

Europäisches Patentamt European Patent Office Office européen des brevets



(11) **EP 1 568 756 A1**

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

31.08.2005 Bulletin 2005/35

(51) Int Cl.7: C10L 1/14

(21) Application number: 05251006.2

(22) Date of filing: 22.02.2005

(84) Designated Contracting States:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR Designated Extension States:

AL BA HR LV MK YU

(30) Priority: 24.02.2004 EP 04251003

(71) Applicant: Infineum International Limited
Oxfordshire OX13 6BB (GB)

(72) Inventor: Sutkowski, Andrew C Oxon, OX26 6YE (GB)

(74) Representative: Capaldi, Michael Joseph et al

Infineum UK Limited Law Department P.O. Box 1

Milton Hill

Abingdon, Oxfordshire OX13 6BB (GB)

(54) Conductivity improving additive for fuel oil compositions

(57) A fuel oil containing a conductivity improving additive comprising the combination of: (a) an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with an alkylene polyamine and (b) a conductivity improver comprising (i) an olefin polysulfone and (ii) a polymeric polyamine reaction product of epichlorohydrin and an aliphatic primary monoamine or an N-aliphatic hydrocarbyl alkylene diamine, or the sulfonic acid salt of the polymeric polyamine reaction product or (c) the combination of an oil soluble succinimide

dispersant comprising a functionalized hydrocarbon reacted with a heavy polyamine and (d) a conductivity improver comprising a hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer, wherein the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from about 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000.

Description

20

30

35

40

45

50

[0001] This invention relates to fuel oils which exhibit improved conductivity properties, to novel additive systems for providing such properties and to the use of such additives for improving the conductivity of fuel oils.

[0002] U.S. Patent 6,391,070, issued May 21,2002 to Schield discloses a composition having increased electrical conductivity, which includes a) a liquid hydrocarbon; b) an anti-static amount of at least one hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer, wherein the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from about 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000; and c) an anti-static amount of at least one hydrocarbon soluble polysulfone copolymer of at least one olefin and sulfur dioxide. These polymers are described by Schield in U. S. Patent 5,672,183 as containing a cationic quaternary ammonium monomer.

[0003] U.S. Patent 5,792,730 discloses the use of dispersants prepared from heavy polyamines as additives for lubricants and fuels.

[0004] The present invention is based upon the discovery that the use in combination of an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with an alkylene polyamine or with a heavy alkylene polyamine with certain commercial conductivity improvers results in a synergistic effect upon the conductivity properties of a fuel oil having little or no inherent conductivity.

[0005] The invention is particularly useful for the formulation of turbine combustion fuel oils which are generally those hydrocarbon fuels having boiling ranges within the limits of about 150° to 600°F (65 to 315°C) and are designated by such terms as JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1. JP-4 and JP-5 are fuels defined by U.S. military specification MIL-T-5624-N and JP-8 is defined by U.S. Military Specification MILT83133-D. Jet A, Jet A-1 and Jet B are defined by ASTM specification D1655.

[0006] In accordance with the present invention there has been discovered an improved fuel oil composition comprising a fuel oil having an inherent conductivity of less than 15 pS/m and a two component additive system; wherein the two component additive system comprises the combination of:

- (a) an oil soluble succinimide dispersant additive prepared from a functionalized hydrocarbon or polymer reacted with an alkylene polyamine; and,
- (b) a conductivity improver comprising (i) an olefin polysulfone and (ii) a polymeric polyamine reaction product of epichlorohydrin and an aliphatic primary monoamine or an N-aliphatic hydrocarbyl alkylene diamine, or the sulfonic acid salt of the polymeric polyamine reaction product,
- or the combination of:
- (c) an oil soluble succinimide dispersant additive prepared from a functionalized hydrocarbon or polymer reacted with a heavy polyamine; and,
- (d) a conductivity improver comprising a hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer, wherein the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from about 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000.

[0007] The oil soluble succinimide dispersant (a) may be represented by the formula: HRN(alkylene-NR)nH wherein n has an average value between 1 and about 11, and in one embodiment about 2 to about 7, the "alkylene" group has from 1 to about 10 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and each R is independently hydrogen, an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms. Some examples of alkylene polyamines include methylene polyamines, ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, etc. Specific examples of such polyamines include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene diamine, tripropylene tetramine, tetraethylene pentamine, hexaethylene heptamine, pentaethylene hexamine, or a mixture of two or more thereof. Ethylene polyamines such as tetraethylene pentamine and pentaethylene hexamine are preferred. Suitable alkylene polyamines also include those termed "heavy polyamines" as defined hereinbelow.

[0008] The weight ratio of the olefin polysulfone to the polymeric polyamine in component (b) is preferably in the range of 40:1 to 1:40.

[0009] The heavy polyamine as the term is used herein includes higher oligomers or mixtures of higher oligomers of polyalkylene, e.g. polyethylene, amines containing, e.g., essentially no tetraethylenepentamine, at most small amounts of pentaethylenehexamine, but primarily oligomers with 6 to 12, preferably 7 to 12, nitrogens per molecule, with 2 or more primary amines per molecule, and more branching than conventional polyamine or polyamine mixtures. The heavy polyamine comprises more than 28 wt.% (e.g. > 32 wt.%) total nitrogen and an equivalent weight of primary amine groups of 120-160 grams per equivalent. Commercial dispersants are based on the reaction of carboxylic acid moieties with a polyamine such as tetraethylenepentamine (TEPA) with five nitrogens per molecule. Commercial TEPA is a distillation cut and contains oligomers with three and four nitrogens as well. Other commercial polyamines known

generically as PAM, contain a mixture of ethylene amines where TEPA and pentaethylene hexamine (PEHA) are the major part of the polyamine, usually less than about 80%. Typical PAM is commercially available from suppliers such as the Dow Chemical Company under the trade name E-100 or from the Union Carbide Company as HPA-X. This mixture typically consists of less than 1.0 wt.% low molecular weight amine, 10-15 wt.% TEPA, 40-50 wt.% PEHA and the balance hexaethyleneheptamine (HEHA) and higher oligomers. Typically PAM has 8.7-8.9 milliequivalents of primary amine per gram (an equivalent weight of 115 to 112 grams per equivalent of primary amine) and a total nitrogen content of about 33-34 wt.%.

[0010] Alkylene polyamines in general, including heavy polyamines, exhibit synergy with the olefin polysulfonic/polymeric polyamine conductivity improver while only the heavy polyamines exhibit synergy with the copolymeric conductivity improver.

[0011] The oil soluble dispersant additive used in the present invention is prepared by a derivatization (imidization), using an alkylene polyamine, of functionalized hydrocarbons or polymers wherein the polymer backbones have a number average molecular weight (Mn) of greater than 300. Preferably 800 to 7500, most preferably 900 to 3000. The preferred number average molecular weight depends on the properties of the particular backbone. For example, for ethylene alpha olefin copolymers the preferred molecular weight is 1500 to 5000 (e.g. 2000 - 4000). For polybutenes the preferred molecular weight is 900 to 3000. A typical example of functionalized polymer is polyisobutenyl succinic anhydride (PIBSA) which is a reaction product of polyisobutene and maleic anhydride. This reaction can occur via halogen-assisted functionalization (e.g. chlorination), the thermal "ene" reaction, or free radical addition using a catalyst (e.g. a peroxide). These reaction are well known in the art. In the present invention the functionalized backbones are subsequently derivatized with an alkylene polyamine. In the case of PIBSA, the reaction with the polyamine yields a polyisobutenyl succinimide.

[0012] The weight average molecular weight of the polysulfone will be in the range of 10,000 to 1,500,000 with the preferred range being 50,000 to 900,000 and the most preferred molecular weight range being in the range of about 100,000 to 500,000. The olefins useful for the preparation of the polysulfones may have about 6 to 20 carbon atoms, preferably about 6 to 18 carbon atoms, with 1-decene polysulfone being particularly preferred. The preparation of these materials is known in the art as described for example in U.S. Patent 3,917,466. The polymeric polyamine component is prepared by heating an amine with epichlorohydrin in the molar proportions of 1:1 to 1:1.5 in the range of 50°C to 100°C. Suitable aliphatic primary amines will have about 8 to 24 carbon atoms, preferably about 8 to 12 carbon atoms, with the aliphatic group being preferably an alkyl group. If the amine used is an N-aliphatic hydrocarbyl alkylene diamine, the aliphatic hydrocarbyl group will have 8 to 24 carbon atoms and will preferably be alkyl and the alkylene group will have 2 to 6 carbon atoms. The preferred N-aliphatic hydrocarbyl alkylene diamine is N-aliphatic hydrocarbyl 1,3-propylenediamine which are commercially available. A preferred commercially available polymeric polyamine is believed to be the polymeric reaction product of N-tallow-1,3-propylenediamine with epichlorohydrin sold as "Polyflo 130" sold by Universal Oil Co. The polymeric polyamine reaction product will have a degree of polymerization of about 2 to 20. The description of these materials is also disclosed in U.S. Patent 3,917,466.

[0013] Preferably, the polymeric polyamine reaction product component will be used in the form of a sulfonic acid salt. Useful are oil soluble sulfonic acids such as alkane sulfonic acid or an aryl sulfonic acid. Particularly suitable is dodecyl benzene sulfonic acid or dinonyl naphthalene sulphonic acid.

[0014] The hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer is described in and may be made by the procedures of U.S. Patent No. 5,672,183, the entirety of which is incorporated by reference herein. In a preferred embodiment, the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000. In another embodiment, the cationic vinyl monomer is a cationic quaternary ammonium vinyl monomer, and in a preferred embodiment is a cationic quaternary ammonium acrylate monomer or a cationic quaternary ammonium methacrylate monomer. In another embodiment, the cationic vinyl monomer corresponds to the formula:

55

10

15

20

30

35

40

45

50

wherein Z is selected from the group consisting of nitrogen, phosphorus and sulfur, X is a non-halogen atom, R is selected from the group consisting of $-C(=0)O_-$,

C(=O)NH-, straight chain and branched alkylene groups, divalent aromatic groups and divalent alicyclic groups, R³ is selected from the group consisting of hydrogen and methyl, R⁴ is a straight chain or branched alkylene of up to about twenty carbon atoms (C₁-C₂₀), and R⁵, R⁶ and R⁷ are independently each a straight chain or branched alkyl of up to about twenty carbon atoms, provided however that if Z is sulfur R⁷ is absent. Optionally, a copolymer of an alkyl vinyl monomer and a nitrile-containing monomer may be used in conjunction with the copolymer of alkylvinyl monomer and cationic vinyl monomer.

5

20

30

35

40

45

50

[0015] The oil-soluble succinimide dispersants are used in the compositions of the present invention (on an active ingredient basis, i.e., without regard to carrier oil or solvent) in amounts ranging from 5 - 400 ppm, preferably about 10 - 160 ppm (by weight), such as about 10 - 60 ppm.

[0016] The polysulfonic-polyamine mixture conductivity improver or the alkylvinyl monomer-cationic vinyl monomer copolymer conductivity improver may each be used in amounts from 0.10-5 ppm, preferably about 0.25-1 ppm.

[0017] The compositions of this invention may also contain a phenolic antioxidant and the amount of phenolic antioxidant compound incorporated may vary over a range of about 1 - 100 ppm, preferably about 10 - 50 ppm, such as about 25 ppm by weight.

[0018] The preferred antioxidant phenolic compounds are the hindered phenolics which are those which contain a sterically hindered hydroxyl group. These include those derivatives of dihydroxy aryl compounds in which the hydroxyl groups are in the o- or p- position to each other. Typical phenolic antioxidants include the hindered phenols substituted with alkyl groups of a total of 6 or more carbon atoms and the alkylene-coupled derivatives of these hindered phenols. Examples of phenolic materials of this type are 2,6-di-t-butyl-4-methyl phenol (BHT, butylated hydroxy toluene); 2-t-butyl-4-heptyl phenol; 2-t-butyl-4-octyl phenol; 2-t-butyl-4-dodecyl phenol; 2,6-di-t-butyl-4-heptyl phenol; 2,6-di-t-butyl-4-dodecyl phenol; 2-methyl-6-di-t-butyl-4-heptyl phenol; and 2-methyl-6-di-t-butyl-4-dodecyl phenol. Examples of ortho coupled phenols include 2,2'-bis(6-t-butyl-4-heptyl phenol); 2,2'-bis(6-t-butyl-4-octyl phenol); and 2,2'-bis(6-t-butyl-4-dodecyl phenol). Sulfur containing phenols can also be used. The sulfur can be present as either aromatic or aliphatic sulfur within the phenolic antioxidant molecule. BHT is especially preferred, as are 2,6- and 2,4-di-t-butylphenol and 2,4,5- and 2,4,6-triisopropylphenol, especially for use in jet fuels.

[0019] The compositions will preferably contain about 0.1 - 50 ppm of a metal deactivator, preferably 1 - 10 ppm by weight. Examples of suitable metal deactivators include:

- (a) Benzotriazoles and derivatives thereof, for example, 4- or 5-alkylbenzotriazoles (e.g. tolutriazole) and derivatives thereof; 4,5,6,7-tetrahydrobenzotriazole and 5,5'-methylenebisbenzotriazole; Mannich bases of benzotriazole or tolutriazole, e.g. 1-[bis(2-ethylhexyl)aminomethyl]tolutriazole and 1-[bis(2-ethylhexyl)aminomethyl]benzotriazole; and alkoxyalkylbenzotriazoles such as 1-(nonyloxymethyl)-benzotriazole, 1-(1-butoxyethyl)benzotriazole and 1-(1-cyclohexyloxybutyl)-tolutriazole;
 - (b) 1,2,4-triazoles and derivatives thereof, for example, 3-alkyl(or aryl)-1,2,4-triazoles, and Mannich bases of 1,2,4-triazoles, such as 1-[bis(2-ethylhexyl)aminomethyl-1,2,4-triazole; alkoxyalkyl-1,2,4-triazoles such as 1-(1-butoxytheyl)-1,2,4-triazole; and acylated 3-amino-1,2,4-triazoles;
 - (c) Imidazole derivatives, for example, 4,4'-methylenebis(2-undecyl-5-methylimidazole) and bis[(N-methyl)imidazole-2-yl]carbinol octyl ether;
 - (d) Sulfur-containing heterocyclic compounds, for example 2-mercaptobenzothiazole, 2,5-dimercapto-1,3,4-thiadiazole and derivatives thereof; and 3,5-bis[di(2-ethyl-hexyl)aminomethyl]-1,3,4-thiadiazolin-2-one; and
 - (e) Amino compounds and imino compounds, such as N,N'-disalicylidene propylene diamine, which is preferred, salicylaminoguanadine and salts thereof.

[0020] The fuel oil compositions of this invention may also contain one or more other additives commonly employed in fuels and present in such amounts so as to provide their normal attendant functions. Examples are cold flow improvers such as ethylene-unsaturated ester copolymers, comb polymers containing hydrocarbyl groups pendant from a polymer backbone, polar nitrogen compounds, compounds having a cyclic ring system having at least two substituents of the formula -A-NR¹⁵R¹⁶ where A is linear or branched hydrocarbylene and R¹⁵ and R¹⁶ are C₉-C₄₀ hydrocarbyl, hydrocarbon polymers such as ethylene alpha-olefin copolymers, polyoxyethylene esters, ethers and ester/ether mixtures such as behenic diesters of polyethylene glycol. Other additives include lubricity additives such as fatty acids, dimers of fatty acids, esters of fatty acids or dimers of fatty acids, corrosion inhibitors, anti-icing additives such as ethylene glycol monomethyl ether or diethylene glycol monomethyl ether, biocides, thermal stability additives, anti-rust agents, anti-foam agents, demulsifiers, detergents, dispersants, cetane improvers, stabilisers, antioxidants, static dissipator additives and the like.

[0021] The fuel oil may be a hydrocarbon fuel such as a petroleum-based fuel oil for example gasoline, kerosene or distillate fuel oil. 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 dis-

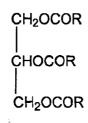
tillate fuels are kerosene, jet fuels, diesel fuels, low sulfur diesel fuels and ultra low sulfur diesel fuels, automotive gas oil, heating oils, premium heating oils and heavy fuel oils. The heating oil or diesel fuel may be a straight atmospheric distillate, or it may contain minor amounts, e.g. up to 35 wt.%, of vacuum gas oil or cracked gas oils or of both.

[0022] 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).

[0023] The fuel oil may have a sulfur concentration of 0.2% by weight or less based on the weight of the fuel. Preferably, the sulfur concentration is 0.05% by weight or less, such as 0.035% by weight or less or 0.01% by weight or less. The art describes methods for reducing the sulfur concentration of hydrocarbon middle distillate fuels, such methods including solvent extraction, sulfuric acid treatment, and hydrodesulfurisation. The additive of the invention is advantageous in the fuels having low sulfur contents, providing lubricity improvement and detergency.

[0024] Also, the fuel oil may be a biofuel, i.e. come from an animal or vegetable source, for example a vegetable or animal oil or both or derivatives thereof, or a mineral oil as described above in combination with biofuel.

[0025] Vegetable oils are mainly triglycerides of monocarboxylic acids, e.g. containing 10-25 carbon atoms of the structure shown below:



25

30

35

45

15

20

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

[0026] Generally, such oils contain glycerides of a number of acids, the number and kind varying with the source vegetable of the oil.

[0027] Examples of oils are rapeseed oil, tall oil, coriander oil, soyabean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almond oil, palm kernel oil, coconut oil, mustard seed oil, beef tallow and fish oils. Rapeseed oil, which is a mixture of fatty acids esterified with glycerol, is preferred as it is available in large quantities and can be obtained in a simple way by pressing from rapeseed.

[0028] Examples of derivatives thereof are alkyl esters, such as methyl esters, of fatty acids of the vegetable or animal oils. Such esters can be made by transesterification. The preferred alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linoleic acid and erucic acid.

[0029] Commercial mixtures of the stated kind are obtained for example by cleavage and esterification of natural fats and oils by their transesterification with lower aliphatic alcohols. For production of lower alkyl esters of fatty acids, it is advantageous to start from fats and oils with high iodine number, such as, for example, sunflower oil, rapeseed oil, coriander oil, castor oil, soyabean oil, cottonseed oil, peanut oil or beef tallow. Lower alkyl esters of fatty acids based on a new variety of rapeseed oil, the fatty acid component of which is derived to more than 80 wt.% from unsaturated fatty acids with 18 carbon atoms, are preferred.

[0030] The invention is particularly useful for the formulation of turbine combustion fuel oils (jet fuels) which are generally those hydrocarbon fuels having boiling ranges within the limits of about 150° to 600°F (65 to 315°C) and are designated by such terms as JP-4, JP-5, JP-7, JP-8, Jet A, Jet A-1. JP-4 and JP-5 are fuels defined by U.S. military specification MIL-T-5624-N and JP-8 is defined by U.S. Military Specification MIL-T83133-D. Jet A, Jet A-1 and Jet B are defined by ASTM specification D1655.

[0031] The invention will now be described by way of example only.

50 EXAMPLES

[0032] The three fuels described below were tested.

55

Fuel Details:				
		Base Fuel 2	Base Fuel 3	Base Fuel 4
Test	Units	Result	Result	Result
Density @15°C	Kg/L	814	829	835
Distillation				
IBP	°C	168	174.6	216.6
10%		184.2	228.9	240.7
50%		210.2	274.0	277.0
90%		235.2	322.7	327.6
FBP		255	349.2	358.1
RESIDUE	vol%	1.1	2.0	2.0
LOSS	vol%	1	0	0
FIA Analysis	vol%			
Aromatics		15.2		28.2
Total Sulfur IP 336/95	%m/m	0.0006	<0.001	0.0036
Flash Point (Abel) IP 170/99		54		
Freezing point IP16/98		-54		
Viscosity at -20C IP71		5.48		
Existent gum		<1		
СР				-20
CFPP			-9	-19

40	Code	Description of Additive
	Dispersant A	a succinimide made from a polyisobutenyl (Mn 950) succinic anhydride reacted with a heavy polyamine having a 10-12% pentaethylene hexamine content, 32% nitrogen and 7.7 meq/g of primary nitrogen, the succinimide having 3.85% nitrogen.
45	Dispersant B	a succinimide made from a polyisobutenyl (Mn 1000) succinic anhydride and the same heavy polyamine used to make Dispersant A, the succinimide having 4.74% nitrogen.
	Dispersant C	a succinimide made from a polyisobutenyl (Mn 950) succinic anhydride reacted with a commercial PAM mixture of ethylene polyamines, the succinimide having 2.0% nitrogen.
50	Dispersant D	a succinimide made from a polyisobutenyl (Mn 1000) succinic anhydride reacted with tetraethylene pentamine the succinimide having 1.35% nitrogen
	Dispersant E	a succinimide made from a polyisobutenyl (Mn 2250) succinic anhydride reacted with pentaethylene hexamine the succinimide having 0.7% nitrogen
	Stadis 450	66% toluene, 13.3% 1-decene polysulfone, 13.3% polyamine (a reaction product of N-tallow-1,3-propylenediamine and epichlorohydrin) and 7.4% dodecylbenzene sulfonic acid.
55	T3514	a commercial hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer sold as "T3514" by Baker Petrolite as a conductivity improver.

Fuel Conductivity Tests

5

[0033] The fuels described above were tested for conductivity using an EMCEE 1152 conductivity meter. The results are given in Table 1 below. Tests were carried out on the fuel without any additives, fuels 2, 3 and 4 containing each of Dispersant A and B (which were dispersants made with heavy polyamines), Stadis 450 and T3514, the latter two being commercial conductivity additives. Fuels containing a combination of this invention exhibit a synergistic cooperative effect in low conductivity fuels not predictable from the values obtained when the additives are tested individually. "BF" refers to Base Fuel. Dispersants C, D and E (made with conventional ethylene polyamines, i.e., not the heavy type) were tested only in fuel 2 and showed synergy with the "Stadis 450" commercial conductivity improver. Dispersants made from the heavy polyamines show synergy with both types of commercial conductivity improvers.

	Additive	ppm	Conductivity (pS/m) BF 3	Conductivity (pS/m) BF 4	Conductivity (pS/m) BF 2
15	Base Fuel	0	18	1.7	3
	Stadis 450	0.25	39.7	38.7	55
	T3514	0.25	46.7	9.7	58
	Dispersant A	33	65	34.7	523
20	Dispersant A + Stadis 450	33 + 0.25	96.7	131.3	707
	Predicted Dispersant A + Stadis 450		104.7	73.4	578
25	Dispersant A + T3514	33 + 0.25	93.7	78	617
	Predicted Dispersant A + T3514		111.7	44.4	581
	Dispersant B	40	150	106.3	825
30	Dispersant B + Stadis 450	40 + 0.25	189.7	202.3	954
	Predicted Dispersant B + Stadis 450		189.7	145	880
35	Dispersant B + T3514	40 + 0.25	195.3	153.3	923
	Predicted Dispersant B + T3514		196.7	116	883
40	Dispersant C	25			188
40	Dispersant C + Stadis 450	25 + 0.25			317
	Predicted Dispersant C + Stadis 450				243
45	Dispersant D	19			100
	Dispersant D + Stadis 450	19 + 0.25			240
50	Predicted Dispersant D + Stadis 450				155
	Dispersant E	29			35
55	Dispersant E + Stadis 450	29 + 0.25			147
00	Predicted Dispersant E + Stadis 450				90

Claims

5

10

15

25

30

40

45

- 1. An improved fuel oil composition, the composition comprising a fuel oil having an inherent conductivity of less than 15 pS/m and a two component additive system; wherein the two component additive system comprises the combination of:
 - (a) an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with an alkylene polyamine; and
 - (b) a conductivity improver comprising (i) an olefin polysulfone and (ii) a polymeric polyamine reaction product of epichlorohydrin and an aliphatic primary monoamine or an N-aliphatic hydrocarbyl alkylene diamine, or the sulfonic acid salt of the polymeric polyamine reaction product, or the combination of :
 - (c) an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with a heavy polyamine, and
 - (d) a conductivity improver comprising a hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer, wherein the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from about 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000.
- 20 2. A composition according to claim 1, wherein the dispersant is a polyisobutenyl succinimide.
 - 3. A composition according to claim 1 or claim 2 further comprising an antioxidant.
 - 4. A composition according to any preceding claim further comprising a metal deactivator.
 - 5. A composition according to any of claims 2 to 4, wherein the polyisobutenyl has a molecular weight of 900 3000.
 - **6.** A composition according to any preceding claim further comprising one or more additives selected from the group consisting of cold flow improvers, lubricity additives, corrosion inhibitors, anti-icing additives, biocides, thermal stability additives, anti-foam agents, anti-rust agents, demulsifiers, detergents, dispersants, stabilisers, static dissipator additives and cetane improvers.
 - 7. A composition according to any preceding claim, wherein the fuel oil is a turbine combustion fuel oil.
- 35 **8.** A composition according to any of claim 1 to 6, wherein the fuel oil is a diesel fuel or a heating oil.
 - **9.** A conductivity improving additive comprising the combination of :
 - (a) an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with an alkylene polyamine; and
 - (b) a conductivity improver comprising (i) an olefin polysulfone and (ii) a polymeric polyamine reaction product of epichlorohydrin and an aliphatic primary monoamine or an N-aliphatic hydrocarbyl alkylene diamine, or the sulfonic acid salt of the polymeric polyamine reaction product, or the combination of:
 - (c) an oil soluble succinimide dispersant comprising a functionalized hydrocarbon reacted with a heavy polyamine, and
 - (d) a conductivity improver comprising a hydrocarbon soluble copolymer of an alkylvinyl monomer and a cationic vinyl monomer, wherein the copolymer has an alkylvinyl monomer unit to cationic vinyl monomer unit ratio of from about 1:1 to about 10:1, the copolymer having an average molecular weight of from about 800 to about 1,000,000.
 - **10.** The use of an additive according to claim 9 to improve the conductivity of a fuel oil.

55

50



EUROPEAN SEARCH REPORT

Application Number EP 05 25 1006

	DOCUMENTS CONSIDER	RED TO BE RELEVANT			
Category	Citation of document with indic of relevant passages		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CI.7)	
X,D	US 3 917 466 A (HENRY 4 November 1975 (1975		10	C10L1/14	
Υ	* the whole document	*	1-9		
X,D	US 5 672 183 A (SCHIE 30 September 1997 (19		10		
Υ	* the whole document	*	1-9		
X,D	US 2001/048099 A1 (SC 6 December 2001 (2001		10		
Υ	* the whole document		1-9		
Υ	US 5 089 028 A (AVERY 18 February 1992 (199 * column 5, line 57 - claims 1,3 *	2-02-18)	1-9		
A	US 5 254 138 A (KUREK 19 October 1993 (1993 * column 3, line 16 -	(-10-19)	1-10 *	TECHNICAL FIELDS SEARCHED (Int.Cl.7)	
				C10L	
	The present search report has bee	n drawn up for all claims Date of completion of the search		Examiner	
	Munich	26 April 2005	Ke	eipert, O	
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document		E : earlier patent d after the filing d D : document cited L : document cited	T: theory or principle underlying the in E: earlier patent document, but public after the filing date D: document cited in the application L: document cited for other reasons		
			 : member of the same patent family, corresponding document 		

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 05 25 1006

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26-04-2005

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 3917466	A	04-11-1975	CA DE FR GB JP JP JP	1533418 988910 51069503	A1 A1 A	18-09-19 06-05-19 28-05-19 22-11-19 29-02-19 16-06-19 12-07-19
US 5672183	A	30-09-1997	AT CA DE DK EP ES JP NO PT WO	2267057 69725138 69725138 909305 0909305 2208888 3631497 2001507380	D1 T2 T3 A1 T3 B2 T A	15-10-20 08-01-19 30-10-20 22-07-20 15-12-20 21-04-19 16-06-20 23-03-20 05-06-20 17-02-19 27-02-20 08-01-19
US 2001048099	A1	06-12-2001	AU CA EP JP TW WO	5553401 2404458 1274819 2004509173 574366 0181512	A1 A2 T B	07-11-20 01-11-20 15-01-20 25-03-20 01-02-20 01-11-20
US 5089028	А	18-02-1992	AU AU EP JP WO	646089 8519391 0542904 5508436 9202601	A A1 T	10-02-19 02-03-19 26-05-19 25-11-19 20-02-19
US 5254138	Α	19-10-1993	NONE	:		

FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82