

12

EUROPEAN PATENT APPLICATION

21 Application number: **88308455.0**

51 Int. Cl.4: **C 10 L 1/14**

22 Date of filing: **13.09.88**

30 Priority: **18.09.87 GB 8722016**

43 Date of publication of application:
22.03.89 Bulletin 89/12

64 Designated Contracting States:
BE DE ES FR GB IT NL SE

71 Applicant: **EXXON CHEMICAL PATENTS INC.**
200 Park Avenue
Florham Park New Jersey 07932 (US)

72 Inventor: **Davies, Brian William**
1 Brook Farm Cottages The Cleave
Harwell Oxon OX11 0EW (GB)

More, Iain
15 Lee Avenue
Abingdon Oxon OX14 3UT (GB)

Costello, June Kathleen
5 Folly Crescent
Highworth Wiltshire (GB)

Brown, Gerald Ivan
3 Orchard Gardens West Challow
Wantage Oxon OX12 9TL (GB)

Tack, Robert Dryden
64 Alexander Close Lodge Fields
Abingdon Oxon OX14 1XB (GB)

74 Representative: **Bawden, Peter Charles et al**
EXXON CHEMICAL LIMITED EXXON CHEMICAL
TECHNOLOGY CENTRE PO Box 1
Abingdon Oxfordshire OX13 6BB (GB)

54 **Fuel oil additives.**

57 An additive suitable for adding to a fuel oil, e.g. a distillate fuel oil containing between 5 and 10 wt% wax at 10°C below cloud point, comprises a fused mixture of (A) a paraffin wax containing 20 to 45 carbon atoms per molecule and (B) a flow improver, for example (1) a copolymer of ethylene and a vinyl ester, e.g. ethylene/vinyl acetate copolymer, (2) a copolymer of an ester of fumaric acid and a vinyl ester, e.g. alkyl fumarate/vinyl acetate copolymer or (3) an amine salt of, an amide of or a half amine salt, half amide of a dicarboxylic acid or anhydride, e.g. half amine salt/half amide of phthalic acid and dihydrogenated tallow amine.

By the use of the additive of this invention which can be in the form of relatively small slabs, blocks etc, distribution problems are considerably reduced compared with previously used additives which are invariably solutions of additives in solvents, requiring the transport of drums of liquid.

EP 0 308 176 A1

Description

FUEL OIL ADDITIVES

This invention relates to fuel oil additives and to fuel oils containing such additives.

Heating oils and other distillate petroleum fuels, e.g. diesel fuels, contain normal paraffin hydrocarbon waxes which, at low temperatures, tend to precipitate in large crystals in such a way as to set up a gel structure which causes the fuel to lose its fluidity. The lowest temperature at which the fuel will still flow is generally known as the pour point. When the fuel temperature reaches or goes below the pour point and the fuel is no longer freely flowable, difficulty arises in transporting the fuel through flow lines and pumps, as for example when attempting to transfer the fuel from one storage vessel to another by gravity or under pump pressure or when attempting to feed the fuel to a burner. Additionally, the wax crystals that have come out of solution tend to plug fuel lines, screens and filters. This problem has been well recognized in the past and various additives have been suggested for depressing the pour point of the fuel oil. One function of such pour point depressants has been to change the nature of the crystals that precipitate from the fuel oil, thereby reducing the tendency of the wax crystals to set into a gel. Small size crystals are desirable so that the precipitated wax will not clog the fine mesh screens that are provided in fuel transport, storage, and dispensing equipment. It is thus desirable to obtain not only fuel oils with low pour points (flow points) but also oils that will form small wax crystals so that the clogging of filters will not impair the flow of the fuel at low operating temperatures.

Effective wax crystal modification (as measured by CFPP (Cold Filter Plugging Point) and other operability tests, as well as by cold climate chassis dynamometer and obviously field performance) can be achieved by flow improvers, mostly ethylene-vinyl acetate copolymer (EVA) based, in distillates containing up to 5% n-paraffin at 10°C below cloud point, as determined by gravimetric or DSC methods. Additive response in these distillates is normally stimulated by adjusting ASTM D-86 distillation characteristics of these distillates (increase of [FBP - 90%] above 20°C and distillation range [90 - 20]% distillation to values above 100°C, FBP above 355°C).

These practices are not however effective when treating high wax content distillates, like those encountered in the Far East, which although featuring mostly similar distillation characteristics (e.g. [FBP - 90%] distillation and [90-20]% distillation range) have much higher wax content (between 5 and 10%). They also have different C number distributions, particularly in the C₂₂ plus range.

We have now discovered that the flow properties of high wax containing distillate fuels can be improved by the addition thereto of an additive mixture which has considerable advantages over previous proposals.

According to this invention an additive suitable for adding to a fuel oil comprises a fused mixture of (A) a paraffin wax containing 20 to 45 carbon atoms per molecule and (B) a flow improver.

By the use of the additive of this invention which can be in the form of relatively small slabs, blocks etc, distribution problems are considerably reduced compared with previously used additives which are invariably solutions of additives in solvents, requiring the transport of drums of liquid. Also it has been found that there is synergy between the wax (A) and the other component (B) which has often been used as a flow improver in the past.

Component (A) of the fused mixture is a paraffin wax containing 20 to 45 carbon atoms per molecule. In practice this will almost inevitably comprise a mixture of paraffins of different chain lengths. The paraffin mix is preferably an n-alkane or a mixture of n-alkanes, but branched chain alkanes can be used. Suitable paraffin waxes are those having 25 to 35 carbon atoms per molecule. A typical paraffin wax for use as component (A) has the following composition:

<u>% by weight</u>	<u>Paraffin</u>
0.028	C ₂₀
0.245	C ₂₁
1.309	C ₂₂
3.750	C ₂₃
7.118	C ₂₄
8.730	C ₂₅
9.996	C ₂₆
8.847	C ₂₇
8.083	C ₂₈
6.769	C ₂₉

5.703	C ₃₀	
4.343	C ₃₁	
3.533	C ₃₂	5
2.520	C ₃₃	
1.788	C ₃₄	
1.093	C ₃₅	10
0.655	C ₃₆	
0.361	C ₃₇	
0.190	C ₃₈	15
0.078	C ₃₉	
0.044	C ₄₀	20

The hydrocarbon contents were determined by Gas Liquid Chromatography (GLC).

Component (B) is a flow improver. Preferably the flow improver is an additive which when added to diesel or heating oil at concentrations of between 0.01 and 0.3 wt% interacts with the crystallising waxes and allows fuel to flow, or pass filters, at a temperature which would not be possible in its absence. Suitable tests for measuring flow improvement are CFPP, slow cool filterability tests (eg PCT), Pour Point, vehicle operability, crystal size measurements etc. Typically, a flow improver produces a Δ CFPPT($^{\circ}$ C) of at least 1° C, normally several degrees when subjecting a fuel containing between 0.01 and 0.3 wt% of the flow improver to the cold filter plugging point test (CFPPT). In addition, the addition of a flow improver very often produces smaller crystals than observed in the base fuel which results in the treated fuel passing finer meshes eg PCT range of filters, (at least one mesh better) than untreated fuel. Typically, flow improver treated fuel (between 0.01 and 0.3 wt%) will pass at least a 60 mesh filter.

Details of the Cold Filter Plugging Point Test (CFPPT) are as follows:-

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 least one degree 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. 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 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 ($^{\circ}$ C) which is the difference between the fail temperature of the untreated fuel (CFPP₀) and the fuel treated with the flow improver (CFPP₁) i.e. Δ CFPP = CFPP₀ - CFPP₁.

The Filterability Test is as follows:-

In this slow cool test fuel samples (300 ml) are cooled at a known cooling rate (1° C/hour) to a target temperature, normally this is about 10° C below the wax appearance point of the fuel. The filterability of the treated fuel is then measure by determining the smallest filter mesh through which 200 ml of fuel passes in 10s when subjected to a 500 mm Hg vacuum. A series of different mesh size filters are available and these are normally numbered as outlined below.

Microns

	(nominal)	750	500	375	300	200	150	125	100	75	60	45
5	Mesh size	20	30	40	50	80	100	120	150	200	250	350
	Mesh No	1	2	3	4	5	6	7	8	9	10	11

----->

increasing operability

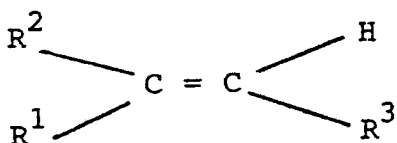
The 120 mesh (Mesh No 7) is indicative of good operability.

The pour point test is similar to CFPP in that the fuel samples undergo rapid cooling. In this test the fuel samples (approx 45 ml) are cooled using a series of baths of different temperature. The fluidity of the sample is monitored every 3°C until no flow is observed when the fuel sample is tilted through 90°C for 5 seconds. The temperature 3°C below which no flow occurs is reported as the pour point of the sample.

In practice the flow improver (B) can be one of the following:-

- (i) Linear copolymers of ethylene and some other comonomer, for example a vinyl ester, an acrylate, a methacrylate, an α -olefine, styrene, etc,
- (ii) Comb polymers, ie polymers with C₁₀-C₃₀ alkyl side chain branches;
- (iii) Linear polymers derived from ethylene oxide, for example polyethylene glycol esters and amino derivatives thereof;
- (iv) Monomeric compounds, for example amine salts and amides of polycarboxylic acids such as citric acid.

The unsaturated comonomers from which the linear copolymer (i) are derived and which may be copolymerized with ethylene, include unsaturated mono and diesters of the general formula:



wherein R² is hydrogen or methyl; R¹ is a -OOCR⁴ group or hydrocarbyl wherein R⁴ is hydrogen or a C₁ to C₂₈, more usually C₁ to C₁₇, and preferably a C₁ to C₈ straight or branched chain alkyl groups or R¹ is a -COOR⁴ group wherein R⁴ is as previously described but is not hydrogen and R³ is hydrogen or -COOR⁴ as previously defined. The monomer, when R¹ and R³ are hydrogen and R² is -OOCR⁴ includes vinyl alcohol esters of C₁ to C₂₉, more usually C₁ to C₁₈ monocarboxylic acid, and preferably C₂ to C₅ monocarboxylic acid. Examples of vinyl esters which may be copolymerized with ethylene include vinyl acetate, vinyl propionate and vinyl butyrate or isobutyrate, vinyl acetate being preferred. We prefer 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 United States patent No 3961916.

Other linear copolymers (i) are derived from comonomers of the formula:



R⁵ is H or alkyl, R⁶ is H or methyl and X is -COOR⁷ or hydrocarbyl where R⁷ is alkyl. This includes acrylates, CH₂ = COOR⁷, methacrylates, CH₂ = CMeCOOR⁷, styrene CH₂ = CH.C₆H₅ and olefins CHR⁵ = CR⁶R⁸ where R⁸ is alkyl. The group R⁷ is preferably C₁ to C₂₈, more usually C₁ to C₁₇ and more preferably a C₁ to C₈ straight or branched chain alkyl group. For the olefins R⁵ and R⁶ are preferably hydrogen and R⁸ a C₁ to C₂₀ alkyl group. Thus suitable olefins are propylene, hexene-1, octene-1, dodecene-1 and tetradecene-1.

For this type of copolymer it is preferred that the ethylene content is 50 to 65 weight per cent although higher amount can be used eg 80 weight % for ethylene-propylene copolymers.

It is preferred that these copolymers have a number average molecular weight as measured by vapour phase osmometry of 1000 to 6000, preferably 1000 to 3000.

Particularly suitable linear copolymeric flow improvers (i) are copolymers of ethylene and a vinyl ester.

The vinyl ester can be a vinyl ester of a monocarboxylic acid, for example one containing 1 to 20 carbon atoms per molecule. Examples are vinyl acetate, vinyl propionate and vinyl butyrate. Most preferred however is vinyl acetate.

Usually the copolymer of ethylene and a vinyl ester will consist of 3 to 40, preferably 3 to 20, molar proportions of ethylene per molar proportion of the vinyl ester. The copolymer usually has a number average

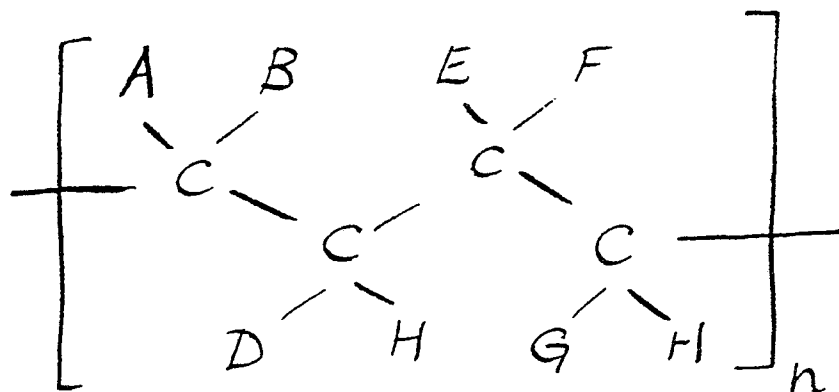
molecular weight of between 1000 and 50,000, preferably between 1,500 and 5,000. The molecular weights can be measured by cryoscopic methods or by vapour phase osmometry, for example by using a Mechrolab Vapour Phase Osmometer Model 310A.

Other particularly preferred linear copolymeric flow improvers are (i) copolymers of an ester of fumaric acid and a vinyl ester. The ester of fumaric acid can be either a mono- or a di-ester and alkyl esters are preferred. The or each alkyl group can contain 6 to 30, preferably 10 to 20 carbon atoms, and mono- or di-(C₁₄ to C₁₈) alkyl esters are especially suitable, either as single esters or as mixed esters. Generally di-alkyl esters are preferred to mono- esters.

Suitable vinyl esters with which the fumarate ester is copolymerised are those described above in connection with ethylene/vinyl ester copolymers. Vinyl acetate is particularly preferred.

The fumarate esters are preferably copolymerised with the vinyl ester in a molar proportion of between 1.5:1 and 1:1.5, for example about 1:1. These copolymers usually have a number average molecular weight of from 1000 to 100,000, as measured for example by Vapour Phase Osmometry such as by a Mechrolab Vapour Pressure Osmometer.

Comb polymers (ii) have the following general formula:



where

A is H, Me or CH₂CO₂R' (where R' = C₁₀ - C₂₂ alkyl) (Me = methyl)

B is CO₂R or R'' (where R'' = C₁₀ - C₃₀ alkyl, PhR' (Ph = phenyl)

D is H or CO₂R'

E is H or Me, CH₂CO₂R'

F is OCOR'' (R''' = C₁ - C₂₂ alkyl), CO₂R', Ph, R' or PhR'

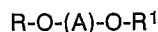
G is H or CO₂R'

and n is an integer

In general terms, such polymers include a dialkyl fumarate/vinyl acetate copolymer eg ditetradecyl fumarate/vinyl copolymer; a styrene dialkyl maleate ester copolymer eg styrene/dihexadecyl maleate copolymer; a poly dialkyl fumarate, eg poly (di octadecyl fumarate); an α -olefin dialkyl maleate copolymer eg copolymer of tetradecene and di hexadecyl maleate, a dialkyl itaconate/vinyl acetate copolymer eg dihexadecyl itaconate/vinyl acetate; poly-(n-alkyl methacrylates) eg poly(tetradecyl methacrylate); poly (n-alkyl acrylates) eg poly (tetra decyl acrylate); poly - alkenes eg poly (1-octadecene) etc.

Linear polymer derived from ethylene oxide (ii) include the poly oxyalkylene esters, ethers, esters/ethers, amide/esters and mixtures thereof, particularly those containing at least one, preferably at least two C₁₀ to C₃₀ linear saturated alkyl groups of a polyoxyalkylene glycol group of molecular weight 100 to 5,000, preferably 200 to 5,000, the alkylene group in said polyoxyalkylene glycol containing from 1 to 4 carbon atoms. European patent publication No 0,061,985 A2 describe some of these additives.

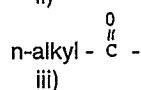
The preferred esters, ethers or ester/ethers may be structurally depicted by the formula:



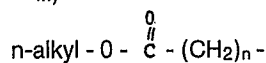
where R and R¹ are the same or different and may be

i) n-alkyl

ii)



iii)



iv)

n-alkyl - O - $\overset{\text{O}}{\parallel}$ C (CH₂)_n - C - $\overset{\text{O}}{\parallel}$ C - the alkyl group being linear and saturated and containing 10 to 30 carbon atoms, and A represents the polyoxyalkylene segment of the glycol in which the alkylene group has 1 to 4 carbon atoms, such as polyoxymethylene, polyoxyethylene or polyoxytrimethylene moiety which is substantially linear; some degree of branching with lower alkyl side chains (such as in polyoxypropylene glycol) may be tolerated but it is preferred the glycol should be substantially linear.

Suitable glycols generally are the substantially linear polyethylene glycol (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 C₁₈-C₂₄ fatty acid, especially behenic acids. The esters may also be prepared by esterifying polyethoxylated fatty acids or polyethoxylated alcohols.

Examples of the monomeric compounds (iv) as flow improver include an amine salt of, a mono amide or a diamide of, or a half amine salt, half amide of a dicarboxylic acid, tricarboxylic acid or anhydride thereof. The preferred acid is an aromatic acid, such as the dicarboxylic acids, phthalic acid and 2:3 naphthalene dicarboxylic acid. Aliphatic acids such as maleic acid or alkyl or alkenyl succinic acid may be used. An example of a tricarboxylic acid is citric acid.

The amine salt or half amine salt can be derived from a primary, secondary or tertiary amine but the amide can only be derived from a primary or secondary amine. The amines are preferably aliphatic amines and the amine is preferably a secondary amine in particular an aliphatic secondary amine of the formula R¹R²NH. Preferably R¹ and R² which can be the same or different contain at least 10 carbon atoms, especially 12 to 22 carbon atoms, e.g. dodecyl, tetradecyl, octadecyl, eicosyl and docosyl (behenyl).

A particularly preferred compound is the half amine salt, half amide of the dicarboxylic acid in which the amine is a secondary amine. Especially preferred is the half amine salt, half amide of phthalic acid and dihydrogenated tallow amine - Armeen 2HT (approx 4 wt% n-C₁₄ alkyl, 30 wt% n-C₁₆ alkyl, 60 wt% n-C₁₈ alkyl, the remainder being unsaturated).

As an alternative to using one flow improver one could use a mixture of two or more of them.

It is essential that the mixture of (A) and (B) is fused so that the mixture becomes a substantially homogeneous mixture. This can be conveniently achieved by heating the mixture of (A) and (B) slowly with stirring until the highest melting component has melted. Thereafter the mixture is allowed to cool and a solid mass of a substantially homogeneous mixture of (A) and (B) will be obtained. The exact temperatures will depend on the melting point of the components but usually heating to between 65°C and 75°C is sufficient and the mixture usually becomes solid at a temperature of between 45°C and 55°C. Provided there is not too much solvent and substantially all can be evaporated on heating, any of compounds (1), (2) and (3) can be mixed with (A) as a solution in a solvent.

The weight ratio of (A) to (B) can vary but weight ratios of 1:1 to 20:1 are suitable, e.g. 8:1 to 12:1, for example about 10:1.

The fused mixture can be allowed to cool in moulds providing the desired shape of additive mixture or it can be allowed to cool in a large area mould and cut up into smaller pieces later. Various shapes include for example slabs, blocks, pastilles, cubes and cuboids.

The additive of this invention is suitable for adding to a fuel oil and the fuel oil is preferably one in which there is less than 0.5 weight % of fuel oil containing paraffins having a carbon chain length of more than 25 carbon atoms.

The fuel oil can be for example a distillate fuel. The distillate fuel can be 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° to 500°C (ASTM D1160), preferably those boiling in the range 150°C to 400°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. A representative specification for a diesel fuel includes a minimum flash point of 38°C and a 90 percent distillation point between 282°C and 338°C. (See ASTM Designations D-396 and D-975).

Generally the fuel oil for which the additive of this invention is particularly suited is a distillate fuel containing between 5 and 10 wt% of wax at 10°C below cloud point. Such distillate fuels usually have a narrow carbon distribution, i.e. fuels in which less than 0.2 weight % of the fuel contains paraffins longer than C₂₇.

A typical distillate fuel containing 5 to 10 wt% wax at 10°C below cloud point has the following ASTM D-86 characteristics:

Initial Boiling Point	213°C	
5.0%	235°C	
10.0%	244°C	5
20.0%	256°C	
30.0%	263°C	
40.0%	279°C	10
50.0%	289°C	
60.0%	299°C	
70.0%	303°C	15
80.0%	321°C	
90.0%	335°C	20
95.0%	344°C	
Final Boiling Point	361°C	

25

The amount of wax is usually about 8 weight percent at 10°C below cloud point.

The amount of additive i.e. Components (A) + (B) added to the distillate fuel is a minor proportion by weight, e.g. between 0.05 and 5.0 wt%, for example between 0.1 and 2.0 wt% based on the weight of fuel. Therefore a suitable fuel oil composition comprises a major proportion by weight of a fuel oil and 0.05 to 5.0% by weight of a mixture of (A) a paraffin wax containing 20 to 45 carbon atoms per molecule and (B) a flow improver.

30

Also in accordance with this invention is the use as a cold flow improver in a fuel oil of a fused mixture of (A) a paraffin wax containing 20 to 45 carbon atoms per molecule and a flow improver. The fused mixture is usually added in a proportion of between 0.05 and 5.0 wt%, e.g. between 0.1 and 2.0 wt% based on the weight of fuel.

35

Example 1

10g of a wax was weighed into a beaker with 10g of a flow improver and heated to 70°C with stirring. After thorough mixing the mixture was allowed to cool with a thermometer placed in it. The mixture started to solidify at 58°C and was completely solid although slightly soft at 48°C. The mixture just melted when placed in a 55°C oven overnight, but set very soon after being removed from it remained pliable and soft down to approximately 45°C. At 30°C the mixture is very hard and shows no signs of any movement.

40

The wax (A) was a mixture of n-alkanes and had the following composition:

45

50

55

60

65

	<u>% by weight</u>	<u>Paraffin</u>
5	0.028	C ₂₀
	0.245	C ₂₁
10	1.309	C ₂₂
	3.750	C ₂₃
	7.118	C ₂₄
15	8.730	C ₂₅
	9.996	C ₂₆
	8.847	C ₂₇
20	8.083	C ₂₈
	6.769	C ₂₉
	5.703	C ₃₀
25	4.343	C ₃₁
	3.533	C ₃₂
	2.520	C ₃₃
30	1.788	C ₃₄
	1.093	C ₃₅
35	0.655	C ₃₆
	0.361	C ₃₇
	0.190	C ₃₈
40	0.078	C ₃₉
	0.044	C ₄₀

45 The hydrocarbon contents were determined by Gas Liquid Chromatography (GLC).

Two different flow improvers were used in two different runs. The first flow improver (B1) was a mixture of ethylene/vinyl acetate copolymers and fumarate ester/vinyl acetate copolymers. It consisted of 63.2 weight % of an ethylene/vinyl acetate copolymer containing 36 weight % of vinyl acetate units, 20.8 weight % of an ethylene/vinyl acetate copolymer containing 13 weight % of vinyl acetate units, 9.4 weight % of ditetradecyl fumarate/vinyl acetate copolymer and 6.5 weight % of the diester of fumaric acid/vinyl acetate copolymer in

50 which the ester is derived from a mixture of tetradecyl and hexadecyl alcohols. The second flow improver (B2) was a mixture of 93 weight % of an ethylene/vinyl acetate copolymer containing 36 weight % of vinyl acetate units and 7 weight % of an ethylene/vinyl acetate copolymer containing 13 weight % of vinyl acetate units.

This procedure was repeated with different weight ratios of flow improver to wax i.e. 1:3, 1:5 and 1:10.

55 The 8 different flow improver/wax blends thus prepared were added at different concentrations to a distillate fuel oil having the following characteristics:

IBP - 205° C
 D20 - 245° C
 60 D50 - 278° C
 D90 - 335° C
 FBP - 355° C

Each of the blends (A + B) added to the fuel oil was subjected to the Cold Filter Plugging Point Test (CFPPT) and the CFPP(°C) determined. This is the fail temperature of the fuel treated with the flow improver.

65 The results obtained are as follows:

Flow Improver Treat (wt.%)	1:1		1:3		1:5		1:10	
	Wax Treat (wt.%) (A)	CFPP(°C)	Wax (wt.%) (A)	CFPP(°C)	Wax (wt.%) (A)	CFPP(°C)	Wax (wt.%) (A)	CFPP(°C)
(B1)								
0.05	0.05	5.0	0.15	5.0	0.25	4.0	0.5	3.5
0.10	0.10	3.0	0.30	3.0	0.50	1.5	1.0	0.5
0.15	0.15	2.0	0.45	1.0	0.75	-3.5	1.5	-5.5
0.20	0.20	1.5	0.60	-3.5	1.00	-5.5		
0.05	0	4.5						
0.10	0	4.0						
0.15	0	3.0						
0.20	0	3.5						
(B2)								
0.05	0.05	4.5	0.15	5.0	0.25	4.0	0.5	2.5
0.10	0.10	3.0	0.30	3.5	0.50	2.2	1.0	0.5
0.15	0.15	2.0	0.45	0.0	0.75	1.1	1.5	2.5
0.20	0.20	0.5	0.60	-0.5	1.00	1.0		
0.05	0	4.5						
0.10	0	2.5						
0	0	4.5						
0.15	0	3.0						
0.20	0	2.5						

It can be seen that in general improved results are achieved by using the combination of A + B, especially a weight ratio of A:B of 10:1.

5

Claims

- 10 1. An additive suitable for adding to a fuel oil comprising a fused mixture of (A) a paraffin wax containing 20 to 45 carbon atoms per molecule and (B) a flow improver.
2. An additive according to claim 1 in which Component (A) of the mixture is a mixture of n-alkanes of 27 to 33 carbon atoms per molecule.
- 15 3. An additive according to either of claims 1 and 2 wherein the flow improver (B) is an additive which when added to a diesel or heating oil at a concentration of between 0.01 and 0.3 weight % interacts with the crystallizing waxes and allows fuel to flow or pass filters at a temperature which would not be possible in its absence.
4. An additive according to any one of the preceding claims in which the flow copolymer (B) is a copolymer of ethylene and a vinyl ester, an acrylate, a methacrylate, an α -olefin or styrene.
- 20 5. An additive according to claim 4 in which the copolymer of ethylene and the vinyl ester consists of 3 to 40 molar proportions of ethylene per molar proportion of vinyl ester and has a number average molecular weight of between 1000 and 50,000.
6. An additive according to any one of the preceding claims in which flow improver (B) of the mixture is a copolymer of ethylene and vinyl acetate.
- 25 7. An additive according to any one of claims 1 to 4 in which flow improver (B) of the mixture is a copolymer of a dialkyl ester of fumaric acid and a vinyl ester.
8. An additive according to claim 7 in which the copolymer is a copolymer of a dialkyl ester of fumaric acid and a vinyl ester in which the molar proportion of fumarate ester to vinyl ester is between 1:1.5 and 1.5:1 and which has a number average molecular weight of 1000 to 100,000.
- 30 9. An additive according to any one of the claims 1 to 3 wherein the flow improver is a comb polymer.
10. An additive according to any one of claims 1 to 3 wherein the flow improver is a linear polymer derived from ethylene oxide.
11. An additive according to any one of claims 1 to 3 in which the flow improver (B) of the mixture is an amine salt of, a mono amide or a diamide of, or a half amine salt, half amide of a dicarboxylic acid, tricarboxylic acid or anhydride thereof.
- 35 12. An additive according to claim 11 in which the flow improver (B) is a half amine salt, half amide of phthalic acid and dihydrogenated tallow amine.
13. An additive according to any one of the preceding claims in which the weight ratio of (A) to (B) is between 1:1 and 20:1.
- 40 14. The use as a cold flow improver in a fuel oil of the additive mixture according to any one of the preceding claims.
15. The use according to claim 12 in which the fuel oil is one in which there is less than 0.5 weight % of fuel oil containing paraffins having a carbon chain length of more than 25 carbon atoms.

45

50

55

60

65



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	FR-A-1 525 531 (ESSO RESEARCH AND ENGINEERING CO.) * Whole document * ---	1-6,13-15	C 10 L 1/14
Y	GB-A-1 266 037 (ESSO RESEARCH AND ENGINEERING CO.) * Whole document; page 2, lines 78-94 in particular * ---	1-6,13-15	
Y	GB-A- 893 175 (BRITISH PETROLEUM) * Whole document * ---	1-4,9,13,14	
Y	US-A-2 917 375 (HUDSON) * Whole document * ---	1-4,9,13,14	
A	US-A-3 649 228 (McLAREN) * Claims; examples 1C,2C; column 11, lines 20-42 * ---	1-6,13-15	
A	US-A-2 125 875 (BARNARD) * Whole document * ---	1-3,13-15	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	EP-A-0 153 177 (EXXON) * Claims * ---	1-3,7,14,15	C 10 L
A	EP-A-0 203 812 (EXXON) * Whole document * ---	1-15	
A	US-A-3 271 121 (YOUNG et al.) * Whole document * ---	4	
A	FR-A-1 572 843 (MOBIL OIL CORP.) * Abstract; examples * ---	9	
A	EP-A-0 061 895 (EXXON) * Claims; examples * -----	1-15	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 08-11-1988	Examiner DE LA MORINERIE B.M.S.B.
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		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	