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Description

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

Heating oils and other distillate petroleum fuels, e.g. diesel fuels, contain normal alkane waxes which, at low temperatures, tend to precipitate as 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 no longer freely flows, 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.

The crystals coming out of solution also tend to plug fuel lines, screens and filters at temperatures above the pour point. These problems have been well recognised in the past and various additives have been suggested for depressing the pour point of the fuel oil and reducing the size of the wax crystals. One function of such additives 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 and other operability tests, as well as simulated and field performance) can be achieved by flow improvers, mostly ethylene-vinyl acetate copolymer (EVA) based, in distillates containing up to 4 wt%-n-alkanes at 10 °C below cloud point, as determined by gravimetric or DSC methods. Additive response in these distillates is normally stimulated by the refiner adjusting ASTM D-86 distillation characteristics of the distillates to increase the tail 90% to Final Boiling Point to deltas between 20 °C and 25 °C.

It has been proposed in US-A-3620696 that the response of the low wax content middle distillate fuels available in the United States in 1968 to copolymers of ethylene and vinyl esters prepared according to FR-A-1461008 may be improved by the incorporation of a small amount of a paraffin wax to furnish from 0.03 to 2 wt.% of wax of average molecular weight within the range of from 300 to 650. Similarly, US-A-3640691 proposes that the response of the same types of middle distillate to similar additives may be improved by the addition of a paraffinic distillate fraction containing normal alkanes higher than n-hexacosane and as high as n-tetracontane to provide from 0.1 to 2 wt.% of normal alkanes of C₂₄ and higher. In these patents as little as 0.1 wt.% and a maximum of 2.0 wt.% of the C₂₄ and higher added wax are shown to improve response.

These practices are not, however, effective when treating high wax content narrow boiling distillates, like those encountered in the Far East and Australia, which although featuring similar distillation characteristics have much higher wax contents (between 5 and 10% at 10 °C below the cloud point as measured by DSC or gravimetric analysis) and different carbon number distribution, particularly in the C₂₂ to C₂₈ range. Particularly difficult to treat fuels are those with a high wax content and a relatively low final boiling point, i.e. no higher than 370 °C sometimes below 360 °C, which have high wax contents over a narrow carbon number distribution. The most difficult to treat are those fuels obtained from high wax crudes such as those from the crudes in Australia and the Far East where the total n-alkane content of the distillate can be greater than 20%, the total content being C₁₂ and higher n-alkanes as measured by Gas Liquid Chromatography.

More recently it has been proposed in JP-A-615811586 that a middle distillate responsive to flow improvers may be obtained by adjusting the total wax content of the fuel to between 5.5 and 12 wt.%, preferably by blending of high and low wax content fuels, the wax content being that precipitated with methyl ethyl ketone from 1 gram of the fuel at -20 °C. This technique is not a satisfactory indication of the wax content of the fuel to be treated by the additives since it is the wax precipitated between the cloud point of the fuel and its operability point which is treated by the additive and which is important to the low temperature characteristics of the fuel. We have found that the ability of these fuels to respond to flow improvers is not dependent on the total wax content of the fuel.

A typical hard to treat distillate fuel containing 5 to 10 wt.% wax at 10 °C below its cloud point and/or greater than 20 wt.% n-alkanes C₁₂₊ has the following ASTM D-86 characteristics:

Initial Boiling Point	212 °C
5%	234 °C
10%	243 °C
20%	255 °C
30%	263 °C
40%	279 °C
50%	288 °C
60%	298 °C
70%	303 °C
80%	321 °C
90%	334 °C
95%	343 °C
Final Boiling Point	361 °C

We have discovered that in contrast to the recommendations of JP-A-615811586 the response of such distillate fuels to flow improvers can be improved by the addition thereto of materials to broaden the carbon number distribution of the n-alkane content within a defined range.

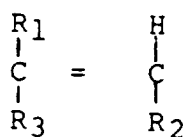
According to this invention a liquid fuel composition comprises a major proportion by weight of a distillate fuel containing between 4 and 10 wt.% wax at 10 °C below cloud point and having a narrow n-alkane distribution, i.e. containing substantially no paraffins longer than n-triacontane (C₃₀), a low temperature flow improver at 0.001 to 2.0 wt.% based on the weight of the distillate fuel and added n-alkanes which provide C₂₄ and higher alkanes in a proportion greater than 0.35 wt.% of the fuel.

Also according to this invention is the use as a cold flow improver for a distillate fuel containing between 4 and 10 wt.% of wax at 10 °C below cloud point and having a narrow carbon distribution, i.e. containing substantially no paraffins longer than n-triacontane (C₃₀), of a mixture of a distillate fuel low temperature flow improver and added n-alkanes whose C₂₄ and higher is greater than 0.35 wt.% of the weight of the fuel.

The flow improvers that are employed in this invention may be any of those generally available although we prefer to use the type comprising copolymers of ethylene and at least one second unsaturated monomer. The second unsaturated monomer can be another monoolefin, e.g. a C₃ to C₁₈ alpha-monoolefin or it can be an unsaturated ester, as for example, vinyl acetate, vinyl butyrate, vinyl propionate, lauryl methacrylate, ethyl acrylate or the like. The second monomer can also be a mixture of an unsaturated mono or diester and a branched or straight chain alpha monoolefin. Mixtures of copolymers can also be used, as for example mixtures of a copolymer of ethylene and vinyl acetate with an alkylated polystyrene or with an acylated polystyrene. Alternative materials are the amino succinic acid derivatives, esters such as polyacrylates and esterified maleic anhydride copolymers, polyalpha olefins, etc.

The preferred distillate fuel flow improver useful in this invention is a copolymer consisting of 1 to 40, and preferably 1 to 20, more preferably 3 to 20 molar proportions of ethylene per molar proportion of the ethylenically unsaturated monomer, which latter monomer can be a single monomer or a mixture of such monomers in any proportion, said polymer being oil soluble and having a number average molecular weight in the range of about 1,000 to 50,000, preferably about 1,000 to about 5,000. Molecular weights can be measured by cryoscopic methods or by vapor phase osmometry, for example by using a Mechrolab Vapor Phase Osmometer Model 310A.

The unsaturated monomers, which may be homopolymerised or copolymerised with ethylene or with each other include unsaturated acids, acid anhydrides, and mono and diesters of the general formula:



wherein R₁ is hydrogen or methyl; R₃ is a -OOCR₄ or -COOR₄ group wherein R₄ is hydrogen or a C₁ to C₁₆, preferably C₁ to C₄ straight or branched chain alkyl group and R₃ is hydrogen or -COOR₄. The monomer, when R₁ to R₃ are hydrogen and R₂ is -OOCR₄, includes vinyl alcohol esters of C₂ to C₁₇ monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl

myristate, vinyl palmitate, etc. When R_2 is $-\text{COOR}_4$ such esters include C_8 oxo alcohol acrylate, methyl acrylate, methyl methacrylate, lauryl acrylate, isobutyl methacrylate, palmityl alcohol ester of alpha-methacrylic acid, C_{13} oxo alcohol esters of methacrylic acid, etc. Examples of monomers wherein R_1 is hydrogen and R_2 and R_3 are $-\text{OOCR}_4$ groups, include mono C_{12} oxo alcohol fumarate, di-isopropyl maleate; di-lauryl fumarate; ethyl methyl fumarate; fumaric acid, maleic acid, etc., or where R_2 is H and R_1 is COOR_4 and R_3 is $\text{CH}_2 \text{COOR}_4$ such as the itaconates.

Other unsaturated monomers copolymerizable with ethylene to prepare pour point depressants or flow improvers useful in this invention include C_3 to C_{16} branched chain or straight-chain alpha monoolefins, as for example, propylene, n-octene-1, 2-ethyl decene-1, n-decene-1, etc.

Small proportions, e.g. about 0 to 20 mole percent, of a third monomer, or even of a fourth monomer, can also be included in the copolymers, as for example a C_2 to C_{16} branched or straight-chain alpha monoolefin, e.g. propylene, n-octene-1, n-decene-1, etc. Thus, for example, copolymers of 3 to 40 moles of ethylene with one mole of a mixture of 30 to 99 mole percent of unsaturated ester and 70 to 1 mole percent of olefin could be used.

The copolymers that are formed are random copolymers consisting primarily of an ethylene polymer backbone along which are distributed side chains of hydrocarbon or oxy-substituted hydrocarbon.

The alcohols used in preparing the esters mentioned above are isomeric mixtures of branched chain aliphatic primary alcohols prepared from olefins, such as polymers and copolymers of C_3 to C_4 monoolefins, reacted with carbon monoxide and hydrogen in the presence of a cobalt-containing catalyst such as cobalt carbonyl, at temperatures of about 300°F to 400°F (about 150°C to 205°C), under pressures of about 1,000 to 3,000 p.s.i. (about 70 to 210 bar) to form aldehydes. The resulting aldehyde product is then hydrogenated to form the alcohol, the latter being recovered by distillation from the hydrogenated product.

It is also preferred that the copolymers have a low degree of side chain branching; particularly they contain less than 10, preferably less than 8, methyl terminated side chains (other than the ester groups) per 100 methylene groups as measured by nuclear magnetic resonance, particularly 500 megahertz proton NMR analysis.

The flow improver is used in a concentration in the range of from about 0.001 to about 2 wt.%, preferably from about 0.005 to about 0.2 percent by weight, based on the weight of the distillate fuel being treated.

The second additive provides the n-alkanes greater than C_{24} and preferably has a carbon number distribution from about 20 to about 40. We prefer also that the additive consist predominantly of linear alkanes although it may also contain a small amount of branched hydrocarbons. The additive may be in the form of a refinery stream such as a heavy atmospheric gas oil, vacuum gas oil or heavy cracked gas oil which provides alkanes having carbon numbers in the required range. It is believed that the additive nucleates the crystallisation of the n-alkanes in the fuel and also co-crystallises with the first n-alkanes to precipitate from the fuel. The preferred n-alkane distribution of the additive therefore depends upon the particular fuel. Whilst the C_{24} and higher n-alkane component should be greater than 0.35 wt.% based on the fuel we prefer that it be greater than 0.5 wt.%.

Other additives may also be used to give further improvements in low temperature properties, for example a diamide or preferably a half amide, half amine salt of a dicarboxylic acid or anhydride such as phthalic anhydride, and a secondary amine, the alkyl groups preferably containing 12 to 20 carbon atoms, may be added. A particularly preferred compound is the half amide, half amine salt of phthalic acid and dihydrogenated tallow amine - Armeen 2HT (approx. 4 wt.% n- C_{14} alkyl, 30 wt.% n- C_{16} alkyl, 60 wt.% n- C_{18} alkyl, the remainder being unsaturated). The amount of diamide or half amide, half amine salt which is added is usually 0.001 to 2 wt.%, preferably 0.005 to 0.2 wt.%, based on the weight of distillate fuel.

Examples of other additives are the glycol esters such as those defined in our EP-B-0 061 895 and the esters and amines of maleic anhydride copolymers such as those defined in EP-A-0214786, and polyolefines and chlorinated polyolefines and the amines or amides of alkyl succinic anhydrides.

The cold flow properties of the distillate fuel can be further improved by adding thereto a wax-naphthalene condensate. A typical condensate is prepared by chlorinating a wax containing n- and branched C_{18} to C_{39} paraffins (C_{26} average) to obtain a chlorinated wax containing about 15 weight % chlorine. The chlorowax thus obtained is polymerised with naphthalene via an alkylation reaction to give a condensate containing alternating wax and naphthalene units.

The amount of condensate added is usually 0.00005 to 0.1 wt.% based on the weight of the distillate fuel.

The additives of the present invention may be supplied as concentrates for incorporation into the bulk fuel, such a concentrate comprising a solution containing from 30 to 70 wt.%, preferably 40 to 60 wt.%, of a mixture of copolymer of ethylene and another ethylenically unsaturated monomer and the n-alkane

composition.

The following Additives were used in the Examples,

Additive 1 63 wt.% solution of a mixture of two ethylene vinyl acetate copolymers, marketed by Exxon Chemicals as ECA 8400. (This additive was not used alone.)

Additive 2 Additive 1 plus 10 wt.% of a wax naphthalene condensate.

Additive 3 a mixture of (1) an ethylene-vinyl acetate copolymer (2 parts by weight), (2) a wax-naphthalene condensate and (3) 1 part by weight of a half amide-half amine salt of phthalic acid and dihydrogenated tallow amine (Armeen 2HT). The amount of wax-naphthalene condensate was 5 weight per cent of the total weight of copolymer (1) and half amide-half amine salt (2).

Additive 4 A 45 wt.% solution of a high branched ethylene vinyl acetate copolymer of molecular weight about 2000 and vinyl acetate content about 30 wt.% prepared according to FR-A-1461008.

Additive 5 A blend of ethylene vinyl acetate copolymers and fumarate vinyl acetate copolymers marketed by Exxon as Paraflow 206.

Additive 6 A concentrate in an aromatic diluent of about 50 wt.% of a mixture of two ethylene-vinyl acetate copolymers in a ratio of about 75 wt.% of wax growth arrestor and about 25 wt.% of nucleator. The wax growth arrestor consists of ethylene and about 38 wt.% vinyl acetate, and has a number average molecular weight of about 2500-3500. The nucleator consists of ethylene and about 16 wt.% vinyl acetate and has a number average molecular weight of about 3000 (VPO). It is identified in GB-A-1374051 as copolymer H.

Example 1

To a high wax content distillate fuel having a +6° C cloud point obtained from a Chinese crude having the following ASTM D-86 characteristics:

Initial Boiling Point	212.8° C
5%	234.8° C
10%	243.8° C
20%	255.8° C
30%	263.4° C
40%	279.1° C
50%	288.8° C
60%	298.6° C
70%	303.3° C
80%	321.0° C
90%	334.8° C
95%	343.8° C
Final Boiling Point	361.0° C

and a wax content of about 8 weight % at 10° C below cloud point was added 7 volume per cent of a vacuum gas oil (VGO) having n-alkanes substantially in the C₂₅ to C₃₅ range and ASTM D-86 distillation characteristics as follows:

Initial Boiling Point	252.0° C
10%	301.5° C
50%	358.0° C
90%	435.0° C
Final Boiling Point	480.0° C

The n-alkane distributions of the fuel and the vacuum gas oil were

	Fuel	VGO
C ₁₂	0.71	
C ₁₃	1.08	
C ₁₄	1.80	
C ₁₅	2.59	
C ₁₆	2.25	
C ₁₈	2.53	0.40
C ₁₉	2.37	0.81
C ₂₀	2.19	1.81
C ₂₁	2.12	2.59
C ₂₂	1.70	3.74
C ₂₃	0.97	4.39
C ₂₄	0.43	4.29
C ₂₅	0.18	3.94
C ₂₆	0.08	3.24
C ₂₇	0.03	2.36
C ₂₈	0.02	1.95
C ₂₉	0.01	1.02
C ₃₀	0.003	0.73
C ₃₁		0.44
C ₃₂		0.26
C ₃₃		0.15
C ₃₄		0.14
C ₃₅		0.09
C ₃₆		0.03
C ₃₇		0.05
C ₃₈		0.02

	<u>A</u>	<u>B</u>
Base Fuel wt%	100	95
Vacuum Gas Oil wt%		5

IBP	212	210
20%	256	258
50%	289	292
90%	335	340
FBP	361	370

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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 centigrade drop in temperature starting from not less than 5 °C above 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 inches (about 2.9 cm²). 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 temperature at which the last filtration commenced is recorded and reported as the cold filter plugging point.

CFPP response to Additive 2 (° C)		
0 ppm	+6	+6
1000 ppm	+5	+1

With 1250 ppm of Additive 3 the cold filter plugging point was -1 °C.

Example 2

In this example the addition of a vacuum gas oil (VGO) of cloud point +12 °C with maximum n-alkane C₃₂ is compared with the addition of a Heavy Cracked Distillate of cloud point +35 °C, (max n-alkane 33) to a base fuel of cloud point + 3 °C produced from Australian Bass Strait crude, having a 8.8 wt.% wax content as measured by wax precipitation to a temperature 10 °C below the cloud point.

The composition of the components was:

<u>Distillation</u>	<u>VGO</u> <u>Gas Chroma-</u> <u>tography</u>	<u>Heavy</u> <u>Cracked</u> <u>D.86</u>	<u>Base</u> <u>Fuel</u> <u>D.86</u>
IBP	221	230	224
10%	295	336	247
20%	319	348	256
50%	361	366	276
90%	430	387	316
95%	446	400	325
FBP	491		334

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Wax Content Wt % 3.0 15.4 8.8

n-alkane distribution
(wt% in fuel)

5	C ₁₀			0.21
	C ₁₁			0.41
10	C ₁₂	0.06		0.83
	C ₁₃	0.13	0.03	2.24
	C ₁₄	0.27	0.10	3.52
15	C ₁₅	0.44	0.14	3.75
	C ₁₆	0.65	0.17	3.71
	C ₁₇	0.87	0.22	3.51
	C ₁₈	1.04	0.27	3.26
20	C ₁₉	1.20	0.53	3.08
	C ₂₀	1.46	1.16	2.17
	C ₂₁	1.28	2.75	0.96
25	C ₂₂	1.13	3.50	0.19
	C ₂₃	0.88	4.25	0.04
	C ₂₄	0.64	7.94	0.01
30	C ₂₅	0.47	2.87	
	C ₂₆	0.40	1.76	
	C ₂₇	0.35	1.08	
35	C ₂₈	0.28	0.48	
40	C ₂₉	0.25	0.24	
	C ₃₀	0.14	0.09	
	C ₃₁	0.08	0.04	
45	C ₃₂	0.02	0.01	
	C ₃₃	-	0.01	

The base fuel contained 27.3 wt.% of alkanes C₁₂ and higher.

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The Following Blends were prepared:

	1	2	3
Kerosene wt%	10	10	-
Base Fuel wt %	75	75	100
VGO wt %	15	-	-
Heavy Cracked wt %	-	15	-

The D.86 Distillation of the blends was as follows:

IBP	201	202	224
20%	250	251	256
50%	279	281	276
90%	335	350	316
FBP	370	391	334
Added C ₂₄ + n-alkane	0.39	2.18	-

The CFPP response to the following additives was as follows:

Amount of Additive	Blend 1		Blend 2		Blend 3	
	Additive 4	Additive 5	Additive 4	Additive 5	Additive 4	Additive 5
0 ppm	-1	-1	5	5	-3	-3
500 ppm	-1	-1	2	-2	-3	-3
1000 ppm	-2	-2	-1	-9	-3	-3
1500 ppm	-2	-2	-1	-10	-3	-3

Example 3

In this example the addition to a base fuel of cloud point +7°C of component with C₃₂ - C₃₃ n-alkanes is compared with the addition of Heavy Gas Oil streams (HGO-1 and HGO-2) containing higher n-alkanes obtained from a waxy Chinese Crude from Daqing.

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The components were as follows:

		<u>Base</u>	<u>VGO-A</u>	<u>VGO-B</u>	<u>HGO-1</u>	<u>HGO-2</u>
5		<u>Fuel</u>				
	Distillation					
	Type	D.86	GC	GC	GC	GC
10	IBP	194	207	309	159	151
	10%	241	270	351	295	278
	20%	257	292	368	332	312
15	50%	289	325	400	397	391
	90%	342	380	447	461	485
	95%	353	401	460	475	504
20	FBP	361	449	488	509	544

n-alkane Distribution

25	C ₁₀	0.25				
	C ₁₁	0.71				
	C ₁₂	1.45				0.12
30	C ₁₃	2.10	0.35			0.25
	C ₁₄	2.89	1.00		0.23	0.47
	C ₁₅	3.22	1.55		0.60	0.81
35	C ₁₆	3.42	2.68		0.86	1.24
	C ₁₇	3.33	3.76		0.64	1.60
	C ₁₈	3.14	5.02		1.28	1.74
40	C ₁₉	2.90	5.23	0.78	2.17	1.85
	C ₂₀	2.67	4.16	1.98	2.22	1.97
	C ₂₁	2.29	2.95	3.27	2.28	2.15
45	C ₂₂	1.75	1.92	3.91	3.17	2.17

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	C ₂₃	1.34	1.46	4.85	3.66	2.16
	C ₂₄	0.73	0.87	4.33	3.47	2.00
5	C ₂₅	0.45	0.74	4.22	3.98	2.19
	C ₂₆	0.22	0.44	3.06	3.37	1.84
	C ₂₇	0.09	0.30	2.26	3.09	1.78
10	C ₂₈	0.04	0.19	1.52	2.47	1.54
	C ₂₉	0.01	0.11	0.94	1.90	1.37
	C ₃₀		0.07	0.55	1.17	1.07
15	C ₃₁		0.04	0.31	0.83	1.01
	C ₃₂		0.01	0.13	0.48	0.78
	C ₃₃		0.01	0.10	0.30	0.62
20	C ₃₄			0.05	0.19	0.47
	C ₃₅				0.11	0.42
	C ₃₆				0.03	0.24
	C ₃₇				0.03	0.21
25	C ₃₈					0.14
	C ₃₉					0.11
	C ₄₀					0.07
30	C ₄₁					0.05
	C ₄₂					0.04
	C ₄₃					0.03

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The base fuel contained 32 wt.% of alkanes C₁₂ and higher.

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The following blends were prepared:

	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>	<u>F</u>	<u>G</u>	<u>H</u>	<u>I</u>
Base Fuel (wt%)	100	97	95	97	95	97	95	97	95
VGO-A (wt%)		3	5	-	-	-	-	-	-
VGO-B (wt%)		-	-	3	5	-	-	-	-
HGO-1 (wt%)		-	-	-	-	3	5	-	-
HGO-2 (wt%)		-	-	-	-	-	-	3	5

D.86 Distillation

IBP	194	192	192	194	195	190	189	191	188
20%	257	242	258	258	259	258	258	258	258
50%	289	290	290	292	294	291	293	291	292
90%	342	343	343	346	348	346	348	346	348
FBP	361	361	362	369	375	369	375	369	371
C ₂₄ + added	-	0.08	0.14	0.52	0.87	0.64	1.07	0.48	0.80
n-alkane									

CFPP value when treated with Additive 2 was (°C)

0 ppm	+6	+7	+7	+6	+9	+7	+8	+4	+4
1000 ppm	+6	+6	+6	+5	+4	0	0	+1	+4
1500 ppm	+5	+6	+6	+2	+1	-1	-1	-2	+4

Example 4

This example illustrates the improvement in response to flow improvers by replacing heavy atmospheric gas oil (HGO) with heavy cracked gas oil (HCO), Base Fuel 1 had a cloud point of -1 °C and use Fuel 2 of -2 °C.

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The Components used were as follows:

		<u>Base</u> <u>Fuel 1</u>	<u>HGO</u>	<u>Heavy Cycle</u> <u>(HCO)</u>	<u>Base</u> <u>Fuel 2</u>
5					
	Distillation Type	D.86	D.86	D.86	D.86
	IBP	226	276	230	220
10	10%	248	300	336	249
	20%	256	310	348	258
	50%	272	326	366	276
15	90%	304	346	400	314
	95%	312	350	400	322
	FBP	322	360		330
20	Wax Content at 10°C below the cloud point	9.9	21.50	15.40	

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N-alkane Distribution

5	C ₁₂	0.93	0.08		0.70
	C ₁₃	2.31	0.25	0.03	1.94
	C ₁₄	3.77	0.47	0.10	3.48
	C ₁₅	3.13	0.75	0.14	3.85
10	C ₁₆	3.15	1.15	0.17	3.52
	C ₁₇	3.02	1.96	0.22	3.20
	C ₁₈	2.66	3.47	0.27	3.11
15	C ₁₉	2.00	6.02	0.53	3.25
	C ₂₀	1.22	8.82	1.16	2.59
	C ₂₁	0.44	8.09	2.75	1.59
20	C ₂₂	0.13	5.35	3.50	0.32
	C ₂₃	0.03	2.70	4.25	0.04
	C ₂₄		1.30	7.94	0.02
	C ₂₅		0.53	2.87	
25	C ₂₆		0.20	1.76	
	C ₂₇		0.08	1.08	
	C ₂₈		0.02	0.48	
30	C ₂₉		0.01	0.24	
	C ₃₀		0.003	0.09	
	C ₃₁			0.04	
35	C ₃₂			0.01	
	C ₃₃			0.01	
	C ₃₄				

The Base Fuel 1 contained 22.8 wt.% n-alkanes C₁₂ and higher and Base Fuel 2 27.6 wt.%.

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The following blends were prepared:

		<u>A</u>	<u>B</u>
5			
	Base Fuel 1 wt %	85	85
	HGO wt %	15	-
10	HCO wt %	-	15
	Distillation D.86		
15	IBP	227	227
	20%	260	260
	50%	279	280
20	90%	318	340
	FBP	339	390
25	Added C ₂₄ + n-alkanes	0.32	2.18
	CFPP Response to Additive 5		
30	0 ppm	-2	+3
	300 ppm	-	-4
	1000 ppm	-2	-9

Example 5

40 Using the Base Fuel 2 referred to in Example 4, the following blends were prepared:

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Blends

5		<u>J</u>	<u>K</u>
	Kerosene wt %	15	15
10	Base Fuel 2 wt %	70	70
	HCO wt %	-	15
	H MGO wt.%	15	-

CFPP Response

20	0 ppm	1	3
	200 ppm Additive 4	-	3
	1000 ppm Additive 4	1	-4
	200 ppm Additive 6	-	-5
25	1000 ppm Additive 6	1	-8
	200 ppm Additive 5	-	-5
	1000 ppm Additive 5	1	-10
30	C ₂₄ + added n-alkanes	0.32	2.18

35 In this example, the quantities of additive specified are the actual amounts of polymer.
 The effect of using several other commercial available low temperature flow improvers was also evaluated and found to be as follows:

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	ppm of active ingredient used	Additive used	J	K
	200	Additive 3	1	-4
	1000	Additive 3	1	-10
5	200	Amoco 2042E	1	-6
	1000	Amoco 2042E	1	-9
	200	Keroflux H	1	-4
	1000	Keroflux H	1	-7
	200	BASF CE 5323	1	-6
10	1000	BASF CE 5323	1	-8
	200	BASF CE 5486	1	-3
	1000	BASF CE 5486	1	-9
	200	Bayer FI 1814	1	-7
	1000	Bayer FI 1814	1	-9
15	200	Hoechst Dodiflow 3592	1	-2
	1000	Hoechst Dodilow 3592	1	-4
	200	Sumitomo FI 20	1	-5
	1000	Sumitomo FI 20	1	-9
	200	Elf 8320	1	0
20	1000	Elf 8320	1	-5
	200	Elf 8327	1	4
	1000	Elf 8327	1	1

Claims

1. A liquid fuel composition comprising a major proportion by weight of a distillate fuel containing between 4 and 10 wt % wax at 10 °C below cloud point and containing substantially no paraffins longer than n-triacontane, a low temperature flow improver at 0.001 to 2.0 wt % based on the weight of the distillate fuel and added n-alkanes which provide added C₂₄ and higher alkanes in an amount greater than 0.35 wt %, based on the weight of the fuel.
2. A composition according to claim 1, wherein the distillate fuel contains about 8 weight % of wax at 10 °C below cloud point.
3. A composition according to claim 1 or claim 2, wherein the amount of flow improver is 0.005 to 0.2 percent by weight based on the weight of distillate fuel.
4. A composition according to any one of the preceding claims where the added n-alkanes have a carbon number distribution from 20 to 40.
5. A composition according to any one of the preceding claims wherein the amount of n-alkanes of C₂₄ and higher added to the distillate fuel is greater than 0.5 wt % of the distillate fuel.
6. A composition according to any one of the preceding claims in which the n-alkanes are added by blending the distillate with a vacuum gas oil, a heavy cracked gas oil, or a heavy atmospheric gas oil.
7. A composition according to claim 6, in which 5 to 10% by weight of vacuum gas oil or heavy atmospheric gas oil is used.
8. A composition according to claim 6 or claim 7, wherein vacuum gas oil comprising n-alkanes substantially in the C₂₅ to C₃₅ range is used.
9. A composition according to claim 6 or claim 7, wherein heavy atmospheric gas oil comprising n-alkanes substantially in the C₁₄ to C₃₇ range is used.
10. A composition according to any one of the preceding claims in which the fuel has a final boiling point below 370 °C.

11. The use as a cold flow improver for distillate fuel containing between 4 and 10 wt % of wax at 10 °C below cloud point and containing no paraffins longer than n-triacontane, of
 - (a) a mixture of n-alkanes which provides at least 0.35 weight %, based on the weight of the fuel, of alkanes C₂₄ and higher and
 - (b) 0.001 to 2 weight %, based on the weight of the fuel, of a low temperature flow improver.
12. The use according to claim 11 which provides at least 0.5 wt % added alkanes C₂₄ and higher.
13. The use according to claim 11 or claim 12 in which the n-alkanes are added as a component in vacuum gas oil or heavy gas oil.
14. The use according to any of claims 11 to 13, in which the n-alkanes contain from 20 to about 40 carbon atoms.
15. A liquid fuel composition comprising a major proportion by weight of a distillate fuel containing between 4 and 10 wt % wax at 10 °C below cloud point and containing substantially no paraffins longer than n-triacontane, 0.001 to 2.0 wt % based on the weight of the distillate fuel of a copolymer of ethylene and an ethylenically unsaturated monomer and 5 to 10% by volume based on the volume of distillate fuel and copolymer of a vacuum gas oil, heavy cracked gas oil, or a heavy atmospheric gas oil.
16. A method of improving the cold flow of a distillate fuel containing between 4 and 10 wt% wax at 10 °C below cloud point and containing substantially no paraffins longer than n-triacontane, which comprises adding thereto from 0.001 to 2.0 wt%, based on the weight of the fuel, of a low temperature flow improver and n-alkanes which provide C₂₄ and higher alkanes in an amount greater than 0.35 wt%, based on the weight of the fuel.

Patentansprüche

1. Flüssige Brennstoffzusammensetzung, die einen größeren Gewichtsanteil eines Destillatbrennstoffs, der bei 10 °C unter dem Trübungspunkt zwischen 4 und 10 Gew.% Paraffin und im wesentlichen keine Paraffine, die länger als n-Triacontan sind, enthält, 0,001 bis 2,0 Gew.%, bezogen auf das Gewicht des Destillatbrennstoffs, eines Tieftemperatur-Fließverbesserers und zugesetzte n-Alkane umfaßt, die zugesetzte C₂₄ und höhere Alkane in einer Menge von mehr als 0,35 Gew.%, bezogen auf das Gewicht des Brennstoffs, liefern.
2. Zusammensetzung nach Anspruch 1, bei der der Destillatbrennstoff bei 10 °C unter dem Trübungspunkt etwa 8 Gew.% Paraffin enthält.
3. Zusammensetzung nach Anspruch 1 oder 2, bei der die Menge des Fließverbesserers 0,005 bis 0,2 Gew.%, bezogen auf das Gewicht des Destillatbrennstoffs, beträgt.
4. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der die zugesetzten n-Alkane eine Kohlenstoffzahlverteilung von 20 bis 40 besitzen.
5. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der die dem Destillatbrennstoff zugesetzte Menge an C₂₄ und höheren n-Alkanen größer als 0,5 Gew.% des Destillatbrennstoffs ist.
6. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der die n-Alkane zugesetzt werden, indem das Destillat mit einem Vakuumgasöl, einem schweren gecrackten Gasöl oder einem schweren atmosphärischen Gasöl vermischt wird.
7. Zusammensetzung nach Anspruch 6, bei der 5 bis 10 Gew.% Vakuumgasöl oder schweres atmosphärisches Gasöl verwendet wird.
8. Zusammensetzung nach Anspruch 6 oder 7, bei der Vakuumgasöl verwendet wird, das n-Alkane im wesentlichen im C₂₅- bis C₃₅-Bereich umfaßt.

9. Zusammensetzung nach Anspruch 6 oder 7, bei der schweres atmosphärisches Gasöl verwendet wird, das n-Alkane im wesentlichen im C₁₄- bis C₃₇-Bereich umfaßt.
10. Zusammensetzung nach einem der vorhergehenden Ansprüche, bei der der Brennstoff einen Endsiedepunkt unter 370 °C besitzt.
11. Verwendung als Kaltfließverbesserer für Destillatbrennstoff, der bei 10 °C unter dem Trübungspunkt zwischen 4 und 10 Gew.% Paraffin und im wesentlichen keine Paraffine, die länger als n-Triacontan sind, enthält, von
 - (a) einer Mischung aus n-Alkanen, die mindestens 0,35 Gew.%, bezogen auf das Gewicht des Brennstoffs, C₂₄ und höhere n-Alkane liefern und
 - (b) 0,001 bis 2 Gew.%, bezogen auf das Gewicht des Brennstoffs, eines Tieftemperatur-Fließverbesserers.
12. Verwendung nach Anspruch 11, die mindestens 0,5 Gew.% zugesetzte C₂₄ und höhere Alkane liefert.
13. Verwendung nach Anspruch 11 oder 12, bei der die n-Alkane als eine Komponente in Vakuumgasöl oder schwerem Gasöl zugesetzt werden.
14. Verwendung nach einem der Ansprüche 11 bis 13, bei der die n-Alkane 20 bis etwa 40 Kohlenstoffatome enthalten.
15. Flüssige Brennstoffzusammensetzung, die einen größeren Gewichtsanteil eines Destillatbrennstoffs, der bei 10 °C unter dem Trübungspunkt zwischen 4 und 10 Gew.% Paraffin und im wesentlichen keine Paraffine, die länger als n-Triacontan sind, enthält, 0,001 bis 2,0 Gew.%, bezogen auf das Gewicht des Destillatbrennstoffs, eines Copolymers aus Ethylen und einem ethylenisch ungesättigten Monomer und 5 bis 10 Vol.%, bezogen auf das Volumen von Destillatbrennstoff und Copolymer, eines Vakuumgasöls, schweren gecrackten Gasöls oder schweren atmosphärischen Gasöls umfaßt.
16. Verfahren zur Verbesserung des Kaltfließverhaltens eines Destillatbrennstoffs, der bei 10 °C unter dem Trübungspunkt zwischen 4 und 10 Gew.% Paraffin und im wesentlichen keine Paraffine, die länger als n-Triacontan sind, enthält, bei dem diesem 0,001 bis 2 Gew.%, bezogen auf das Gewicht des Brennstoffs, eines Tieftemperatur-Fließverbesserers und n-Alkane zugesetzt werden, die C₂₄ und höhere Alkane in einer Menge von mehr als 0,35 Gew.%, bezogen auf das Gewicht des Brennstoffs, liefern.

Revendications

1. Composition de combustible liquide comprenant une proportion dominante, en poids, d'un combustible distillé contenant 4 à 10 % en poids de cire à une température inférieure de 10 °C au point de trouble et ne contenant pratiquement aucune paraffine supérieure au n-triacontane, un agent améliorant l'écoulement à froid à basse température en une quantité de 0,001 à 2,0 % en poids sur la base du poids du combustible distillé et des n-alcanes ajoutés qui fournissent des n-alcanes ajoutés ayant 24 ou plus de 24 atomes de carbone en une quantité supérieure à 0,35 % en poids, sur la base du poids du combustible.
2. composition suivant la revendication 1, dans laquelle le combustible distillé contient environ 8 % en poids de cire à une température inférieure de 10 °C au point de trouble.
3. Composition suivant la revendication 1 ou la revendication 2, dans laquelle la quantité d'agent améliorant l'écoulement est comprise dans l'intervalle de 0,005 à 0,2 % en poids sur la base du poids du combustible distillé.
4. Composition suivant l'une quelconque des revendications précédentes, dans laquelle les n-alcanes ajoutés possèdent une distribution des nombres d'atomes de carbone de 20 à 40.
5. Composition suivant l'une quelconque des revendications précédentes, dans laquelle la quantité des n-alcanes ayant 24 ou plus de 24 atomes de carbone ajoutés au combustible distillé est supérieure à 0,5

% en poids du combustible distillé.

6. Composition suivant l'une quelconque des revendications précédentes, dans laquelle les n-alcanes sont ajoutés par mélange du distillat à un gas-oil sous vide, un gas-oil lourd de craquage ou un gas-oil atmosphérique lourd.
7. Composition suivant la revendication 6, dans laquelle une quantité de 5 à 10 % en poids de gas-oil sous vide ou de gas-oil atmosphérique lourd est utilisée.
8. Composition suivant la revendication 6 ou la revendication 7, dans laquelle un gas-oil sous vide comprenant des n-alcanes essentiellement dans la plage de C₂₅ à C₃₅ est utilisé.
9. Composition suivant la revendication 6 ou la revendication 7, dans laquelle un gas-oil atmosphérique comprenant des n-alcanes essentiellement dans la plage de C₁₄ à C₃₇ est utilisé.
10. Composition suivant l'une quelconque des revendications précédentes, dans laquelle le combustible possède un point d'ébullition final inférieur à 370 °C.
11. Utilisation comme agent améliorant l'écoulement à froid, pour un combustible distillé contenant 4 à 10 % en poids de cire à une température inférieure de 10 °C au point de trouble et ne contenant aucune paraffine supérieure au n-triacontane,
 - (a) d'un mélange de n-alcanes qui fournit au moins 0,35 % en poids, sur la base du poids du combustible, d'alcanes ayant 24 ou plus de 24 atomes de carbone, et
 - (b) de 0,001 à 2 % en poids, sur la base du poids du combustible, d'un agent améliorant l'écoulement à basse température.
12. Utilisation suivant la revendication 11, qui fournit au moins 0,5 % en poids d'alcanes ajoutés ayant un nombre d'atomes de carbone égal ou supérieur à 24.
13. Utilisation suivant la revendication 11 ou la revendication 12, dans laquelle les n-alcanes sont ajoutés comme constituant dans un gas-oil sous vide ou un gas-oil lourd.
14. Utilisation suivant l'une quelconque des revendications 11 à 13, dans laquelle les n-alcanes contiennent 20 à environ 40 atomes de carbone.
15. Composition de combustible liquide comprenant une proportion dominante, en poids, d'un combustible distillé contenant 4 à 10 % en poids de cire à une température inférieure de 10 °C au point de trouble et ne contenant pratiquement aucune paraffine supérieure au n-triacontane, 0,001 à 2,0 % en poids, sur la base du poids du combustible distillé, d'un copolymère d'éthylène et d'un monomère à insaturation éthylénique, et 5 à 10 % en volume, sur la base du volume du combustible distillé et du copolymère, d'un gas-oil sous vide, d'un gas-oil lourd de craquage ou d'un gas-oil atmosphérique lourd.
16. Procédé pour améliorer l'écoulement à froid d'un combustible distillé contenant 4 à 10 % en poids de cire à une température inférieure de 10 °C au point de trouble et ne contenant pratiquement aucune paraffine supérieure au n-triacontane, qui comprend l'addition à ce combustible de 0,001 à 2,0 % en poids, sur la base du poids du combustible, d'un agent améliorant l'écoulement à basse température et de n-alcanes qui fournissent des alcanes ayant un nombre d'atomes de carbone égal ou supérieur à 24 en une quantité supérieure à 0,35 % en poids, sur la base du poids du combustible.