Carboxy Compounds

Examples are those described in EP-A-0261957 which describes the use of compounds of the general formula

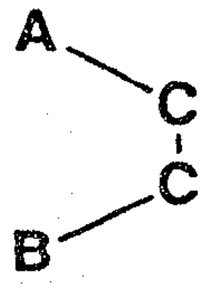


in which -Y-R^2 is $SO_3^{(-)(+)}NR^3_3R^2$, -$SO_3^{(-)(+)}HNR^3_2R^2$,

-$SO_3^{(-)(+)}H_2NR^3R^2$, -$SO_3^{(-)(+)}H_3NR^2$,
-$SO_2NR^3R^2$ or -SO_3R^2;
-X-R^1 is -Y-R^2 or -$CONR^3R^1$,
-$CO_2^{(-)(+)}NR^3_3R^1$, -$CO_2^{(-)(+)}HNR^3_2R^1$,
-R^4-$COOR_1$, -NR^3COR^1,
-R^4OR^1, -R^4OCOR^1, -R^4,R^1,
-$N(COR^3)R^1$ or $Z^{(-)(+)}NR^3_3R^1$;
-$Z^{(-)}$ is $SO_3^{(-)}$ or -$CO_2^{(-)}$;

R^1 and R^2 are alkyl, alkoxy alkyl or polyalkoxy alkyl containing at least 10 carbon atoms in the main chain;

R^3 is hydrocarbyl and each R^3 may be the same or different and R^4 is nothing or is C_1 to C_5 alkylene and in



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

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

OIL

The oil may be a crude oil, i.e. oil obtained directly from drilling and before refining, the compounds of this invention being suitable for use as flow improvers or dewaxing aids therein.

The oil may be fuel oil suitably a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of about 110°C to about 500°C, e.g. 150° to about 400°C. The fuel oil can comprise atmospheric distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. The most common petroleum distillate fuels are kerosene, jet 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.

The fuel oil may be an animal, vegetable or mineral oil and may also be synthetic. It may also contain other additives such as stabilisers, dispersants, antioxidants and corrosion inhibitors. Also, the fuel oil may have a sulphur concentration of 0.2% by weight or less based on the weight of the fuel, preferably 0.05% or less, more preferably 0.01% or less.

The concentration of the demulsifier in the oil may for example be up to 2,000 ppm of additive (active ingredient) by weight per weight of fuel, but preferably not greater than 50 ppm when used in combination with other additives, with a preferred lower limit of 5 ppm. The concentration of such other additives may be 10 to 2000 ppm (active ingredient) by weight per weight of fuel, preferably 25 to 500 ppm, more preferably 100 to 200 ppm. If used on its own, the demulsifier may have a concentration of up to 1000 ppm by weight, preferably up to 500 ppm, more preferably up to 300 ppm.

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

CONCENTRATE

The concentrates of the present invention are convenient as a means for incorporating the additive into bulk oil such as distillate fuel, which incorporation may be done by methods known in the art. The concentrates may also contain other additives as required and preferably contain from 3 to 75 wt%, more preferably 3 to 60 wt%, most preferably 10 to 50 wt% of the additives preferably in solution in oil. Examples of carrier liquid are organic solvents including

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

The additives of the invention may be incorporated into bulk oil by other methods such as those known in the art. If co-additives are required, they may be incorporated into the bulk oil at the same time as the additives of the invention or at a different time.

EXAMPLES

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

ADDITIVES

The following additives were used and will be referred to under their designated numbers:

1. Demulsifiers

1: a linear adipate made by esterification of adipic acid with polypropylene glycol under acidic conditions to give an adipate ester.

2: a product made by oxyalkylating dipropylene glycol under basic conditions to give an intermediate product which is reacted with a diglycidyl ether epoxy resin.

3: an oxyalkylated polyether resin made by oxyalkylating dipropylene glycol under basic conditions to give an intermediate product similar to that obtained in preparing Demulsifier 2, which product is reacted with a diglycidyl ether epoxy resin to give a product which is further oxyalkylated with propylene oxide.

2. **Other Additives**

4: 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.

5: an ethylene-vinyl acetate copolymer of number average molecular weight 3300 as measured by GPC and containing 36% by weight of vinyl acetate.

6: a N,N-dialkylammonium salt of 2-N^1,N^1-dialkyl-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.

7: an itaconate polymer of number average molecular weight about 4000 as measured by GPC prepared by polymerising a monomer in cyclohexane solvent using a free radical catalyst, the monomer containing linear alkyl groups of 18 carbon atoms.

8: a copolymer of styrene and esterified fumaric acid wherein the alkyl groups have 14 carbon atoms, the copolymer having a number average molecular weight of 15000 as measured by GPC and proportions of styrene and esterified fumaric acid in the ratio of 1:1 (mole:mole).

9: a demulsifier consisting of an alkylated phenol-formaldehyde resin condensate made by the acid catalysed condensation of a C_9 alkylated phenol with formaldehyde followed by oxyalkylating under basic conditions with ethylene oxide.

10: an ethylene-vinyl acetate copolymer of number average molecular weight of 3,300 as measured by GPC and containing 29% by weight of vinyl acetate.

FUELS

The following fuels were used:

Fuel	WAT (°C)	Density (g/ml)	D-86 Distillation (°C)	
			90-20	FBP-90
A	0.8	0.8368	128	30
B	-0.2	0.8400	91	30

Fuel	% Wax (at 10°C below Cloud Point)	Cloud Point (°C)	D-86 Distillation (°C)			
			IBP	20%	90%	FBP
C	2.0	-3	174	233	343	369

KEY: WAT is Wax Appearance Temperature as measured by Differential Scanning Calorimetry (DSC).
ASTM D-86:
90-20 is the difference between the temperatures at which 90 and 20% of the fuel (by volume) had distilled.
FBP-90 is the difference between the final boiling point of the fuel and the temperature at which 90% of the fuel (by volume) has distilled.
FBP, IBP are final and initial boiling points.
CP as measured by IP 219/82.

TESTS

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

Cold Filter Plugging Point (CFPP)

The test was carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Volume 52, Number 510, June 1966, pp. 173-285. This

test was designed to correlate with the cold flow of a middle distillate fuel oil in automotive diesel engines.

Simulated Filter Plugging Point (SFPP)

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

Wax Appearance Temperature (WAT)

This is a measure of the onset of crystallisation and hence the Cloud Point and was determined by Differential Scanning Calorimetry (DSC). Thus, a small sample (25 µl) of test fuel is cooled at 2°C/minute from a temperature at least 30°C above the expected cloud point of the fuel. An exotherm is observed when crystallisation commences in the sample and the WAT is measured by an extrapolation technique using a Mettler TA 2000B differential scanning calorimeter.

RESULTS

The results are shown in the tables below.

Table 1

Example	Additive(s) (Concentration in ppm)	CFPP (°C)	SFPP (°C)
1	None	-2	Not measured
2	X (415)	-1	-3
3	1 (8)	0	2
4	2 (8)	-1	2
5	1 (8); X (415)	-12	-11
6	2 (8); X (415)	-12	-12

KEY: Fuel A was used in each of Examples 1 to 6
Additive X was a mixture of Additives 4, 5, 6, 7 and 8 in the weight ratio of 1:3:2:3:2.

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Table 2

Example	Fuel	Additive (Concentration in ppm)	Delta WAT (°C)
7	A	None	0
8	A	3 (300)	5.8
9	A	2 (300)	3.5
10	B	None	0
11	B	3 (300)	1.8
12	B	2 (300)	1.5

KEY: Delta WAT is the difference in WAT between the untreated and the treated fuel and therefore measures Cloud Point Depression.

The results of Table 1 show the synergy of demulsifier additives (i.e. 1 and 2) with other additives in filterability tests, and those of Table 2 show the effectiveness of demulsifier additives (i.e. 2 and 3) in producing cloud point depression.

Table 3

Example	Additive (Concentration in ppm)			SFPP
	10	6	9	°C
13		None		FAIL (-8)
14			20	FAIL (-8)
15	100		20	-10
16	100	200	20	-12
17	100			FAIL (-8)
18	100	200		-9

Examples 13 to 18 were carried out in Fuel C. The results show that SFPP performance was enhanced when the demulsifier (Additive 9) was used in combination with one or both of the cold flow additives (Additives 10 and 6) as in Examples 15 and 16.

CLAIMS:

1. An additive composition comprising:

(i) one or more non-metallic flow improving oil soluble addition products or condensates capable of improving, either jointly or singly, one or more cold flow properties of a crude oil or fuel oil; and

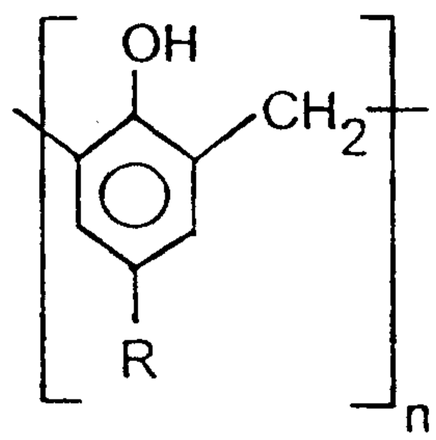
(ii) a non-metallic oil soluble demulsifier for crude oil- or fuel oil-water emulsions, said demulsifier having a hydrophobic part and a hydrophilic part and being selected from Groups I and II below where Group I is a condensate comprising, as the hydrophobic part, a part derived from a precursor having one or more groups capable of a condensation reaction to form oxyalkylated groups, bonded to one or more oxyalkylated groups comprising the hydrophilic part, and Group II is a compound having a sulphonate or sulphonic acid group as the hydrophilic part, attached to the hydrophobic part; provided that the component (i) is not a combination of a substituted succinic acid derivative and an ethylene-vinyl acetate copolymer.

2. The composition of claim 1 in admixture with a major proportion of a crude oil or a fuel oil, the composition constituting a minor proportion.

3. The composition of claim 1 dispersed in a liquid medium compatible with a crude oil or a fuel oil to form a concentrate.

4. The composition of any one of claims 1 to 3 wherein the demulsifier is of Group 1 where the hydrophobic part is derived from a precursor having one or more hydroxy groups, one or more of which hydroxy groups having been condensed to form the oxyalkylated groups bonded thereto.

5. The composition of claim 4 wherein the precursor has the general formula:



where R represents an aliphatic hydrocarbyl group having from 3 to 24 carbon atoms, and n represents an integer from 4 to 20.

6. The composition of claim 4 wherein the precursor is a linear mono- or poly-hydroxy compound, one or more of the hydroxy groups of which have been condensed to form the oxyalkylated groups.

7. The composition of any one of claims 1 to 4 wherein the demulsifier is of Group 1 where the hydrophobic part is derived from a precursor having one or more primary, secondary or tertiary amino groups or quaternary ammonium groups, one or more of which groups having been condensed to form the oxyalkylated groups bonded thereto.

8. The composition of any one of claims 1 to 7 wherein the demulsifier is of Group 1 where the or each oxyalkylated group has up to 50 oxyalkyl units per group capable of a condensation reaction, each such oxyalkyl unit having from 2 to 6 carbon atoms.

9. The composition of claim 2 or any one of claims 4 to 8 wherein the oil is a fuel oil and the demulsifier is present therein in a proportion by weight that is not greater than 50 ppm.

10. The composition of claim 2 or any one of claims 4 to 8 wherein the oil is a middle distillate fuel oil.

11. The composition of any one of claims 1 to 10 wherein the flow improving addition product or condensate is selected from one or more of:

(a) an ethylene-vinyl ester copolymer

(b) a comb-like polymer

(c) a polar nitrogen-containing compound or compounds comprising an amine

salt or an amide or both formed by reacting at least one molar proportion of

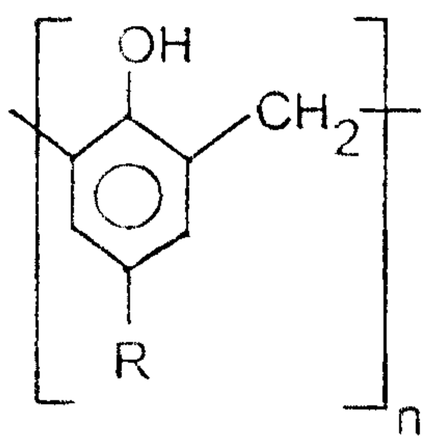
a hydrocarbyl substituted amine with a molar proportion of a hydrocarbyl

acid having 1 to 4 carboxylic acid groups or its anhydride.

12. The use of an additive composition as defined in claim 1 for improving the cold flow properties of a crude oil or a fuel oil.

13. The use of claim 12 wherein the demulsifier is of Group 1 where the hydrophobic part is derived from a precursor having one or more hydroxy groups, one or more of which hydroxy groups having been condensed to form the oxyalkylated groups bonded thereto.

14. The use of claim 13 wherein the precursor has the general formula:



where R represents an aliphatic hydrocarbyl group having from 3 to 24 carbon atoms, and n represents an integer from 4 to 20.

15. The use of claim 13 wherein the precursor is a linear mono- or poly-hydroxy

compound, one or more of the hydroxy groups of which have been condensed to form the oxyalkylated groups.

16. The use of claim 12 or 13 wherein the demulsifier is of Group 1 where the hydrophobic part is derived from a precursor having one or more primary, secondary or tertiary amino groups or quaternary ammonium groups, one or more of which groups having been condensed to form the oxyalkylated groups bonded thereto.

17. The use of any one of claims 12 to 16 wherein the demulsifier is of Group 1 where the or each oxyalkylated group has up to 50 oxyalkyl units per group capable of a condensation reaction, each such oxyalkyl unit having from 2 to 6 carbon atoms.

18. The use of any one of claims 12 to 17 wherein the oil is a fuel oil and the demulsifier is present therein in a proportion by weight that is not greater than 50 ppm.

19. The use of any one of claims 12 to 18 wherein the oil is a middle distillate fuel oil.

20. The use of any one of claims 12 to 19 wherein the flow improving addition product or condensate is selected from one or more of:

(a) an ethylene-vinyl ester copolymer

(b) a comb-like polymer

(c) a polar nitrogen-containing compound or compounds comprising an amine

salt or an amide or both 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.

21. The use of any one of claims 12 to 20 wherein the demulsifier has a Relative Solubility Number of from 4 to 25.