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(54) **Use of an additive in a fuel oil composition as a flow improver**

Verwendung eines Additives in einer Brennstoffölzusammensetzung als Fliessverbesserer

Utilisation d'un additif dans une composition de fuel-oil comme agent améliorant l'écoulement

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EP 0 343 981 B2

Description

Description for the following Contracting States : DE, ES, FR, GB, IT

This invention relates to fuel oil compositions containing a flow improver.

Wax separation in crude oils, middle distillate fuels, heavy and residual fuels and lubricating oils limits their flow at low temperatures. The usual method of overcoming these problems is to add wax crystal modifying compounds that cause the wax crystals to be smaller (nucleators) and/or to be smaller and to grow into more compact shapes (growth inhibitors).

Another difficulty is that small wax crystals can stick together and form larger agglomerates and these agglomerates as well as the individual crystals can block the filter screens through which the individual crystals would pass and they will settle more rapidly than do the individual, small crystals.

We have now found that the wax crystals may be modified so as to improve filterability and reduce the pour point and the tendency of the wax crystals to agglomerate may be reduced by the addition of certain amino or quaternary ammonium salts.

JP Patent Publication No. 56-54038 describes fuel oils containing copolymers of olefins and maleic anhydride derivatised to amide or amide/amine salt groups, in combination with certain other additives. JP Patent Application No. 61-211397 describes fuel oils containing an esteramide or esteramidoamine salt of a specific α-olefin/maleic anhydride copolymer.

EP-A-0 283 293 describes flow improver polymers containing more than one amide group derived from a secondary amine.

According to this invention, there is provided use in a fuel oil composition as a flow improver, alone or in combination with another flow improver, of an additive comprising a polymer or copolymer containing more than one amino group in the form of a salt of a primary or tertiary amine or a quatemary ammonium salt, said copolymer being derived from an intermediate polymer or copolymer containing acid or anhydride groups and selected from one or more of the following:

I. a polymer of one or more unsaturated ester also including a free acid group or from a copolymer of unsaturated ester monomers at least one of which has a free acid group,

II. a copolymer of an unsaturated carboxylic acid ester with an unsaturated carboxylic anhydride,

III. a polymer or copolymer obtained by partial hydrolysis of a polymer or copolymer containing ester groups so as to obtain carboxylic acid or anhydride groups,

IV. a polymer or copolymer obtained by reaction of a polymer as defined in III above with a carboxylic anhydride,

and reaction with an amino compound selected from primary or tertiary alkyl amines and tetraalkyl ammonium halides, said polymer or copolymer having at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms.

The liquid hydrocarbon fuel oils can be distillate fuel oils, such as the middle distillate fuel oils, e.g. a diesel fuel, aviation fuel, kerosene, fuel oil, jet fuel, heating oil, etc. Generally, suitable distillate fuels are those boiling in the range of 120°C to 500°C (ASTM D86). preferably those boiling in the range 150°C to 400°C. A representative heating oil specification calls for a 10 percent distillation point no higher than about 226°C, a 50 percent point no higher than about 272°C and a 90 percent point of at least 282°C and no higher than about 338°C to 343°C, although some specifications set the 90 percent point as high as 357°C. Heating oils are preferably made of a blend of virgin distillate, e.g. gas oil, naphtha, etc. and cracked distillates, e.g. catalytic cycle stock.

The polymer containing more than one amino group can be prepared by reacting a polymer having a plurality of carboxylic acid or anhydride groups with a primary or tertiary amine.

To prepare the quaternary ammonium salts the polymers can be reacted with a tetra-hydrocarbyl ammonium halide. Alternatively, they may be prepared by reaction of a tertiary amine with a hydrocarbyl halide and so the polymer from which the desired polymer is derived should have halide groups and be reacted respectively with a tertiary amine.

Examples of, and further details of, the different types of polymer ((I to IV) of this invention which can be further reacted to produce the desired polymer containing two or more amine salt groups are as follows:

(I) Copolymers of a dialkyl fumarate, maleate, citraconate or itaconate; copolymers of vinyl acetate with a monoalkyl fumarate, maleate, citraconate or itaconate; copolymers of an alkyl acrylate or an alkyl methacrylate with a monoalkyl fumarate, maleate, citraconate or itaconate; and copolymers of a dialkyl fumarate, maleate, citraconate or itaconate with a monoalkyl fumarate and with vinyl acetate.

Particularly suitable examples of type I polymers are a copolymer of vinyl acetate and a monoalkyl fumarate and a dialkyl fumarate where the alkyl groups are 1:1 mixtures of dodecyl and tetra decyl and copolymers of vinyl

acetate and either mono dodecyl, mono tetra decyl or mono hexadecyl fumarate.

(II) These copolymers on reaction with a primary or secondary amine can give half amide/half amine salts due to reaction with the anhydride group. Specific examples are copolymers (a) of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride, or (b) of vinyl esters, e.g. vinyl acetate or vinyl stearate with maleic anhydride, or (c) of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride and vinyl acetate.

Particularly suitable examples of Type II polymers are copolymers of didodecyl fumarate, vinyl acetate and maleic anhydride; di-tetradecyl fumarate, vinyl acetate and maleic anhydride, dihexadecyl fumarate, vinyl acetate and maleic anhydride; or the equivalent copolymers where instead of the fumarate the itaconate is used.

(III) The partially hydrolysed polymer is reacted with an amine to produce the desired polymer containing two or more amine salt groups. Thus, one may partially hydrolyse polymers of acrylates, methacrylates, alkyl fumarates, alkyl maleates or copolymers thereof or copolymers thereof with an olefin.

In all of the above mentioned types of suitable polymer (I, II and III) the desired amine salt is obtained by reacting the polymer containing carboxylic acid or anhydride groups with a primary-, secondary- or tertiary amine to obtain the corresponding amine salt, (optionally also with a alcohol whence an ester-amine salt is formed). Very often, for example when reacting polymers containing an anhydride group, the resulting amino groups will be amine salts and amides. Such polymers can be used, provided that they contain at least two amine salt groups.

To prepare a quaternary ammonium salt any of the above described polymers (I, II or III) is reacted with a tetra hydrocarbyl ammonium halide or the polymers are converted so that they contain halide groups instead of carboxylic acid groups or they are formed by polymerising with an unsaturated halide, for example vinyl chloride. They would then be reacted with a tertiary amine so as to form the quaternary ammonium salt.

(IV) Suitable polymers of unsaturated esters are homo polymers of acrylates, methacrylates, alkyl fumarates or copolymers thereof with an olefin, for example ethylene or a copolymer of vinyl acetate with an olefin. A specific example is an ethylene-vinyl acetate copolymer. After partial hydrolysis the polymer is reacted with an acid anhydride, e.g. succinic or maleic anhydride and the resulting product can be reacted with a p- or t-amine to obtain the corresponding amine salt, or with a tetrahydrocarbyl ammonium halide to obtain the corresponding quaternary ammonium salt.

As stated, said polymer, or copolymer has at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms. Preferably there are 12 to 18 carbon atoms in at least one of said groups. Any such group which is preferably a straight chain or branched alkyl groups, can be present either attached directly or through a carboxylate group to the backbone of the polymer or attached to the nitrogen atom of the amine salt or quaternary ammonium salt group. The polymers may also contain such groups attached both to the nitrogen atom and to the backbone or to the carboxylate group. Thus in Type I, II and III polymers the alkyl groups of the mono- and di-alkyl fumarate, of the alkyl acrylate or of the alkyl methacrylate from which the polymers are derived can contain at least 10 carbon atoms. Particularly suitable monomers are therefore di dodecyl fumarate, di tetra decyl fumarate, di octadecyl fumarate and the corresponding mono alkyl fumarates and mixtures thereof. Also dodecyl, tetradecyl, hexadecyl and octadecyl acrylates and methacrylates are particularly suitable. In type III polymers one could use for example di-decyl, di-dodecyl, di-tetradecyl maleates.

As an alternative or an addition one can introduce the long chain group into the polymer by using a long chain p- or t-amine or tetrahydrocarbyl ammonium halide or mixtures thereof in forming the salt.

The amines can be represented by the formulae

$$R^1NH_2$$

and

$$R^1R^2R^3N$$

and the tetrahydrocarbyl ammonium halide by the formula

$$R^1R^2R^3R^4NX$$

wherein R^1, R^2, R^3, and R^4 are hydrocarbyl groups, preferably alkyl groups and wherein at least one of R^1, R^2, R^3 and R^4 preferably contains at least 10 carbon atoms, for instance 12 to 18 carbon atoms, for example dodecyl, tetradecyl, hexadecyl and octadecyl and wherein X is halogen, preferably chlorine.

Suitable polyamines can be represented by the formulae $H_2N[RHN]_xH$ where R is a divalent hydrocarbyl group, preferably alkylene or hydrocarbyl substituted alkylene and x is an integer.

Examples of suitable primary amines are hexyl amine, octyl amine, and those containing at least 10 carbon atoms, for instance decyl amine, tetradecyl amine, octadecyl amine, eicosylamine, the mixed amine RNH_2 (Armeen C) where R is 0.5 wt % C_6 alkyl, 8 wt % C_8 alkyl, 7 wt % C_{10} alkyl, 50 wt % C_{12} alkyl, 18 wt % C_{14} alkyl, 8 wt % G_{16} alkyl, 1.5 wt % C_{18} alkyl and 7.0 wt % C_{18}/C_{19} unsaturated.

Examples of suitable tertiary amines are tri hexyl amine, tri octyl amine and those containing alkyl groups with at least 10 carbon atoms, for instance, hexyl di-decyl amine, tri decyl amine and tri hexadecyl amine.

Examples of suitable quaternary ammonium halides are tri-octyl-methyl ammonium chloride, and those containing alkyl groups with at least 10 carbon atoms, for instance tri-dodcyl-methyl ammonium chloride, tri-tetradecyl, dodecyl ammonium chloride and hexadecyl, dimethyl, phenyl amine.

The polymer salts of this invention usually have a number average molecular weight of 1,000 to 500,000, for example 10,000 to 100,000.

Particularly suitable examples of amino group-containing polymers for use in the present invention are:

(1) A copolymer of 50.0 mole % vinyl acetate, 45.0 mole % di C_{12}/C_{14} alkyl (1:1) fumarate and 5 mole % maleic anhydride reacted with 5 mole % trioctylamine to produce the half amide, half amine salt of the carboxylic acid groups derived from the maleic anhydride units of the copolymer.

(2) A copolymer as (1) above but formed by the reaction of 5 mole % of trioctyl-methyl ammonium chloride and 5 mole % of sodium hydroxide in the minimum amount of water instead of trioctylamine. This results in the quaternary ammonium salt of the polymer.

(3) A copolymer of di-tetradecyl fumarate, vinyl acetate and maleic anhydride, (the mole ratio of acetate:fumarate: anhydride being approximately 50:45:5) reacted with a mixture of dodecylamine and tetradecylamine.

(4) Copolymers as (1) to (3) above where the copolymer is based on equimolar proportions of alkyl fumarate and vinyl acetate but where the amount of maleic anhydride is 10 mole % based on the total weight of the fumarate and vinyl acetate.

Improved results are often achieved when the fuel compositions of this invention incorporate other additives known for improving the cold flow properties of distillate fuels generally. Examples of these other additives are the polyoxyalkylene esters, ethers, ester/ethers, amide/esters and mixtures thereof, particularly those containing at least one, preferably at least two C_{10} to C_{30} linear saturated alkyl groups of a polyoxyalkylene glycol 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. EP-A-0,061,895 describe some of these additives.

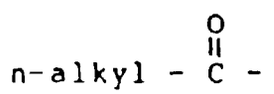
The preferred esters, ethers or ester/ethers may be structurally depicted by the formula:

$$R^5\text{-O-(A)-O-}R^6$$

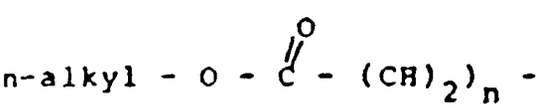
where R^5 and R^6 are the same or different and may be:

(i) n-alkyl-

(ii)



(iii)



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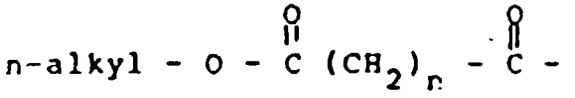
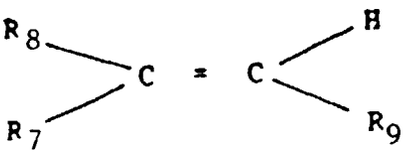


the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyoxyalkylene segement of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred the glycol should be substantially linear.

Suitable glycols generally are the 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 and it is preferred to use a C_{18}-C_{24} fatty acid, especially behenic acids. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols. A particularly preferred additive of this type is polyethylene glycol dibehenate, the glycol portion having a molecular weight of about 600 and is often abbreviated as PEG 600 dibehenate. Similar polyethylene glycol dibehenates where the glycol portion has molecular weights of about 200 and 400 are often abbreviated as PEG 200 and PEG 400 respectively.

Other suitable additives for fuel composition of this invention are ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers which may be copolymerised with ethylene include unsaturated mono and diesters of the general formula:



wherein R^8 is hydrogen or methyl, R^7 is a -$OOCR^{10}$ group wherein R^{10} is hydrogen 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^7 is a -$COOR^{10}$ group wherein R^{10} is as previously defined but is not hydrogen and R^9 is hydrogen or -$COOR^{10}$ as previously defined. The monomer, where R^7 and R^9 are hydrogen and R^8 is -$OOCR^{10}$, includes vinyl alcohol esters of C_1 to C_{29}, more usually C_1 to C_{18}, monocarboxylic acid, and preferably C_2 to C_{29}, more usually C_2 to C_{18}, monocarboxylic acid, and preferably C_2 to C_5 monocarboxylicacid. Examples of vinyl esters which may be copolmerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. It is preferred that the copolymers contain from 20 to 40 wt % of the vinyl ester, more preferably from 25 to 35 wt % vinyl ester. They may also be mixtures of two copolymers such as those described in US-A-3,961,916. It is preferred that these copolymers have a number average molecular weight as measured by vapor phase osmometry of 1,000 to 6,000, preferably 1,000 to 3,000.

Other suitable additives for fuel compositions of the present invention are polar compounds, either ionic or nonionic, which have the capability in fuels of acting as wax crystal growth inhibitors. Polar nitrogen containing compounds have been found to be especially effective when used in combination with the glycol esters, ethers or ester/ethers. These polar compounds are generally amine salts and/or amides formed by reaction of at least one molar proportion of hydrocarbyl substituted amines with a molar proportion of hydrocarbyl acid having 1 to 4 carboxylic acid groups or their anhydrides; ester/amides may also be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US-A-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-C_{40}, preferably C_{14} to C_{24} alkyl segment.

Suitable amines include primary, secondary, tertiary and quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, hydrogenated tallow amine and the like. Examples of secondary amines include dioctadecyl amine, methyl-behenyl amine and the like. Amine mixtures are also suitable and many amines derived from natural materials are mixtures. The 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 for preparing these nitrogen compounds (and their anhydrides) include cyclohexane, 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid, naphthalene dicarboxylic acid and the like. Generally, these acids will have about 5-13 carbon atoms in the cyclic moiety. Preferred acids are benzene dicarboxylic acid such as phthalic acid, tere-phthalic acid, and iso-phthalic 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 di-hydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

The relative proportions of additives used in the mixtures are preferably from 0.05 to 20 parts by weight, more preferably from 0.1 to 5 parts by weight of the amine salt - or quaternary ammonium salt - containing polymer to 1 part of the other additives, such as the polyoxyalkylene esters, ether, ester/ether or amide ether.

The amount of amine salt - or quaternary ammonium salt - containing polymer added to the liquid hydrocarbon fuel is preferably 0.0001 to 5.0 wt. %, for example, 0.001 to 0.5 wt %, especially 0.01 to 0.05 wt %, (active matter) based on the weight of hydrocarbon fuel.

The polymer may conveniently be dissolved in a suitable solvent to form a concentrate of from 20 to 90, e.g., 30 to 80 weight % of the polymer in the solvent. Suitable solvents include kerosene, aromatic naphthas, mineral lubricating oils, etc.

EXAMPLE 1

In this Example a vinyl acetate dialkyl fumarate copolymer AA was compared with two amine salt-containing copolymers, BB and CC and a quaternary ammonium salt-containing copolymer DD when added to two distillate fuel oils F1 and F2 having the following characteristics:

		F1	F2
D-86 Distillation:	IBP	222°C	238°C
	20%	275°C	281°C
	90%	336°C	331°C
	FBP	360°C	352°C
Wax Appearance Point		-3°C	-3.5°C
Base CFPPT*		-3°C	-3°C

* Cold Filter Plugging Point Test.

Details of the polymers are as follows:

AA: A copolymer of equimolar proportions of vinyl acetate and C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate (Comparative).

BB: A terpolymer of 50.0 mol % of vinyl acetate, 45.0 mole % of C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate and 5 mole % of maleic anhydride reacted with 5 mole % of trioctylamine.

DD: A copolymer of 47.5 mole % of vinyl acetate, 47.5 mole % of C_{12} alkyl/C_{14} alkyl (1:1) diakyl fumarate and 5 mole % of maleic anhydride reacted with 5 mole % of trioctyl methyl ammonium chloride and 5 mole % of NaOH in the minimum amount of water where NaCl separated.

Each of polymers AA, BB and DD was mixed with half its weight of a 1:1:1 mole mixture of PEG 200 behenate, PEG 400 dibehenate and PEG 600 behenate and in each case the blend of polymer and PEG behenates were added to the fuel F1 and fuel F2 at an active matter concentration of 0.1% (1000 pm) and the results obtained when tested in the CFPPT were as follows:

Polymer	Fuel F1	Fuel F2
AA (Comparative)	-11	-10
BB	-13	-12
DD	-14	-13

It can be seen that the polymers BB and DD show superior results to those shown by polymer AA which does not possess an amino group.

Details of the CFPPT are as follows:

THE COLD FILTER PLUGGING POINT TEST (CFPPT)

The cold filter properties of the blend were determined by the Cold Filter Plugging Point Test (CFPPT). This test is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Vol. 52, No. 510, June 1966, pp. 173-185. In brief, a 40 ml. sample of the oil to be tested is cooled by a bath maintained at about -34°C. Periodically (at each one degree of Centigrade drop in temperature starting from 2°C above the cloud point) the cooled oil is tested for its ability to flow through a fine screen in a time period. This cold property is tested with a device consisting of a pipette to whose lower end is attached an inverted funnel positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area of about 0.45 square inch (2.9 10^{-4} m^2). The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml. of oil. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds. The results of the test are quoted as Δ CFPPT (°C) which is the difference between the fail temperature of the untreated fuel ($CFPP_0$) and the fuel treated with the flow improver ($CFPP_{1)}$, i.e.

$$\Delta \text{ CFPP} = CFPP_0 - CFPP_1$$

EXAMPLE 2

In this Example various amine-salt containing polymers based on alkyl fumarate-vinyl acetate-maleic anhydride mixed with the polyethylene glycol dibehenate, the glycol portion having a MW of about 600 (PEG 600 dibehenate) were added to a distillate fuel oil blend known as F3 having the characteristics given in Table 1.

The various polymers blended in each case with PEG 600 dibehenate in a weight ratio of 4 parts of polymer per part of PEG 600 dibehenate were as follows:

Polymer-Salt	Details
C	The mono-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 10 mole % maleic anhydride copolymer.
F	The mono-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer.
G	The di-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer.

PROGRAMMED COOLING TEST (PCT)

This is a slow cooling test designed to correlate with the pumping of a stored heating oil. The cold flow properties of the described fuels containing the additives are determined by the PCT as follows. 300 ml of fuel are cooled linearly at 1°C/hour to the test temperature and the temperature then held constant. After 2 hours at the test temperature, approximately 20 ml of the surface layer is removed by suction to prevent the test being influenced by the abnormally large wax crystals which tend to form on the oil/air interface during cooling. Wax which has settled in the bottle is dispersed by gentle stirring, then a CFPPT filter assembly is inserted. The tap is opened to apply a vacuum of 500 mm of mercury, and closed when 200 ml of fuel have passed through the filter into the graduated receiver: a PASS is recorded if the 200 ml are collected within ten seconds through a given mesh size or A fail if the flow rate is too slow indicating that the filter has become blocked.

The mesh number passed at the test temperature is recorded.

Determination by the CFPPT were carried out on F3 blends containing polymers C, F and G all blended with PEG 600 dibehenate in a weight ratio of 4;1 respectively. Copolymer X which is included for comparison purposes is a copolymer of vinyl acetate and ditetradecyl fumarate. The results are as follows:

Polymer Salt	Δ CFPP	
	1500 ppm (active ingredient)	3000 ppm (active ingredient)
C	1	2

(continued)

Polymer Salt	Δ CFPP	
	1500 ppm (active ingredient)	3000 ppm (active ingredient)
F	0	3
G	0	2.5
X	1.5	3.5

The PCT (+2°C) was also carried out on F3 blends containing polymers F, G all blended with PEG 600 dibehenate in a weight ratio of 4:1 respectively. The results obtained were as follows:

Polymer Salt	PCT Mesh Passed at 2°C	
	1500 ppm a.i.	3000 ppm a.i.
F	40	80
G	30	80
X	80	150
No polymer (base fuel oil alone)	<20	

The advantages of the blends containing the polymer over the base fuel oil alone can be clearly seen.

TABLE 1

	Wax Content (%)[a]	WAT (°C) [b]	WAP (°C)	D86 Distillation				
				IBP	D20	D50	D90	FBP
F3	4.9/9.8[c]	10.3	7.5	204	262	295	346	362

(a) Wax at 5°C below WAT/10°C below WAT.

(b) Corrected for thermal lag.

(c) Estimated from component values.

EXAMPLE 3

In this Example the polymer salts F, G used in Example 2 were added to F4, a high boiling point distillate fuel and the CFPP (F4 alone) and the Δ CFPP measured in each case. The ASTM D86 distillation details of F4 are as follows:

IBP	172°C
D20	228°C
D50	276°C
D90	362°C
FBP	389°C

The results are given below for each polymer-salt added at 300 ppm and 500 ppm (active ingredient), i.e. 0.03 wt % and 0.05 wt %, to the base fuel oil, F4 and when compared with the untreated fuel oil.

Polymer Salt	Concentration ppm	CFPP		Δ CFPP
F	300	+ 1	+5	1
F	500	-5	-5	9
G	300	+3	+4	0
G	500	-6	-6	10
Base fuel oil alone		+4	+3	

The polymer salts F, G were also blended with a copolymer Y in a mole rato of 1:4 respectively and then added to F4 at concentrations of 300 and 500 ppm (0.03 wt % and 0.05 wt %). Copolymer Y is a 3:1 weight mixture of an ethylene/vinyl acetate copolymer containing 36 weight % of vinyl acetate of molecular weight about 2000 and an eth-

ylene/vinyl acetate copolymer containing 13 weight % vinyl acetate of molecular weight about 3000.

As before the CFPP (treated fuel oil) and the Δ CFPP were measured in each case. The results are as follows:

Polymer Salt	Concentration		CFPP		Δ CFPP
	Y (ppm)	Polymer Salt (ppm)			
F	240	60	-15	-14	18
F	400	100	-15	-15	19
G	240	60	-15	-13	18
G	400	100	-14	-14	18
Base fuel oil alone			+4	+3	

It can be seen that in all cases there is a considerable reduction in the flow point when the polymer salts are added to the base fuel oil.

EXAMPLE 4

Various polymer salts either alone or in admixture with Polymer Y (See Example 3) were added to a distillate fuel oil F5 which had the following ASTM D86 distillation characteristics:

IBP	188°C
D20	236°C
D50	278°C
D90	348°C
FBP	376°C

The results of the CFPPT and the PCT were as follows:

Polymer Salt	Conc. (ppm)	CFPP		Δ CFPP	PCT at -9°C
F	375	-4,	-3	3	40
F	625	-3,	-3	3	60
G	375	-5,	-4	4	40
G	625	-6,	-6	6	60

Concentration ppm			CFPP		Δ CFPP	PCT at -9°C
Y	Polymer					
300	75	F	-16,	-14	15	150
500	125	F	-17,	-18	17	200
300	75	G	-16,	-17	16	120
500	125	G	-16,	-13	14	150

EXAMPLE 5

In this Example polymer salt C (as used in Example 2) was added to a distillate fuel F6 having the D86 distillation properties:

IBP	173°C
D20	222°C
D50	297°C
D90	356°C
FBP	371°C

This polymer salt C was also blended in a 1:1 mole ratio with ethylene-vinyl acetate copolymer mixture (Y) (see Example 3).

The polymer salt and mixture thereof in a mole ratio of 1:1 with Y were added to the fuel oil at concentrations of 300 and 600 ppm (active ingredient) (0.03 and 0.06 wt%) and the resultant blends were subjected to the PCT and the CFPPT. The results are as follows:

Polymer Salt	Polymer	Concentration (ppm)	PCT (-8°C)	CFPP	
C		300	<20	+3	+3
C		600	20	+3	+2
C	Y	300	40	-1	-2
C	Y	600	80	-6	-6

EXAMPLE 6

In this Example the following polymer salt was added to the distillate fuel oil F6 of Example 5. The polymer salt was blended in a 1:1 mole ratio with the copolymer mixture Y as used in Example 3.

The polymer salt blended with copolymer mixture Y was added to the fuel oil at two different concentrations, i.e. 300 and 600 ppm (0.03 wt % and 0.05 wt %) active ingredient and submitted to the PCT and CFPPT. The results obtained were as follows:

Additive + Y (1:1)	Concentration (ppm)	PCT (-8°C)		CFPP	
F	300	-	20		
F	600	-	20	+2	+ 2
F	300	30	40	-1	-2
F	600	80	100	-5	-8
Base fuel oil alone		20	30	+3	+3

It can be seen that in general adding the polymer salt improves the flow properties of the base fuel oil.

Description for the following Contracting States : BE, NL, SE

This invention relates to fuel oil compositions containing a low improver.

Wax separation in crude oils, middle distillate fuels, heavy and residual fuels and lubricating oils limits their flow at low temperatures. The usual method of overcoming these problems is to add wax crystal modifying compounds that cause the wax crystals to be smaller (nucleators) and/or to be smaller and to grow into more compact shapes (growth inhibitors).

Another difficulty is that small wax crystals can stick together and form larger agglomerates and these agglomerates as well as the individual crystals can block the filter screens through which the individual crystals would pass and they will settle more rapidly than do the individual, small crystals.

We have now found that the wax crystals may be modified so as to improve filterability and reduce the pour point and the tendency of the wax crystals to agglomerate may be reduced by the addition of certain amino or quaternary ammonium salts.

JP Patent Publication No. 56-54038 describes fuel oils containing copolymers of olefins and maleic anhydride derivatised to amide or amide/amine salt groups, in combination with certain other additives. JP Patent Application No. 61-211397 describes fuel oils containing an esteramide or esteramidoamine salt of a specific α-olefin/maleic anhydride copolymer.

According to this invention, there is provided use in a fuel oil composition as a flow improver, alone or in combination with another flow improver, of an additive comprising a polymer or copolymer containing more than one amino group in the form of a salt of a primary, secondary or tertiary amine or a quaternary ammonium salt, said copolymer being derived from an intermediate polymer or copolymer containing acid or anhydride groups and selected from one or more of the following:

I. a polymer of one or more unsaturated ester also including a free acid group or from a copolymer of unsaturated ester monomers at least one of which has a free acid group,

II. a copolymer of an unsaturated carboxylic acid ester with an unsaturated carboxylic anhydride,

III. a polymer or copolymer obtained by partial hydrolysis of a polymer or copolymer containing ester groups so as to obtain carboxylic acid or anhydride groups,
IV. a polymer or copolymer obtained by reaction of a polymer as defined in III above with a carboxylic anhydride, and reaction with an amino compound selected from primary, secondary, or tertiary alkyl amines and tetraalkyl ammonium halides,
said polymer or copolymer having at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms.

The liquid hydrocarbon fuel oils can be distillate fuel oils, such as the middle distillate fuel oils, e.g. a diesel fuel, aviation fuel, kerosene, fuel oil, jet fuel, heating oil, etc. Generally, suitable distillate fuels are those boiling in the range of 120°C to 500°C (ASTM D86), preferably those boiling in the range 150°C to 400°C. A representative heating oil specification calls for a 10 percent distillation point no higher than about 226°C, a 50 percent point no higher than about 272°C and a 90 percent point of at least 282°C and no higher than about 338°C to 343°C, although some specifications set the 90 percent point as high as 357°C. Heating oils are preferably made of a blend of virgin distillate, e.g. gas oil, naphtha, etc. and cracked distillates, e.g. catalytic cycle stock.

The polymer containing more than one amino group can be prepared by reacting a polymer having a plurality of carboxylic acid or anhydride groups with a primary, secondary or tertiary amine.

To prepare the quaternary ammonium salts the polymers can be reacted with a tetra-hydrocarbyl ammonium halide. Alternatively, they may be prepared by reaction of a tertiary amine with a hydrocarbyl halide and so the polymer from which the desired polymer is derived should have halide groups and be reacted respectively with a tertiary amine.

Examples of, and further details of, the different types of polymer ((I to IV) of this invention which can be further reacted to produce the desired polymer containing two or more amine salt groups are as follows:

(I) Copolymers of a dialkyl fumarate, maleate, citraconate or itaconate; copolymers of vinyl acetate with a monoalkyl fumarate, maleate, citraconate or itaconate; copolymers of an alkyl acrylate or an alkyl methacrylate with a monoalkyl fumarate, maleate, citraconate or itaconate; and copolymers of a dialkyl fumarate, maleate, citraconate or itaconate with a monoalkyl fumarate and with vinyl acetate.

Particularly suitable examples of type I polymers are a copolymer of vinyl acetate and a monoalkyl fumarate and a dialkyl fumarate where the alkyl groups are 1:1 mixtures of dodecyl and tetra decyl and copolymers of vinyl acetate and either mono dodecyl, mono tetra decyl or mono hexadecyl fumarate.

(II) These copolymers on reaction with a primary or secondary amine can give half amide/half amine salts due to reaction with the anhydride group. Specific examples are copolymers (a) of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride, or (b) of vinyl esters, e.g. vinyl acetate or vinyl stearate with maleic anhydride, or (c) of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride and vinyl acetate.

Particularly suitable examples of Type II polymers are copolymers of didodecyl fumarate, vinyl acetate and maleic anhydride; di-tetradecyl fumarate, vinyl acetate and maleic anhydride, dihexadecyl fumarate, vinyl acetate and maleic anhydride; or the equivalent copolymers where instead of the fumarate the itaconate is used.

(III) The partially hydrolysed polymer is reacted with an amine to produce the desired polymer containing two or more amine salt groups. Thus, one may partially hydrolyse polymers of acrylates, methacrylates, alkyl fumarates, alkyl maleates or copolymers thereof or copolymers thereof with an olefin.

Particularly suitable examples of Type III polymers are partially hydrolysed polymers of alkyl acrylates or methacrylates, e.g. dodecyl acrylate, tetradecyl acrylate or hexadecyl acrylate.

In all of the above mentioned types of suitable polymer (I, II and III) the desired amine salt is obtained by reacting the polymer containing carboxylic acid or anhydride groups with a primary-, secondary- or tertiary amine to obtain the corresponding amine salt, (optionally also with a alcohol whence an ester-amine salt is formed). Very often, for example when reacting polymers containing an anhydride group, the resulting amino groups will be amine salts and amides. Such polymers can be used, provided that they contain at least two amine salt groups.

To prepare a quaternary ammonium salt any of the above described polymers (I, II or III) is reacted with a tetra hydrocarbyl ammonium halide or the polymers are converted so that they contain halide groups instead of carboxylic acid groups or they are formed by polymerising with an unsaturated halide, for example vinyl chloride. They would then be reacted with a tertiary amine so as to form the quaternary ammonium salt.

(IV) Suitable polymers of unsaturated esters are homo polymers of acrylates, methacrylates, alkyl fumarates or copolymers thereof with an olefin, for example ethylene or a copolymer of vinyl acetate with an olefin. A specific example is an ethylene-vinyl acetate copolymer. After partial hydrolysis the polymer is reacted with an acid anhydride, e.g. succinic or maleic anhydride and the resulting product can be reacted with a p-, s- or t-amine to obtain the corresponding amine salt, or with a tetrahydrocarbyl ammonium halide to obtain the corresponding quaternary ammonium salt.

As stated, said polymer, or copolymer has at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms. Preferably there are 12 to 18 carbon atoms in at least one of said groups. Any such group which is preferably a straight chain or branched alkyl groups, can be present either attached directly or through a carboxylate group to the backbone of the polymer or attached to the nitrogen atom of the amine salt or quaternary ammonium salt group. The polymers may also contain such groups attached both to the nitrogen atom and to the backbone or to the carboxylate group. Thus in Type I, II and III polymers the alkyl groups of the mono- and di-alkyl fumarate, of the alkyl acrylate or of the alkyl methacrylate from which the polymers are derived can contain at least 10 carbon atoms. Particularly suitable monomers are therefore di dodecyl fumarate, di tetra decyl fumarate, di octadecyl fumarate and the corresponding mono alkyl fumarates and mixtures thereof. Also dodecyl, tetradecyl, hexadecyl and octadecyl acrylates and methacrylates are particularly suitable. In type III polymers one could use for example di-decyl, di-dodecyl, di-tetradecyl maleates.

As an alternative or an addition one can introduce the long chain group into the polymer by using a long chain p-, s- or t-amine or tetrahydrocarbyl ammonium halide or mixtures thereof in forming the salt.

The amines can be represented by the formulae

$$R^1NH_2,$$

$$R^1R^2NH$$

and

$$R^1R^2R^3N$$

and the tetrahydrocarbyl ammonium halide by the formula

$$R^1R^2R^3R^4NX$$

wherein R^1, R^2, R^3, and R^4 are hydrocarbyl groups, preferably alkyl groups and wherein at least one of R^1, R^2, R^3 and R^4 preferably contains at least 10 carbon atoms, for instance 12 to 18 carbon atoms, for example dodecyl, tetradecyl, hexadecyl and octadecyl and wherein X is halogen, preferably chlorine.

Suitable polyamines can be represented by the formulae $H_2N[RHN]_xH$ and $R^1NH[RNR^1]_xH$ where R^1 is a hydrocarbyl group, R is a divalent hydrocarbyl group, preferably alkylene or hydrocarbyl substituted alkylene and x is an integer.

Examples of suitable primary amines are hexyl amine, octyl amine, and those containing at least 10 carbon atoms, for instance decyl amine, tetradecyl amine, octadecyl amine, eicosylamine, the mixed amine RNH2 (Armeen C) where R is 0.5 wt % C_6 alkyl, 8 wt % C_8 alkyl, 7 wt % C_{10} alkyl, 50 wt % C_{12} alkyl, 18 wt % C_{14} alkyl, 8 wt % C_{16} alkyl, 1.5 wt % C_{18} alkyl and 7.0 wt % C_{18}/C_{19} unsaturated.

Examples of suitable secondary amines are di-octyl amine, and those containing alkyl groups with at least 10 carbon atoms, for instance di-decyl amine, di-docyl amine, di-coco amine (i.e. di mixed C_{12} to C_{14} alkyl amines), di octadecyl amine, hexadecyl, octadecyl amine, dihydrogenated tallow amine (Armeen 2HT) (approx. 4 wt % nC_{14} alky 1, 30% nC_{16} alkyl, 60 wt % C_{18} alkyl, the rest unsaturated) n-coco-propyl di amine (C_{12}/C_{14} alkyl-propyl di amine - Duomeen C), n-tallow-propyl diamine (C_{16}/C_{18} alkyl propyl diamine - Duomeen T).

Examples of suitable tertiary amines are tri hexyl amine, tri octyl amine and those containing alkyl groups with at least 10 carbon atoms, for instance, hexyl di-decyl amine, tri decyl amine and tri hexadecyl amine.

Examples of suitable quaternary ammonium halides are tri-octyl-methyl ammonium chloride, and those containing alkyl groups with at least 10 carbon atoms, for instance tri-dodcyl-methyl ammonium chloride, tri-tetradecyl, dodecyl ammonium chloride and hexadecyl, dimethyl, phenyl amine.

Examples of suitable polyamines are N-octadecyl propane diamine; N'N' dioctadecyl propane diamine, N tetradecyl butane diamine and N,N' dihexadecyl hexane diamine.

The polymer salts of this invention usually have a number average molecular weight of 1,000 to 500,000, for example 10,000 to 100,000.

Particularly suitable examples of amino group-containing polymers for use in the present invention are:

(1) A copolymer of di-tetradecyl fumarate, vinyl acetate and maleic anhydride, (the mole ratio of acetate:fumarate:

anhydride being approximately 50:45:5) reacted with di C_{16}/C_{18} n-alkyl amine (C_{16} alkyl/C_{18} alkyl being approximately 1:2) to produce the half amide, half amine salt of the carboxylic acid groups mainly derived from the maleic anhydride units of the copolymer.

(2) A copolymer of 50.0 mole % vinyl acetate, 45.0 mole % di C_{12}/C_{14} alkyl (1:1) fumarate and 5 mole % maleic anhydride reacted with 5 mole % trioctylamine to produce the half amide, half amine salt of the carboxylic acid groups derived from the maleic anhydride units of the copolymer.

(3) A copolymer as (2) above but formed by the reaction of 10 mole % of di-coco (C_{12} to C_{14} alkyl) amines instead of trioctylamine.

(4) A copolymer as (2) above but formed by the reaction of 5 mole % of trioctyl-methyl ammonium chloride and 5 mole % of sodium hydroxide in the minimum amount of water instead of trioctylamine. This results in the quaternary ammonium salt of the polymer.

(5) A copolymer as (1) above but formed by the reaction of a mixture of dodecylamine and tetradecylamine instead of the dialkylamine.

(6) A copolymer as (1) above but formed by the reaction of n-coco (C_{12} to C_{14} alkyl) propyl diamine instead of the dialkylamine.

(7) Copolymers as (1) to (6) above where the copolymer is based on equimolar proportions of alkyl fumarate and vinyl acetate but where the amount of maleic anhydride is 10 mole % based on the total weight of the fumarate and vinyl acetate.

Improved results are often achieved when the fuel compositions of this invention incorporate other additives known for improving the cold flow properties of distillate fuels generally. Examples of these other additives are the polyoxyalkylene esters, ethers, ester/ethers, amide/esters and mixtures thereof, particularly those containing at least one, preferably at least two C_{10} to C_{30} linear saturated alkyl groups of a polyoxyalkylene glycol 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. EP-A-0,061,895 describe some of these additives.

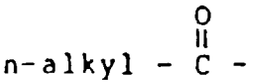
The preferred esters, ethers or ester/ethers may be structurally depicted by the formula:

$$R^5\text{-O-(A)-O-}R^6$$

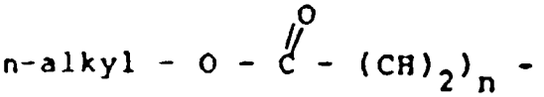
where R^5 and R^6 are the same or different and may be:

(i) n-alkyl-

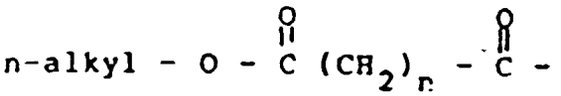
(ii)



(iii)



(iv)

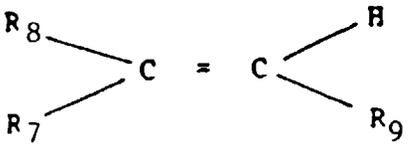


the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyoxyalkylene

segement 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 the glycol should be substantially linear.

Suitable glycols generally are the 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 and it is preferred to use a C_{18}-C_{24} fatty acid, especially behenic acids. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols. A particularly preferred additive of this type is polyethylene glycol dibehenate, the glycol portion having a molecular weight of about 600 and is often abbreviated as PEG 600 dibehenate. Similar polyethylene glycol dibehenates where the glycol portion has molecular weights of about 200 and 400 are often abbreviated as PEG 200 and PEG 400 respectively.

Other suitable additives for fuel composition of this invention are ethylene unsaturated ester copolymer flow improvers. The unsaturated monomers which may be copolymerised with ethylene include unsaturated mono and diesters of the general formula:



wherein R^8 is hydrogen or methyl, R^7 is a -$OOCR^{10}$ group wherein R^{10} is hydrogen 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^7 is a -$COOR^{10}$ group wherein R^{10} is as previously defined but is not hydrogen and R^9 is hydrogen or -$COOR^{10}$ as previously defined. The monomer, where R^7 and R^9 are hydrogen and R^8 is -$OOCR^{10}$, includes vinyl alcohol esters of C_1 to C_{29}, more usually C_1 to C_{18}, monocarboxylic acid, and preferably C_2 to C_{29}, more usually C_2 to C_{18}, monocarboxylic acid, and preferably C_2 to C_5 monocarboxylicacid. Examples of vinyl esters which may be copolmerised with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. It is preferred that the copolymers contain from 20 to 40 wt % of the vinyl ester, more preferably from 25 to 35 wt % vinyl ester. They may also be mixtures of two copolymers such as those described in US-A-3,961,916. It is preferred that these copolymers have a number average molecular weight as measured by vapor phase osmometry of 1,000 to 6,000, preferably 1,000 to 3,000.

Other suitable additives for fuel compositions of the present invention are polar compounds, either ionic or nonionic, which have the capability in fuels of acting as wax crystal growth inhibitors. Polar nitrogen containing compounds have been found to be especially effective when used in combination with the glycol esters, ethers or ester/ethers. These polar compounds are generally amine salts and/or amides formed by reaction of at least one molar proportion of hydrocarbyl substituted amines with a molar proportion of hydrocarbyl acid having 1 to 4 carboxylic acid groups or their anhydrides; ester/amides may also be used containing 30 to 300, preferably 50 to 150 total carbon atoms. These nitrogen compounds are described in US-A-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-C_{40}, preferably C_{14} to C_{24} alkyl segment.

Suitable amines include primary, secondary, tertiary and quaternary, but preferably are secondary. Tertiary and quaternary amines can only form amine salts. Examples of amines include tetradecyl amine, cocoamine, hydrogenated tallow amine and the like. Examples of secondary amines include dioctadecyl amine, methyl-behenyl amine and the like. Amine mixtures are also suitable and many amines derived from natural materials are mixtures. The 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 for preparing these nitrogen compounds (and their anhydrides) include cyclohexane, 1,2 dicarboxylic acid, cyclopentane 1,2 dicarboxylic acid, naphthalene dicarboxylic acid and the like. Generally, these acids will have about 5-13 carbon atoms in the cyclic moiety. Preferred acids are benzene dicarboxylic acid such as phthalic acid, tere-phthalic acid, and iso-phthalic 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 di-hydrogenated tallow amine. Another preferred compound is the diamide formed by dehydrating this amide-amine salt.

The relative proportions of additives used in the mixtures are preferably from 0.05 to 20 parts by weight, more preferably from 0.1 to 5 parts by weight of the amine salt - or quaternary ammonium salt - containing polymer to 1 part of the other additives, such as the polyoxyalkylene esters, ether, ester/ether or amide ether.

The amount of amine salt - or quaternary ammonium salt - containing polymer added to the liquid hydrocarbon fuel is preferably 0.0001 to 5.0 wt. %, for example, 0.001 to 0.5 wt %, especially 0.01 to 0.05 wt %, (active matter) based on the weight of hydrocarbon fuel.

The polymer may conveniently be dissolved in a suitable solvent to form a concentrate of from 20 to 90, e.g., 30 to 80 weight % of the polymer in the solvent. Suitable solvents include kerosene, aromatic naphthas, mineral lubricating oils, etc.

EXAMPLE 1

In this Example a vinyl acetate dialkyl fumarate copolymer AA was compared with two amine salt-containing copolymers, BB and CC and a quaternary ammonium salt-containing copolymer DD when added to two distillate fuel oils F1 and F2 having the following characteristics:

		F1	F2
D-86 Distillation:	IBP	222°C	238°C
	20%	275°C	281°C
	90%	336°C	331°C
	FBP	360°C	352°C
Wax Appearance Point		-3°C	-3.5°C
Base CFPPT*		-3°C	-3°C

* Cold Filter Plugging Point Test.

Details of the polymers are as follows:

AA: A copolymer of equimolar proportions of vinyl acetate and C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate (Comparative).

BB: A terpolymer of 50.0 mol % of vinyl acetate, 45.0 mole % of C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate and 5 mole % of maleic anhydride reacted with 5 mole % of trioctylamine.

CC: A terpolymer of 50.0 mole % of vinyl acetate, 45.0 mole % of C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate and 5 mole % of maleic anhydride reacted with 10 mole % of di-coco (C_{12} to C_{14}) amine.

DD: A copolymer of 47.5 mole % of vinyl acetate, 47.5 mole % of C_{12} alkyl/C_{14} alkyl (1:1) dialkyl fumarate and 5 mole % of maleic anhydride reacted with 5 mole % of trioctyl methyl ammonium chloride and 5 mole % of NaOH in the minimum amount of water where NaCl separated.

Each of polymers AA, BB, CC and DD was mixed with half its weight of a 1:1:1 mole mixture of PEG 200 behenate, PEG 400 dibehenate and PEG 600 behenate and in each case the blend of polymer and PEG behenates were added to the fuel F1 and fuel F2 at an active matter concentration of 0.1% (1000 pm) and the results obtained when tested in the CFPPT were as follows:

Polymer	Fuel F1	Fuel F2
AA (Comparative)	-11	-10
BB	-13	-12
CC	-14	-12
DD	-14	-13

It can be seen that the polymers BB, CC and DD show superior results to those shown by polymer AA which does not possess an amino group.

Details of the CFPPT are as follows:

THE COLD FILTER PLUGGING POINT TEST (CFPPT)

The cold filter properties of the blend were determined by the Cold Filter Plugging Point Test (CFPPT). This test is carried out by the procedure described in detail in "Journal of the Institute of Petroleum", Vol. 52, No. 510, June 1966, pp. 173-185. In brief, a 40 ml. sample of the oil to be tested is cooled by a bath maintained at about -34°C. Periodically (at each one degree of Centigrade drop in temperature starting from 2°C above the cloud point) the cooled oil is tested for its ability to flow through a fine screen in a time period. This cold property is tested with a device

consisting of a pipette to whose lower end is attached an inverted funnel positioned below the surface of the oil to be tested. Stretched across the mouth of the funnel is a 350 mesh screen having an area of about 0.45 square inch (2.9 10^{-4} m^2). The periodic tests are each initiated by applying a vacuum to the upper end of the pipette whereby oil is drawn through the screen up into the pipette to a mark indicating 20 ml. of oil. The test is repeated with each one degree drop in temperature until the oil fails to fill the pipette within 60 seconds. The results of the test are quoted as A CFPPT (°C) which is the difference between the fail temperature of the untreated fuel ($CFPP_0$) and the fuel treated with the flow improver ($CFPP_1$), i.e.

$$\Delta \text{ CFPP} = CFPP_0 - CFPP_1$$

EXAMPLE 2

In this Example various amine-salt containing polymers based on alkyl fumarate-vinyl acetate-maleic anhydride mixed with the polyethylene glycol dibehenate, the glycol portion having a MW of about 600 (PEG 600 dibehenate) were added to a distillate fuel oil blend known as F3 having the characteristics given in Table 1.

The various polymers blended in each case with PEG 600 dibehenate in a weight ratio of 4 parts of polymer per part of PEG 600 dibehenate were as follows:

Polymer-Salt	Details
A	Half amide, half amine salt of di tetradecyl fumarate - vinyl acetate - 10 mole % maleic anhydride copolymer, the amine being R_2NH where R is as given previously for Armeen C.
B	Half amide, half amine salt of di-tetra decyl fumarate-vinyl acetate - 10 mole % maleic anhydride, the amine being n-tallow propyl diamine.
C	The mono-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 10 mole % maleic anhydride copolymer.
D	A copolymer of 50 mole % vinyl acetate, 45 mol % di-tetradecyl fumarate and 5 mole % maleic anhydride reacted in a mole ratio of 1:1 with R_2NH where R = $C_{16/18}$ alkyl to produce the half amide-half amine salt.
E	The half amide-half amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride, the amine being R_2NH where R is as given previously for Armeen C.
F	The mono-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer.
G	The di-trioctyl amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer.
H	Half amide, half amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer, the amine being R_2NH where R = C_{16}/C_{18} alkyl.
I	Half amide, half amine salt of di-tetradecyl fumarate-vinyl acetate - 5 mole % maleic anhydride copolymer, the amine being R_2-NH where R is as given previously for Armeen C.

The CFPPT was determined for a fuel oil blend containing polymer A and this blend was also subjected to the PCT (programmed cooling test), details of which are as follows:

PROGRAMMED COOLING TEST (PCT)

This is a slow cooling test designed to correlate with the pumping of a stored heating oil. The cold flow properties of the described fuels containing the additives are determined by the PCT as follows. 300 ml of fuel are cooled linearly

at 1°C/hour to the test temperature and the temperature then held constant. After 2 hours at the test temperature, approximately 20 ml of the surface layer is removed by suction to prevent the test being influenced by the abnormally large wax crystals which tend to form on the oil/air interface during cooling. Wax which has settled in the bottle is dispersed by gentle stirring, then a CFPPT filter assembly is inserted. The tap is opened to apply a vacuum of 500 mm of mercury, and closed when 200 ml of fuel have passed through the filter into the graduated receiver: a PASS is recorded if the 200 ml are collected within ten seconds through a given mesh size or A fail if the flow rate is too slow indicating that the filter has become blocked.

The mesh number passed at the test temperature is recorded.

The results obtained were as follows:

		Δ CFPP		PCT (+2°C) *	
		1500	3000	1500	3000
Polymer Salt	PEG 600 dibehenate	ppm	ppm	ppm	ppm
4 pt by wt	1 pt by wt	(active ingredient)		(active ingredient)	
A		1	4.5	40	100

* Test temperature.

Further determination by the CFPPT were carried out on F3 blends containing polymers B to I all blended with PEG 600 dibehenate in a weight ratio of 4;1 respectively. Copolymer X which is included for comparison purposes is a copolymer of vinyl acetate and ditetradecyl fumarate. The results are as follows:

Polymer Salt	Δ CFPP	
	1500 ppm (active ingredient)	3000 ppm (active ingredient)
B	1.5	2.5
C	1	2
D	-2*	5.5
E	0.5	3
F	0	3
G	0	2.5
H	0.5	3.5
I	0.5	3
X	1.5	3.5

* Negative sign indicates an increase in CFPP.

The PCT (+2°C) was also carried out on F3 blends containing polymers D, E, F, G, H, and I, all blended with PEG 600 dibehenate in a weight ratio of 4:1 respectively. The results obtained were as follows:

Polymer Salt	PCT Mesh Passed at 2°C	
	1500 ppm a.i.	3000 ppm a.i.
D	60	150
E	30	80
F	40	80
G	30	80
H	100	200
I	30	60
X	80	150
No polymer (base fuel oil alone)	<20	

The advantages of the blends containing the polymer over the base fuel oil alone can be clearly seen.

TABLE 1

	Wax Content (%)[a]	WAT (°C) [b]	WAP (°C)	D86 Distillation				
				IBP	D20	D50	D90	FBP
F3	4.9/9.8[c]	10.3	7.5	204	262	295	346	362

(a) Wax at 5°C below WAT/10°C below WAT.

(b) Corrected for thermal lag.

(c) Estimated from component values.

EXAMPLE 3

In this Example the polymer salts D, E, F, G, H and I used in Example 2 were added to F4, a high boiling point distillate fuel and the CFPP (F4 alone) and the Δ CFPP measured in each case. The ASTM D86 distillation details of F4 are as follows:

IBP	172°C
D20	228°C
D50	276°C
D90	362°C
FBP	389°C

The results are given below for each polymer-salt added at 300 ppm and 500 ppm (active ingredient), i.e. 0.03 wt % and 0.05 wt %, to the base fuel oil, F4 and when compared with the untreated fuel oil.

Polymer Salt	Concentration ppm	CFPP		Δ CFPP
D	300	-3	-3	7
D	500	-6	-5	9
E	300	+3	+4	0
E	500	-4	-5	8
F	300	+1	+5	1
F	500	-5	-5	9
H	300	-5	-2	7
H	500	-6	-6	10
I	300	+1	+2	2
I	500	-8	-5	10
G	300	+3	+4	0
G	500	-6	-6	10
Base fuel oil alone		+4	+3	

The polymer salts D, E, F, G, H and I were also blended with a copolymer Y in a mole rato of 1:4 respectively and then added to F4 at concentrations of 300 and 500 ppm (0.03 wt % and 0.05 wt %). Copolymer Y is a 3:1 weight mixture of an ethylene/vinyl acetate copolymer containing 36 weight % of vinyl acetate of molecular weight about 2000 and an ethylene/vinyl acetate copolymer containing 13 weight % vinyl acetate of molecular weight about 3000.

As before the CFPP (treated fuel oil) and the Δ CFPP were measured in each case. The results are as follows:

Polymer Salt	Concentration		CFPP		Δ CFPP
	Y (ppm)	Polymer Salt (ppm)			
D	240	60	-14	-12	17
D	400	100	-17	-16	20
E	240	60	-14	-13	17
E	400	100	-15	-14	18
F	240	60	-15	-14	18

(continued)

Polymer Salt	Concentration		CFPP		Δ CFPP
	Y (ppm)	Polymer Salt (ppm)			
F	400	100	-15	-15	19
H	240	60	-15	-14	18
H	400	100	-14	-14	18
I	240	60	-12	-13	16
I	400	100	-16	-14	19
G	240	60	-15	-13	18
G	400	100	-14	-14	18
Base fuel oil alone			+4	+3	

It can be seen that in all cases there is a considerable reduction in the flow point when the polymer salts are added to the base fuel oil.

EXAMPLE 4

Various polymer salts either alone or in admixture with Polymer Y (See Example 3) were added to a distillate fuel oil F5 which had the following ASTM D86 distillation characteristics:

IBP	188°C
D20	236°C
D50	278°C
D90	348°C
FBP	376°C

The results of the CFPPT and the PCT were as follows:

Polymer Salt	Conc. (ppm)	CFPP		Δ CFPP	PCT at -9°C
D	375	-3,	-3	3	40
D	625	-4,	-4	4	80
E	375	-5,	-5	5	40
E	625	-5,	-4	4	60
F	375	-4,	-3	3	40
F	625	-3,	-3	3	60
H	375	-3,	-3	3	40
H	625	-4,	-4	4	60
I	375	-3,	-4	3	40
I	625	-5,	-5	5	60
G	375	-5,	-4	4	40
G	625	-6,	-6	6	60

Concentration ppm			CFPP		Δ CFPP	PCT at -9°C
Y	Polymer					
300	75	D	-16,	-18	17	150
500	125	D	-16,	-18	17	200
300	75	E	-14,	-16	15	120
500	125	E	-17,	-16	16	200
300	75	F	-16,	-14	15	150
500	125	F	-17,	-18	17	200

(continued)

Concentration ppm			CFPP		Δ CFPP	PCT at -9°C
Y	Polymer					
300	75	H	-14,	-15	14	120
500	125	H	-14,	-15	14	200
300	75	I	-17,	-14	15	150
500	125	I	-16,	-19	17	200
300	75	G	-16,	-17	16	120
500	125	G	-16,	-13	14	150

EXAMPLE 5

In this Example polymer salt C (as used in Example 2) and another polymer salt J was added to a distillate fuel F6 having the D86 distillation properties:

IBP	173°C
D20	222°C
D50	297°C
D90	356°C
FBP	371°C

Polymer salt J is the half amide, half amine salt of the copolymer of di-tetradecyl fumarate-vinyl acetate - 10 mole % maleic anhydride, the amine being R_2NH where R is C_{16}/C_{18} alkyl.

These polymer salts C and J were also blended in a 1:1 mole ratio with ethylene-vinyl acetate copolymer mixture (Y) (see Example 3).

The polymer salts and mixtures thereof in a mole ratio of 1:1 with Y were added to the fuel oil at concentrations of 300 and 600 ppm (active ingredient) (0.03 and 0.06 wt%) and the resultant blends were subjected to the PCT and the CFPPT. The results are as follows:

Polymer Salt	Polymer	Concentration (ppm)	PCT (-8°C)	CFPP	
J		300	40	+3	+3
J		600	80	+2	+3
J	Y	300	40	-5	-8
J	Y	600	80	-9	-8
C		300	<20	+3	+3
C		600	20	+3	+2
C	Y	300	40	-1	-2
C	Y	600	80	-6	-6

EXAMPLE 6

In this Example polymer salts A and B (as used in Example 2) and J (as used in Example 5) were added to the distillate fuel oil F6 of Example 5. In addition the following polymer salts were also added to this fuel oil. Each polymer salt was blended in a 1:1 mole ratio with the copolymer mixture Y as used in Example 3.

Polymer Salt	
K	Half amide, half amine salt of di-tetradecyl fumarate-vinyl acetate - 10 mole % maleic anhydride copolymer, the amine being RNH_2 where R = C_{16}/C_{18} alkyl.
L	Half amide, half amine salt of di-tetradecyl fumarate-vinyl acetate - 10 mole % maleic anhydride copolymer, the amine being n-coco-propyl diamine.

(continued)

Polymer Salt	
M	As L but where R is as given previously for Armeen C.

Each polymer salt blended with copolymer mixture Y was added to the fuel oil at two different concentrations, i.e. 300 and 600 ppm (0.03 wt % and 0.05 wt %) active ingredient and submitted to the PCT and CFPPT. The results obtained were as follows:

Additive + Y (1:1)	Concentration (ppm)	PCT (-8°C)		CFPP	
K	300	-	20		
K	600	-	20		
K	300	40	60		
K	600	80	100		
L	300	-	20		
L	600	-	20		
L	300	40	60		
L	600	80	100		
J	300	40	60		
J	600	100	120	+2	+1
J	300	60	80		
J	600	80	100	-7	-8
A	300	20	30		
A	600	20	30	+2	+1
A	300	40	60		
A	600	60	80	-9	-11
B	300	-	20		
B	600	-	20	+2	+1
B	300	40	60		
B	600	60	80	-9	-9
F	300	-	20		
F	600	-	20	+2	+2
F	300	30	40	-1	-2
F	600	80	100	-5	-8
M	300	-	20		
M	600	-	20	+2	+1
M	300	30	40		
M	600	80	100		
Base fuel oil alone		20	30	+3	+3

It can be seen that in general adding the polymer salt improves the flow properties of the base fuel oil.

Claims

Claims for the following Contracting States : DE, ES, FR, GB, IT

1. Use in a fuel oil composition as a flow improver, alone or in combination with another flow improver, of an additive comprising a polymer or copolymer containing more than one amino group in the form of a salt of a primary or tertiary amine or a quaternary ammonium salt, said copolymer being derived from an intermediate polymer or copolymer containing acid or anhydride groups and selected from one or more of the following:

   I. a polymer of one or more unsaturated ester also including a free acid group or from a copolymer of unsatu-

rated ester monomers at least one of which has a free acid group,

II. a copolymer of an unsaturated carboxylic acid ester with an unsaturated carboxylic anhydride,

III. a polymer or copolymer obtained by partial hydrolysis of a polymer or copolymer containing ester groups so as to obtain carboxylic acid or anhydride groups,

IV. a polymer or copolymer obtained by reaction of a polymer as defined in III above with a carboxylic anhydride,

and reaction with an amino compound selected from primary or tertiary alkyl amines and tetraalkyl ammonium halides,

said polymer or copolymer having at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms.

2. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride.

3. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a vinyl ester with maleic anhydride.

4. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride and vinyl acetate.

5. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a partially hydrolysed polymer of an alkyl fumarate, maleate, citraconate or itaconate or a copolymer thereof with a C_{10} to C_{30} olefin.

6. Use according to any preceding claim wherein at least one of said hydrogen-and carbon-containing groups has from 12 to 18 carbon atoms.

7. Use according to any preceding claim wherein, in said intermediate polymer or copolymer, the or each said hydrogen- and carbon-containing group is attached directly through a carboxylate group to the backbone of the polymer.

8. Use according to any preceding claim wherein, in said intermediate polymer or copolymer, the or each said hydrogen- and carbon-containing group is attached to the nitrogen atom of the amine salt or of the quaternary ammonium salt.

9. Use according to any preceding claim wherein said amino compound comprises a primary or tertiary alkyl amine containing at least one alkyl group having at least 10 carbon atoms.

10. Use according to any preceding claim wherein said amino compound comprises the tertiary amine trioctylamine.

11. Use according to any preceding claim wherein the amount of amine salt-containing copolymer is from 0.0001 to 5.0 weight % (active matter) based on the weight of said fuel.

12. Use according to any preceding claim which includes another flow improver selected from: a polyoxyalkylene ester, ether, ester/ether, or amide/ether; an ethylene unsaturated ester copolymer flow improver; a polar nitrogen-containing compound; and mixtures thereof.

13. Use according to claim 13 wherein the other flow improver is an ethylene-vinyl acetate copolymer.

Claims for the following Contracting States : BE, NL, SE

1. Use in a fuel oil composition as a flow improver, alone or in combination with another flow improver, of an additive comprising a polymer or copolymer containing more than one amino group in the form of a salt of a primary, secondary or tertiary amine or a quaternary ammonium salt, said copolymer being derived from an intermediate polymer or copolymer containing acid or anhydride groups and selected from one or more of the following:

I. a polymer of one or more unsaturated ester also including a free acid group or from a copolymer of unsaturated ester monomers at least one of which has a free acid group,

II. a copolymer of an unsaturated carboxylic acid ester with an unsaturated carboxylic anhydride,
III. a polymer or copolymer obtained by partial hydrolysis of a polymer or copolymer containing ester groups so as to obtain carboxylic acid or anhydride groups,
IV. a polymer or copolymer obtained by reaction of a polymer as defined in III above with a carboxylic anhydride,

and reaction with an amino compound selected from primary, secondary, or tertiary alkyl amines and tetraalkyl ammonium halides,
said polymer or copolymer having at least one hydrogen- and carbon-containing group where the total number of carbon atoms in said group(s) is at least 10 carbon atoms.

2. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride.

3. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a vinyl ester with maleic anhydride.

4. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a copolymer of a dialkyl fumarate, maleate, citraconate or itaconate with maleic anhydride and vinyl acetate.

5. Use according to claim 1 wherein said intermediate polymer or copolymer comprises a partially hydrolysed polymer of an alkyl fumarate, maleate, citraconate or itaconate or a copolymer thereof with a C_{10} to C_{30} olefin.

6. Use according to any preceding claim wherein at least one of said hydrogen-and carbon-containing groups has from 12 to 18 carbon atoms.

7. Use according to any preceding claim wherein, in said intermediate polymer or copolymer, the or each said hydrogen- and carbon-containing group is attached directly through a carboxylate group to the backbone of the polymer.

8. Use according to any preceding claim wherein, in said intermediate polymer or copolymer, the or each said hydrogen- and carbon-containing group is attached to the nitrogen atom of the amine salt or of the quaternary ammonium salt.

9. Use according to any preceding claim wherein said amino compound comprises a primary, secondary or tertiary alkyl amine containing at least one alkyl group having at least 10 carbon atoms.

10. Use according to any preceding claim wherein said amino compound comprises a secondary or tertiary amine selected from trioctylamine, di(hydrogenated) tallow amine, mixed C_{12} to C_{14} alkyl-propyl diamine, and n-tallow-propyl diamine.

11. Use according to any preceding claim wherein the amount of amine salt-containing copolymer is from 0.0001 to 5.0 weight % (active matter) based on the weight of said fuel.

12. Use according to any preceding claim which includes another flow improver selected from: a polyoxylalkylene ester, ether, ester/ether, or amide/ether; an ethylene unsaturated ester copolymer flow improver; a polar nitrogen-containing compound; and mixtures thereof.

13. Use according to claim 13 wherein the other flow improver is an ethylene-vinyl acetate copolymer.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : DE, ES, FR, GB, IT

1. Verwendung eines Additivs in einer Brennstoffölzusammensetzung als Fließverbesserer, allein oder in Kombination mit einem anderen Fließverbesserer, wobei das Additiv ein Polymer oder Copolymer umfaßt, das mehr als eine Aminogruppe in Form eines Salzes eines primären oder tertiären Amins oder eines quartären Ammonium-

salzes enthält, das Copolymer sich von einem intermediären Polymer oder Copolymer ableitet, das Säure- oder Säureanhydridgruppen enthält und aus einem oder mehreren der folgenden ausgewählt ist:

I. einem Polymer aus einem oder mehreren ungesättigten Estern, das außerdem freie Säuregruppen enthält, oder einem Copolymer aus ungesättigten Estermonomeren, von denen mindestens eines eine freie Säuregruppe aufweist,

II. einem Copolymer aus einem ungesättigten Carbonsäureester und einem ungesättigten Carbonsäureanhydrid,

III. einem Polymer oder Copolymer, das durch partielle Hydrolyse eines Polymers oder Copolymers erhalten worden ist, das Estergruppen enthält, um so Carbonsäure- oder Carbonsäureanhydridgruppen zu erhalten,

IV. einem Polymer oder Copolymer, das durch Umsetzung eines wie oben in III definierten Polymers mit einem Carbonsäureanhydrid erhalten worden ist,

und mit einer Aminoverbindung ausgewählt aus primären oder tertiären Alkylaminen und Tetraalkylammoniumhalogeniden umgesetzt worden ist,
und das Polymer oder Copolymer mindestens eine Wasserstoff und Kohlenstoff enthaltende Gruppe aufweist, wobei die Gesamtzahl der Kohlenstoffatome in dieser Gruppe (diesen Gruppen) mindestens 10 Kohlenstoffatome beträgt.

2. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Dialkylfumarat, -maleat, -citraconat oder -itaconat und Maleinsäureanhydrid umfaßt.

3. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Vinylester und Maleinsäureanhydrid umfaßt.

4. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Dialkylfumarat, -maleat, -citraconat oder -itaconat mit Maleinsäureanhydrid und Vinylacetat umfaßt.

5. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein partiell hydrolysiertes Polymer aus einem Alkylfumarat, -maleat,-citraconat oder -itaconat oder ein Copolymer derselben mit einem C_{10}- bis C_{30}-Olefin umfaßt.

6. Verwendung nach einem der vorhergehenden Ansprüche, bei der mindestens eine der Wasserstoff und Kohlenstoff enthaltenden Gruppen 12 bis 18 Kohlenstoffatome aufweist.

7. Verwendung nach einem der vorhergehenden Ansprüche, bei der in dem intermediären Polymer oder Copolymer die oder jede der Wasserstoff und Kohlenstoff enthaltenden Gruppen direkt über eine Carboxylatgruppe an das Gerüst des Polymers gebunden ist.

8. Verwendung nach einem der vorhergehenden Ansprüche, bei der in dem intermediären Polymer oder Copolymer die oder jede der Wasserstoff und Kohlenstoff enthaltenden Gruppen an das Stickstoffatom des Aminsalzes oder des quartären Ammoniumsalzes gebunden ist.

9. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Aminoverbindung ein primäres oder tertiäres Alkylamin umfaßt, das mindestens eine Alkylgruppe mit mindestens 10 Kohlenstoffatomen enthält.

10. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Aminoverbindung das tertiäre Amin Trioctylamin umfaßt.

11. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Menge an Aminsalz enthaltendem Copolymer 0,0001 bis 5,0 Gew.-% (aktiver Bestandteil), bezogen auf das Gewicht des Brennstoffs, beträgt.

12. Verwendung nach einem der vorhergehenden Ansprüche, bei der ein anderer Fließverbesserer ausgewählt aus einem Polyoxyalkylenester, -ether, -ester/-ether oder -amid/-ether, einem Ethylen/ungesättigter Ester-Copolymerfließverbesserer, einer polaren Stickstoff enthaltenden Verbindung und Mischungen derselben umfaßt ist.

13. Verwendung nach Anspruch 12, bei der der andere Fließverbesserer ein Ethylen/Vinylacetat-Copolymer ist.

Patentansprüche für folgende Vertragsstaaten : BE, NL, SE

1. Verwendung eines Additivs in einer Brennstoffölzusammensetzung als Fließverbesserer, allein oder in Kombination mit einem anderen Fließverbesserer, wobei das Additiv ein Polymer oder Copolymer umfaßt, das mehr als eine Aminogruppe in Form eines Salzes eines primären, sekundären oder tertiären Amins oder eines quartären Ammoniumsalzes enthält, das Copolymer sich von einem intermediären Polymer oder Copolymer ableitet, das Säure- oder Säureanhydridgruppen enthält und aus einem oder mehreren der folgenden ausgewählt ist:

I. einem Polymer aus einem oder mehreren ungesättigten Estern, das außerdem freie Säuregruppen enthält, oder einem Copolymer aus ungesättigten Estermonomeren, von denen mindestens eines eine freie Säuregruppe aufweist,

II. einem Copolymer aus einem ungesättigten Carbonsäureester und einem ungesättigten Carbonsäureanhydrid,

III. einem Polymer oder Copolymer, das durch partielle Hydrolyse eines Polymers oder Copolymers erhalten worden ist, das Estergruppen enthält, um so Carbonsäure- oder Carbonsäureanhydridgruppen zu erhalten,

IV. einem Polymer oder Copolymer, das durch Umsetzung eines wie oben in III definierten Polymers mit einem Carbonsäureanhydrid erhalten worden ist,

und mit einer Aminoverbindung ausgewählt aus primären, sekundären oder tertiären Alkylaminen und Tetraalkylammoniumhalogeniden umgesetzt worden ist,
und das Polymer oder Copolymer mindestens eine Wasserstoff und Kohlenstoff enthaltende Gruppe aufweist, wobei die Gesamtzahl der Kohlenstoffatome in dieser Gruppe (diesen Gruppen) mindestens 10 Kohlenstoffatome beträgt.

2. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Dialkylfumarat, -maleat, -citraconat oder -itaconat und Maleinsäureanhydrid umfaßt.

3. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Vinylester und Maleinsäureanhydrid umfaßt.

4. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein Copolymer aus einem Dialkylfumarat, -maleat, -citraconat oder -itaconat mit Maleinsäureanhydrid und Vinylacetat umfaßt.

5. Verwendung nach Anspruch 1, bei der das intermediäre Polymer oder Copolymer ein partiell hydrolysiertes Polymer aus einem Alkylfumarat, -maleat, -citraconat oder -itaconat oder ein Copolymer derselben mit einem C_{10}- bis C_{30}-Olefin umfaßt.

6. Verwendung nach einem der vorhergehenden Ansprüche, bei der mindestens eine der Wasserstoff und Kohlenstoff enthaltenden Gruppen 12 bis 18 Kohlenstoffatome aufweist.

7. Verwendung nach einem der vorhergehenden Ansprüche, bei der in dem intermediären Polymer oder Copolymer die oder jede der Wasserstoff und Kohlenstoff enthaltenden Gruppen direkt über eine Carboxylatgruppe an das Gerüst des Polymers gebunden ist.

8. Verwendung nach einem der vorhergehenden Ansprüche, bei der in dem intermediären Polymer oder Copolymer die oder jede der Wasserstoff und Kohlenstoff enthaltenden Gruppen an das Stickstoffatom des Aminsalzes oder des quartären Ammoniumsalzes gebunden ist.

9. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Aminoverbindung ein primäres, sekundäres oder tertiäres Alkylamin umfaßt, das mindestens eine Alkylgruppe mit mindestens 10 Kohlenstoffatomen enthält.

10. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Aminoverbindung ein sekundäres oder ter-

tiäres Amin ausgewählt aus Trioctylamin, Di(hydriertes)talgamin, gemischtem C_{12}- bis C_{14}-Alkylpropyldiamin und n-Talgpropyldiamin umfaßt.

11. Verwendung nach einem der vorhergehenden Ansprüche, bei der die Menge an Aminsalz enthaltendem Copolymer 0,0001 bis 5,0 Gew.-% (aktiver Bestandteil), bezogen auf das Gewicht des Brennstoffs, beträgt.

12. Verwendung nach einem der vorhergehenden Ansprüche, bei der ein anderer Fließverbesserer ausgewählt aus einem Polyoxyalkylenester, -ether, -ester/-ether oder -amid/-ether, einem Ethylen/ungesättigter Ester-Copolymer-Fließverbesserer, einer polaren Stickstoff enthaltenden Verbindung und Mischungen derselben umfaßt ist.

13. Verwendung nach Anspruch 12, bei der der andere Fließverbesserer ein Ethylen/Vinylacetat-Copolymer ist.

Revendications

Revendications pour les Etats contractants suivants : DE, ES, FR, GB, IT

1. Utilisation dans une composition de fuel-oil comme agent améliorant l'écoulement, seul ou en association avec un autre agent améliorant l'écoulement, d'un additif comprenant un polymère ou copolymère contenant plus d'un groupe amino sous forme d'un sel d'une amine primaire ou tertiaire ou d'un sel d'ammonium quaternaire, ledit copolymère étant dérivé d'un polymère ou copolymère intermédiaire contenant des groupes acide ou anhydride et consistant en un ou plusieurs des suivants :

I. un polymère d'un ou plusieurs esters insaturés comprenant également un groupe acide libre, ou provenant d'un copolymère de monomères ester insaturé dont au moins un possède un groupe acide libre,
II. un copolymère d'un ester d'acide carboxylique insaturé avec un anhydride carboxylique insaturé,
III. un polymère ou copolymère obtenu par hydrolyse partielle d'un polymère ou copolymère contenant des groupes ester de manière à obtenir des groupes acide ou anhydride carboxylique,
IV. un polymère ou copolymère obtenu par réaction d'un polymère tel que défini dans le paragraphe III précité avec un anhydride carboxylique,
et réaction avec un composé à fonction amino choisi entre des alkylamines primaires ou tertiaires et des halogénures de tétraalkylammonium,
ledit polymère ou copolymère possédant au moins un groupe contenant de l'hydrogène et du carbone, le nombre total d'atomes de carbone dans ledit ou lesdits groupes étant au moins égal à 10.

2. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un fumarate, maléate, citraconate ou itaconate de dialkyle avec l'anhydride maléique.

3. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un ester vinylique avec l'anhydride maléique.

4. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un fumarate, maléate, citraconate ou itaconate de dialkyle avec l'anhydride maléique et l'acétate de vinyle.

5. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un polymère partiellement hydrolysé d'un fumarate, maléate, citraconate ou itaconate d'alkyle ou un de ses copolymères avec une oléfine en C_{10} à C_{30}.

6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle au moins un des groupes contenant de l'hydrogène et du carbone possède 12 à 18 atomes de carbone.

7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle, dans le polymère ou copolymère intermédiaire, le ou chaque groupe contenant de l'hydrogène et du carbone est fixé directement par un groupe carboxylate au squelette du polymère.

8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle, dans le polymère ou copolymère intermédiaire, le ou chaque groupe contenant de l'hydrogène et du carbone est fixé à l'atome d'azote du sel

d'amine ou du sel d'ammonium quaternaire.

9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le composé à fonction amino comprend une alkylamine primaire ou tertiaire contenant au moins un groupe alkyle ayant au moins 10 atomes de carbone.

10. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le composé à fonction amino comprend l'amine tertiaire consistant en trioctylamine.

11. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité de copolymère contenant un sel d'amine va de 0,0001 à 5,0 % en poids (matière active) sur la base du poids du combustible.

12. Utilisation suivant l'une quelconque des revendications précédentes, qui comprend un autre agent améliorant l'écoulement choisi entre : un ester, éther, ester/éther ou amide/éther de polyoxyalkylène ; un agent améliorant l'écoulement consistant en un copolymère d'éthylène et d'un ester insaturé ; un composé azoté polaire ; et leurs mélanges.

13. Utilisation suivant la revendication 12, dans laquelle l'autre agent améliorant l'écoulement est un copolymère éthylène - acétate de vinyle.

Revendications pour les Etats contractants suivants : BE, NL, SE

1. Utilisation dans une composition de fuel-oil comme agent améliorant l'écoulement, seul ou en association avec un autre agent améliorant l'écoulement, d'un additif comprenant un polymère ou copolymère contenant plus d'un groupe amino sous forme d'un sel d'une amine primaire, secondaire ou tertiaire ou d'un sel d'ammonium quaternaire, ledit copolymère étant dérivé d'un polymère ou copolymère intermédiaire contenant des groupes acide ou anhydride et consistant en un ou plusieurs des suivants :

I. un polymère d'un ou plusieurs esters insaturés comprenant également un groupe acide libre, ou provenant d'un copolymère de monomères ester insaturé dont au moins un possède un groupe acide libre,
II. un copolymère d'un ester d'acide carboxylique insaturé avec un anhydride carboxylique insaturé,
III. un polymère ou copolymère obtenu par hydrolyse partielle d'un polymère ou copolymère contenant des groupes ester de manière à obtenir des groupes acide ou anhydride carboxylique,
IV. un polymère ou copolymère obtenu par réaction d'un polymère tel que défini dans le paragraphe III précité avec un anhydride carboxylique,
et réaction avec un composé à fonction amino choisi entre des alkylamines primaires, secondaires ou tertiaires et des halogénures de tétraalkylammonium,
ledit polymère ou copolymère possédant au moins un groupe contenant de l'hydrogène et du carbone, le nombre total d'atomes de carbone dans ledit ou lesdits groupes étant au moins égal à 10.

2. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un fumarate, maléate, citraconate ou itaconate de dialkyle avec l'anhydride maléique.

3. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un ester vinylique avec l'anhydride maléique.

4. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un copolymère d'un fumarate, maléate, citraconate ou itaconate de dialkyle avec l'anhydride maléique et l'acétate de vinyle.

5. Utilisation suivant la revendication 1, dans laquelle le polymère ou copolymère intermédiaire comprend un polymère partiellement hydrolysé d'un fumarate, maléate, citraconate ou itaconate d'alkyle ou un de ses copolymères avec une oléfine en C_{10} à C_{30}.

6. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle au moins un des groupes contenant de l'hydrogène et du carbone possède 12 à 18 atomes de carbone.

7. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle, dans le polymère ou copoly-

mère intermédiaire, le ou chaque groupe contenant de l'hydrogène et du carbone est fixé directement par un groupe carboxylate au squelette du polymère.

8. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle, dans le polymère ou copolymère intermédiaire, le ou chaque groupe contenant de l'hydrogène et du carbone est fixé à l'atome d'azote du sel d'amine ou du sel d'ammonium quaternaire.

9. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le composé à fonction amino comprend une alkylamine primaire, secondaire ou tertiaire contenant au moins un groupe alkyle ayant au moins 10 atomes de carbone.

10. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle le composé à fonction amino comprend une amine secondaire ou tertiaire choisie entre la trioctylamine, la di-amine de suif hydrogéné, une (alkyle en C_{12} à C_{14})-propyl-diamine mixte, et une n-(radical dérivé du suif)-propyl-diamine.

11. Utilisation suivant l'une quelconque des revendications précédentes, dans laquelle la quantité de copolymère contenant un sel d'amine va de 0,0001 à 5,0 % en poids (matière active) sur la base du poids du combustible.

12. Utilisation suivant l'une quelconque des revendications précédentes, qui comprend un autre agent améliorant l'écoulement choisi entre : un ester, éther, ester/éther ou amide/éther de polyoxyalkylène ; un agent améliorant l'écoulement consistant en un copolymère d'éthylène et d'un ester insaturé ; un composé azoté polaire ; et leurs mélanges.

13. Utilisation suivant la revendication 12, dans laquelle l'autre agent améliorant l'écoulement est un copolymère éthylène - acétate de vinyle.