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(54) **Process for the preparation of a flow-improved fuel oil composition.**

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EP 0 301 837 B1

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Description

a) Field of the Invention

5 This invention relates to a method for improving the cold flow properties of a fuel oil composition having a low flowability at low temperature, the composition being prepared from a heavy distillate fuel of petroleum and a low temperature flow improver.

b) Prior Art

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As is well known, among fractions obtained by distilling crude oil, those called as middle and heavy fractions and having boiling points from about 150 °C to 450 °C, respectively, are used extensively as various fuel sources such as kerosene, gas oil, and heavy oil A.

15 Particularly, kerosene and heavy oil A suffer remarkable decrease in flowability at low temperatures (or cold flowability) in winter season and the like due to separation of wax component contained in the oil, which tends to cause severe problems.

For example, under cold conditions of winter season, the wax component contained in kerosene separates out and causes clogging or plugging of minute screen which is incorporated in a filter for preventing impurities provided in midway in a pipeline from a kerosene tank to an engine in a diesel automobile, so that supply of kerosene becomes impossible and as a result the engine stops. Under much lower temperature conditions, kerosene as a whole gels to lose flowability.

Separation of wax component occurs also in heavy oil A, which is used widely for driving engines in fishing boats, for warming greenhouses used in order to accelerate cultivation as well as for heating buildings, resulting in incomplete combustion which gives a serious influence to humans and plants.

25 Various measures have heretofore been taken in order to maintain sufficient flowability of fuel oil at low temperatures.

For example, a method is known in which fuel oil is heated with warm water or with an electric heater in order to prevent decrease in the temperature of the fuel oil due to decrease in the ambient temperature, and to keep the temperature of the fuel oil at certain temperature range. However, this method is practically disadvantageous because it requires amelioration or reconstruction of installments and incur additional cost for energy.

Also, it is known to dilute fuel oils with those fractions which retain cold flowability at relatively low temperatures, e.g., kerosene fractions. This method is not suitable because relatively light fuel oils to which the kerosene fractions belong are in great demand and highly value-added.

35 Another conventional method for improving the cold flowability of fuel oils is to add a cold flow improver to the fuel oils.

The action of the cold flow improver is to give influence upon separation-out of wax from fuel oils to prevent the growth of wax into large-size crystals but retain the wax in the form of minute crystals, thus stabilizing the cold flowability.

40 Various synthetic chemicals have been proposed as a cold flow improver. However, their effect vary extremely depending on the characteristics of fuel oils to which they are added; it is very important to grasp the characteristics of fuel oils which can be subjected to quality control steadily. However, this is very difficult because there are a great variety of crude oil types very complicated operational conditions of distilling apparatus and other factors are involved.

45 In order for the cold flow improver to virtually exhibit its effect upon addition, various considerations have been taken on the characteristics of the fuel oils concerned.

For example, Published Unexamined Japanese Patent Application No. Sho-58-134188 describes improvement in the cold flowability of a middle fraction fuel oil by adding 0.2 to 1.5 parts by weight of an ethylene copolymer and n-paraffin having 26 to 27 carbon atoms to 100 parts by weight of the fuel oil.

50 This method not only requires addition of both the ethylene copolymer and n-paraffin, which causes complication of installments and operation, but also involves increase in the amount of wax separated out at low temperatures because of paraffin, which is a principal causal substance for aggravation of cold flowability due to separating-out of wax, is positively added. As the result, it is often the case that the cold flow improver does not act effectively.

55 In a typical utility where fuel oil is used as a fuel for driving a Diesel engine automobile, fuel oil is passed in a fuel supply pipeline in the midway of which is provided with a strainer which tends to cause early plugging because of separation-out of wax in great amounts, resulting in shortened wax saturation time. Therefore, this solution involving provision of strainer is undesirable.

GB 1,264,684 describes the addition to a middle distillate fuel oil, which contains an indeterminate amount of normal paraffins within the range of about 10 to 26 carbon atoms, of a paraffinic distillate fraction containing C₂₄ to C₄₀ n-paraffins in order to improve the response of the fuel oil to ethylene copolymer flow improvers. The amount of C₂₄+ n-paraffin added to the fuel is from 0.1 to 2wt%.

Published Unexamined Japanese Patent Application No. Sho-61-58116 discloses a composition containing gas oil of which the content of paraffin wax that separates out at a temperature of -20 °C is adjusted to a level of from 5.5 to 12 wt.% and a pour point depressant.

However, this proposal is insufficient because even with gas oil of which the content of paraffin wax separating out at -20 °C is specifically adjusted to a range of from 5.5 to 12 wt.%, it sometimes happens that the addition of a pour point depressant fails to decrease CFPP (cold filter plugging point) at all, and that decrease of CFPP cannot be achieved until a specified pour point depressant is added.

US 4,210,424 describes the preparation and use of a three component additive system for improving cold flow properties of distillate fuel oils. The three component additive system comprises ethylene polymer or copolymer, normal paraffinic wax containing n-paraffins ranging from C₂₃ to C₃₇, and nitrogen compounds such as amides, amine salts and ammonium salts of carboxylic acids or anhydrides.

As described above, it has conventionally been difficult to provide fuel oils of which cold flowability has been improved steadily because the prior art additives are effective only to fuel oils having specific characteristics or because a large amount of a specific substance other than the additive must be added in order to facilitate exhibition of the effect of the prior art additives.

SUMMARY OF THE INVENTION

Therefore, an object of this invention is to obviate the above-described defects of the prior arts and provide a fuel oil mainly composed of medium and/or heavy distillates of crude oil and having an improved cold flowability.

Another object of this invention is to optimize the amount of n-paraffin contained in the middle and/or heavy distillates of crude oil in order to have sufficiently exhibited the effect of a cold flow improver.

As a result of extensive research, this invention has been completed, which provides a method for improving the cold flow properties, measured as decreased cold flow pour point, of base fuel oil composed mainly of middle or heavy distillates of crude oil, the method comprising the following steps:

- (a) determining the amount of n-paraffin having at least 25 carbon atoms and the amount of wax which separates out at a temperature of 10 °C lower than the cloud point,
- (b) if necessary, adjusting the amount of n-paraffin having at least 25 carbon atoms in said base fuel oil to an amount of not smaller than 0.1 by weight, and smaller than 0.6% by weight, and the amount of said wax to smaller than 4% by weight, and
- (c) adding a cold flow improver composed of a copolymer of ethylene and a vinyl ester of unsaturated carboxylic acid, the copolymer having an ethylene content of 60-80% by weight and an average molecular weight of 1000-5000, in an amount of 30 to 1500 ppm.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a graph representing gas chromatogram of test oil No.5 obtained by the technique of gas chromatographic n-paraffin analysis according to example, with the portions calculated as n-paraffin being shadowed with oblique lines.

Fig. 2 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive A, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 36.5 wt.% and a number average molecular weight of 1,690.

Fig. 3 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive B, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 16.5 wt.% and a number average molecular weight of 2,200.

Fig. 4 is a graph showing relationship between the content of n-paraffin having at least 25 carbon atoms contained in various test oils and decrease in the cold filter plugging point (Δ CFPP) upon the addition of 500 ppm of Additive C, i.e., a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 44.6 wt.% and a number average molecular weight of 1,820.

DETAILED DESCRIPTION OF THE INVENTION

In this invention, the term "base fuel oil composed mainly of middle and/or heavy distillates of crude oil" used herein refers to distillate oils obtained by distilling crude oil which is a mixture of a great number of components composed mainly of hydrocarbons having a boiling point of from about 150 ° C. to about 450 ° C.

5 Examples of distillate fractions obtained from general petroleum distilling installments include light gas oil, heavy gas oil, or heavy gas oil hydrogenated using a purifier such as a unifiner, or vacuum gas oil which is obtained by vacuum distilling the distillation residue from normal pressure distillator in a vacuum distillator and its hydrogenated product. They can be used as a blend depending on their application.

If necessary, the base fuel oil can be mixed with a small amount of middle or heavy distillate oil generated in petroleum purifiers, e.g., oils treated in catalytic cracking apparatus, hydrogenolysis apparatus, etc. or residual oils after dewaxing during manufacture of lubricants.

Further, it can be mixed with a small amount of normal pressure residual oil or vacuum residual oil or extracted oil generated during the step of purification of lubricants, as is generally adopted as a method for adjusting heavy oil A.

15 In this invention, the amount of n-paraffin having at least 25 carbon atoms contained in the middle and/or heavy distillate oils of petroleum as base fuel oil can be analyzed in a usual manner using a programmed-temperature gas chromatography apparatus.

More particularly, a trace amount sample is analyzed using a hydrogen flame ionizing detector with a column packed with a filler composed of a partition agent having a weak polarity and a porous carrier, and the content of n-paraffin is obtained from the respective chromatograms of the separated components.

For example, a sample oil is injected into a column of a stain-less steel tube having a diameter of 3 mm and a length of 4,000 mm packed with a column filler (Silicon GE SE-30, 2%, 60/80 mesh, Uniport HP carrier) commercially available from Wako Pure Chemicals Industries, Ltd. and the temperature of the column is elevated starting from 70 ° C to 270 ° C at a rate of 5 ° C/min., and detection is performed by hydrogen flame ionizing method. The electric signals detected are processed with a recorder or data processor as output to outside. The content of n-paraffin can be obtained by calculating n-paraffin peak.

In this invention, the content of n-paraffin having at least 25 carbon atoms contained in the middle and/or heavy distillate oils of petroleum as base fuel oil is not smaller than 0.1 wt.% and smaller than 0.6 wt.%.

30 When the content of n-paraffin having at least 25 carbon atoms is smaller than 0.1 wt%, the effect of improvement in cold filter plugging point with a cold flow improver becomes poor. On the other hand, when it is larger than 0.6 wt%, although sometimes addition of a very large amount, e.g., 2,000 ppm or more, of a cold flow improver permits improvement in cold filter plugging point, total amount of wax which separates out increases, resulting in that the fuel oil obtained tends to be one which cannot be used practically.

35 Preferred amount of n-paraffin having at least 25 carbon atoms with which the effect of cold flow improver added can be exhibited more efficiently is not smaller than 0.2 wt.% and smaller than 0.5 wt.%. In this range, addition of a relatively low amount of cold flow improver enables sufficient decrease in the cold filter plugging point.

Examples of the cold flow improver used in this invention include those described in "Shinpan Sekiyu Seihin Tenkazai" ed. by Toshio Sakurai, Saiwai Shobo, July 1986, pp.192-195. More particularly, ethylene copolymers disclosed in Japanese Patent Publication Nos. Sho-48-23165, Sho-55-33480, and Sho-60-17399, Published Unexamined Japanese Patent Application No. Sho-59-136391.

45 Examples of the ethylene copolymer include those copolymers which contain one or more vinyl esters of saturated fatty acids such as vinyl acetate, vinyl propionate, vinyl butyrate, etc. as a comonomer. They may be a low molecular weight product obtained by decomposing a high molecular weight ethylene copolymer with oxygen, peroxides, heat, etc.

The ethylene copolymer includes those copolymers which have an ethylene content of 60 to 80 wt.%, and a number average molecular weight in the range of from 1,000 to 5,000 measured by vapor pressure equilibrium method.

50 When the ethylene content is below 60 wt.% or not lower than 80 wt.%, or the number average molecular weight is below 1,000 or not lower than 5,000, the effect of improvement in cold filter plugging point is rather poor and a large amount of the improver must be added, which is not advantageous from economical viewpoint.

The ethylene copolymer may be used singly or as a mixture of two or more of it. Although the ethylene copolymer can be mixed with and dissolved in fuel oils as it is, it is industrially preferred to dissolve it in a hydrocarbon based solvent and use it as a 10 to 90 wt.% solution.

55 Among the ethylene copolymers described above, ethylene-vinyl acetate copolymers are particularly preferred because they are not only readily available on industrial scale but also are excellent in the effect

of improving cold flowability.

More preferred ethylene-vinyl acetate copolymers are those copolymers having an ethylene content of 60 to 75 wt.%, and a number average molecular weight of 1,000 to 4,000, with molecular weight distribution being not lower than 4.0, and containing not more than 6 methyl terminated side chains per 100 main-chain methylene groups as well as methyl groups contained in the acetyl group. The copolymers exhibit further decrease in cold filter plugging point.

The molecular weight distribution is obtained from the ratio of weight average molecular weight (M_w)/number average molecular weight (M_n) calculated as standard polystyrene according to gel permeation chromatography (GPC) (cf. "Kobunshi Sokuteihou, Kouzou to Bussei" vol. 1, ed. by Kobunshi Gakkai, Baihukan, 1973, pp.76-89).

Further, the degree of branching as used herein is expressed as the number of methyl terminated side chains per 100 main-chain methylene groups besides methyl groups in the acetoxymethyl groups, and calculated from the results obtained by nuclear magnetic resonance (^1H NMR) method (cf. the method described in "Nippon Kagaku Kai Shi", No. 1, 1980, pp.74-78).

That is, peak ratio based on methyl group and methylene group in proton nuclear magnetic resonance spectrum is obtained. Separately, the vinyl acetate content is obtained by saponification method and the number average molecular weight is obtained by vapor pressure osmotic pressure method. The degree of branching is calculated from the peak ratio, the vinyl acetate content and the number average molecular weight. It is to be noted that assumption is made that both the ends of the main-chain methylene groups are methyl groups and that all the side chains are ethyl groups, and therefore, 2 terminal methyl groups are deduced upon calculation.

The amount of the cold flowability improver used in this invention is in the range of preferably 30 to 1,500 ppm, more preferably 50 to 1,000 ppm based on the weight of the base fuel oil composed of the middle and/or heavy distillates of petroleum.

When the amount of addition is below 30 ppm, decrease in cold filter plugging point is hardly expectable, while with the amount of addition above 1,500 ppm, economical advantage as compared with the results obtained is poor, which is undesirable.

The fuel oil composition of this invention may contain one or more of rust preventives, antioxidants, antistatics, cetane value improvers and anticorrosives.

EXAMPLES

Hereinafter, the fuel oil composition of this invention will be explained concretely by way of examples. However, this invention should not be construed as being limited thereto.

Various analyses and measurements of test oils were performed by the following methods.

- (1) Specific density JIS K2249 (1986)
- (2) Kinematic viscosity JIS K2283 (1986)
- (3) Distillation test JIS K2254 (1986)
- (4) Cloud point JIS K2269 (1986)
- (5) Pour point JIS K2269 (1986)
- (6) CFPP (cold filter plugging point):

Measured using an automated cold filter plugging point tester (A4F2 type manufactured by Yoshida Kagaku Kikai Co., Ltd. according to Cold Filter Plugging Point of Distillate Fuels shown in IP-309 (1976, United Kingdom)

- (7) Amount of wax separated out:

In 50 g of a test oil was dissolved 200 ppm of a cold flowability improver (STABINOL FI-18 (registered trademark), commercially available from SUMITOMO CHEMICAL CO., LTD) and the solution was cooled in a 100 ml graduated cylinder from room temperature to -5°C , -10°C , or a temperature 10°C below the cloud point at a rate of 1°C/hr . Oil component other than wax separated out from the cooled test oil was each removed under vacuum through a filter metal fitting to which $5\ \mu\text{m}$ membrane filter is attached, and 50 ml of cold ethanol/ethyl ether (2/1 by volume) was added to the residual wax component, followed by gentle stirring and then removal of oil component under vacuum.

Further, 50 ml of cold ethanol was added to the residual wax component and the mixture was all introduced into 11G4 glass filter to remove oily component under vacuum. After the wax component which remained on the glass filter was air-dried for one day and one night, the weight of wax component was measured to obtain the amount of wax separated out.

- (8) n-Paraffin content:

The content of n-paraffin in the test oil was obtained using GAS CHROMATOGRAPH GC-9A type

EP 0 301 837 B1

and CHROMATOPACK C-R2AX data processor, manufactured by Shimazu Seisakusho Co., Ltd. n-Triacontane was used as an inner standard substance for quantitative determination. Principal operational conditions are as follows.

Column: Made of stainless steel, 3 mm in inner diameter and 4m in length
 Column filler: Silicon GE SE-30 (manufactured by Wako Pure Chemicals Industry, Ltd.), 2%, 60/80 mesh (Uniport HP carrier)
 Injection Temperature: 270 °C
 Carrier Gas: Helium
 Detector: Hydrogen flame ionizing detector
 Column temperature elevation rate: 5 °C/min. (70 → 270 °C)

Example 1

To Diesel gas oil samples Nos. 1 to 4 of which characteristics are shown in Tables 1 and 2 were added 500 ppm of a cold flowability improver composed of a 50 wt.% xylene solution of various cold flowability improving substances, and CFPP was measured.

The results of evaluation of the effect by temperature decrease from CFPP of the sample oil itself (Δ CFPP) are shown in Table 3.

Table 1

Sample No.	1	2	3	4
Specific Density (15/4 °C)	0.8290	0.8340	0.8480	0.8521
Kinematic Viscosity (30 °C) cSt	4.899	4.556	5.685	5.981
Distillation Test (°C)				
Initial Boiling Point	191	175	244	206
10% Boiling Point	236	229	275	246
90% Boiling Point	346	342.5	327	356.5
Dry Point	368	364	338	382
Cloud Point (CP) °C	0	-3	-6	2
Pour Point °C	-5	-7.5	-10	-10
CFPP °C	-3	-5	-8	-7
Amount of Wax Separated Out (wt%)				
-5 °C	0.84	0.62	0.00	1.21
-10 °C	1.86	1.75	2.25	2.35
CP-10 °C	1.86	2.65	4.63	2.95
Note: CP-10 °C is a temperature 10 °C below the cloud point				

EP 0 301 837 B1

Table 2

Carbon Number of n-Paraffin	n-Paraffin Content (wt.%)			
	No. 1	No. 2	No. 3	No. 4
10	0.04	0.04	0.03	0.00
11	0.63	0.58	0.12	0.00
12	0.68	0.68	0.15	0.10
13	0.88	0.92	0.40	0.34
14	1.51	1.42	0.82	1.59
15	1.94	2.17	1.71	1.20
16	2.30	2.59	3.13	1.73
17	3.40	2.90	4.98	1.56
18	2.42	2.57	3.52	1.55
19	1.54	1.63	2.19	1.46
20	1.23	1.23	1.51	1.30
21	0.81	0.77	0.75	0.84
22	0.61	0.54	0.42	0.73
23	0.41	0.36	0.18	0.46
24	0.27	0.22	0.10	0.38
25	0.16	0.15	0.02	0.27
26	0.10	0.08	0.02	0.16
27	0.05	0.03	0.00	0.11
28	0.02	0.01	0.00	0.06
29	0.00	0.00	0.00	0.02
Total of C ₂₅ ≤	0.33	0.27	0.04	0.62
Note: "Total of C ₂₅ ≤" indicates total of n-paraffin having at least 25 carbon atoms.				

Table 3

Run No.	Cold Flow Improver	Δ CFPP (°C)			
		Sample			
		No.1	No.2	No.3	No.4
1	EVA Copolymer (VA 34 wt.%, Mn 1630)	12	7	0	0
2	EVA Copolymer (VA 28 wt.%, Mn 2050)	10	5	0	0
3	EVA Copolymer (VA 29 wt.%, Mn 2100)	8	4	0	0
4	EVA Copolymer (VA 18 wt.%, Mn 2300)	4	0	0	0

Table 3 (continued)

Run No.	M.W. Distribution	Number of Methyl Terminated Side Chain (groups/100 methylene groups)
1	2.2	3.6
2	2.8	7.2
3	4.4	3.8
4	2.4	5.9

Notes: "VA" stands for vinyl acetate, and "Mn" indicates number average molecular weight.

Example 2

Diesel gas oil samples Nos. 5 and 9 shown in Tables 4 and 5 were mixed with each other at a mixing ratio of 75/25 (Sample No. 6), 50/50 (Sample No. 7), or 25/75 (Sample No. 8), each by volume. The characteristics of mixed test oils are also shown in Tables 4 and 5.

To these sample oils were added 300 ppm or 500 ppm of Additive A composed of a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 36.5 wt.%, a number average molecular weight of 1,690, and a number of methyl terminated side chains of 3.8 groups/100 methylene groups, and CFPP of each mixture was measure.

The results of evaluation of the effect by temperature decrease from CFPP of the sample oil itself (Δ CFPP) are shown in Table 6 and Fig. 2.

EP 0 301 837 B1

Table 4

Sample No.	5	6	7	8	9
Specific Density (15/4 ° C)	0.8405	0.8405	0.8410	0.8410	0.8410
Kinematic Viscosity (30 ° C) cSt	4.582	4.542	4.517	4.430	4.387
Distillation Test (° C)					
Initial Boiling Point	201.5	200	207	214	215
10% Boiling Point	238	240	239	240	242
90% Boiling Point	342	341	340.5	335	330
Dry Point	371	368	363	356	351
Cloud Point (CP) ° C	1	0	-2	-2	-2
Pour Point ° C	-5	-5	-7.5	-7.5	-7.5
CFPP ° C	-1	-3	-3	-4	-5
Amount of Wax Separated Out (wt%)					
-5 ° C	0.90	0.82	0.77	0.61	0.53
-10 ° C	1.64	1.81	2.05	2.32	2.58
CP-10 ° C	1.52	1.81	2.54	2.93	3.41

Note: CP-10 ° C is a temperature 10 ° C below the cloud point.

Table 5

Carbon Number of n-Paraffin	n-Paraffin Content (wt.%)				
	No. 5	No. 6	No. 7	No. 8	No. 9
10	0.30	0.23	0.21	0.20	0.14
11	0.61	0.56	0.53	0.51	0.42
12	0.93	0.90	0.85	0.83	0.81
13	1.78	1.89	1.95	2.10	2.14
14	2.61	2.59	2.59	2.61	2.61
15	2.49	2.58	2.63	2.67	2.72
16	2.29	2.47	2.58	2.64	2.67
17	2.42	2.83	3.06	3.41	3.64
18	2.20	2.44	2.58	2.67	2.81
19	1.45	1.55	1.66	1.78	1.88
20	1.13	1.21	1.32	1.40	1.44
21	0.81	0.85	0.92	0.96	1.01
22	0.69	0.73	0.77	0.80	0.84
23	0.47	0.50	0.50	0.50	0.52
24	0.31	0.31	0.32	0.31	0.30
25	0.28	0.25	0.20	0.14	0.11
26	0.13	0.11	0.10	0.05	0.05
27	0.06	0.05	0.03	0.00	0.00
28	0.01	0.00	0.00	0.00	0.00
29	0.00	0.00	0.00	0.00	0.00
Total of C25≤	0.48	0.41	0.33	0.19	0.15

Notes: "Total of C25≤" indicates total of n-paraffin having at least 25 carbon atoms.
Gas chromatogram of sample oil No. 5 is shown in Fig. 1.

Table 6

	Δ CFPP (°C)				
Sample No.	5	6	7	8	9
Amount of Addition					
300 ppm	2	7	4	1	0
500 ppm	3	12	8	2	1

Example 3

To sample fuel oils shown in Table 7 was added 500 ppm of Additive A described in Example 2, and CFPP was measured.

The results of evaluation of the effect by temperature decrease from CFPP of the sample fuel oil itself (Δ CFPP) are shown in Table 7 and also in Fig. 2.

Further, for comparison, results obtained using Additive B and Additive C are shown in Table 7 and Figs. 3 and 4.

Additive B is a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 16.5 wt.%, a number average molecular weight of 2,200.

Additive C is a 60 wt.% xylene solution of an ethylene-vinyl acetate copolymer having a vinyl acetate content of 44.6 wt.% and a number average molecular weight of 1,820.

Table 7

Sample No.	10	11	12	13	14
Specific Density (15/4°C)	0.8510	0.8444	0.8488	0.8467	0.8418
Kinematic Viscosity (30°C) cSt	5.293	4.895	4.379	4.887	4.131
Distillation Test (°C)					
Initial Boiling Point	197	197	168	210	162.5
10% Boiling Point	259.5	249.5	234	259	216
90% Boiling Point	338	338.5	337	332	343
Dry Point	363	364.5	354	351	362
Cloud Point (CP) °C	-1	-3	-6	-5	-5
Pour Point °C	-2.5	-5	-7.5	-7.5	-7.5
CFPP °C	-3	-3	-6	-5	-5
Amount of Wax Separated Out (wt%)					
-5°C	1.22	0.88	0.00	0.00	0.00
-10°C	2.75	2.03	1.96	2.10	1.80
CP-10°C	3.21	2.46	5.13	4.61	3.90
Content of n-Paraffin (°C)					
Total	20.63	21.07	19.68	21.77	19.42
C20≤	4.21	3.85	3.69	3.44	3.81
C25≤	0.21	0.22	0.05	0.04	0.10
ΔCFPP (°C)					
Additive A	2	3	0	0	1
Additive B	0	1	0	0	0
Additive C	0	1	0	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

Sample No.	15	16	17	18	19
Specific Density (15/4°C)	0.8463	0.8290	0.8340	0.8450	0.8550
Kinematic Viscosity (30°C) cSt	4.050	2.960	4.556	4.720	4.511
Distillation Test (°C)					
Initial Boiling Point	166	191	175	207	208.5
10% Boiling Point	224	236	229	253.5	250.5
90% Boiling Point	334	346	342.5	325.5	318
Dry Point	353	368	364	342	337
Cloud Point (CP) °C	-5	0	-3	-11	-12
Pour Point °C	-7.5	-5	-7.5	-12.5	-12.5
CFPP °C	-5	-3	-5	-11	-13
Amount of Wax Separated Out (wt%)					
-5°C	0.00	0.84	0.62	0.00	0.00
-10°C	1.65	1.68	1.75	0.00	0.00
CP-10°C	3.55	1.68	2.41	5.23	6.71
Content of n-Paraffin (°C)					
Total	20.18	19.63	19.26	17.69	18.60
C20≤	3.52	3.70	3.37	2.02	1.52
C25≤	0.04	0.36	0.24	0.01	0.00
ΔCFPP (°C)					
Additive A	0	11	8	0	0
Additive B	0	3	3	0	0
Additive C	0	3	3	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

Sample No.	20	21	22	23	24
Specific Density (15/4°C)	0.8485	0.8472	0.8510	0.8630	0.8615
Kinematic Viscosity (30°C) cSt	5.482	5.469	5.349	5.202	5.216
Distillation Test (°C)					
Initial Boiling Point	234	224.5	221	204	207
10% Boiling Point	265	263.5	240	247	245
90% Boiling Point	328	325	345	360.5	362
Dry Point	348	340	367	381	381
Cloud Point (CP) °C	-2	-2	4	7	7
Pour Point °C	-5	-7.5	-2.5	0	1
CFPP °C	-5	-5	-4	0	0
Amount of Wax Separated Out (wt%)					
-5°C	0.26	0.61	1.13	1.70	1.65
-10°C	3.13	3.09	3.78	-	-
CP-10°C	3.62	4.11	0.91	1.21	0.74
Content of n-Paraffin (°C)					
Total	24.46	25.30	21.81	13.98	16.69
C20≤	3.61	3.42	4.50	3.98	4.36
C25≤	0.23	0.11	0.46	0.78	0.67
ΔCFPP (°C)					
Additive A	3	0	8	0	0
Additive B	1	0	2	0	0
Additive C	0	0	2	0	0

Note: CP-10°C is a temperature 10°C below the cloud point.

Table 7 (Continued)

5	<u>Sample No.</u>	<u>25</u>
	Specific Density (15/4°C)	0.8602
10	Kinematic Viscosity (30°C) cSt	4.613
	Distillation Test (°C)	
15	Initial Boiling Point	190
	10% Boiling Point	250
	90% Boiling Point	335
20	Dry Point	359
	Cloud Point (CP) °C	0
	Pour Point °C	-2
25	CFPP °C	-2.5
	Amount of Wax Separated Out (wt%)	
30	-5°C	2.06
	-10°C	4.32
	CP-10°C	4.32
35	Content of n-Paraffin (°C)	
	Total	20.77
40	C20≤	4.22
	C25≤	0.27
	Δ CFPP (°C)	
45	Additive A	0
	Additive B	0
50	Additive C	0

Note: CP-10°C is a temperature 10°C below the cloud point.

55 EFFECT OF THE INVENTION

As evident from the above-described examples, sample oils which contained n-paraffin having at least 25 carbon atoms in an amount of below 0.1 wt.% or not smaller than 0.6 wt.% and wax component which

separated out at a temperature 10 °C below the cloud point in an amount of not smaller than 4 wt.% did not exhibit effect of decreasing CFPP by the addition of a cold flowability improver. In contrast, those oils which contained n-paraffin in an amount of not smaller than 0.1 wt.% and below 0.6 wt.% and wax component which separated out at a temperature 10 °C below the cloud point in an amount of below 4 wt. % showed decrease in CFPP with the cold flowability improver. This effect was much more excellent with sample oils of which the C25 ≤ n-paraffin content was not smaller than 0.2 wt.% and below 0.5 wt.%.

Further, CFPP of fuel oils decreased widely particularly when an ethylene-vinyl acetate copolymer having an ethylene content of 60 to 80 wt.% and a number average molecular weight of 1,000 to 4,000 was used as a cold flowability improver. Among them, remarkable effect was observed with those copolymers which had a molecular weight distribution of not greater than 4.0 and contained not more than 6 methyl terminated side chains per 100 methylene units.

Claims

1. A method for improving the cold flow properties, measured as decreased cold flow pour point, of base fuel oil composed mainly of middle or heavy distillates of crude oil, the method comprising the following steps:
 - (a) determining the amount of n-paraffin having at least 25 carbon atoms and the amount of wax which separates out at a temperature of 10 °C lower than the cloud point,
 - (b) if necessary, adjusting the amount of n-paraffin having at least 25 carbon atoms in said base fuel oil to an amount of not smaller than 0.1 by weight, and smaller than 0.6% by weight, and the amount of said wax to smaller than 4% by weight, and
 - (c) adding a cold flow improver composed of a copolymer of ethylene and a vinyl ester of unsaturated carboxylic acid, the copolymer having an ethylene content of 60-80% by weight and an average molecular weight of 1000-5000, in an amount of 30 to 1500 ppm.
2. The method according to claim 1, wherein the determination of the amount of n-paraffin under (a) is carried out using a programmed temperature gas chromatography apparatus.
3. The method according to claim 2, wherein the adjustment of (b) is carried out by blending the oil with another oil with more or less n-paraffin, as appropriate, so as to bring the amount of n-paraffin into the interval between 0.1 and 0.6% by weight.
4. The method according to claim 1 wherein the amount of n-paraffin is not smaller than 0.2 wt.% and smaller than 0.5 wt.%
5. The method according to claim 1 wherein the vinyl ester of the unsaturated carboxylic acid is vinyl acetate.
6. The method according to claim 5 wherein the copolymer of ethylene and vinyl acetate has an ethylene content of 60 to 75 wt.%, a number average molecular weight of 1000 to 4000, and a molecular weight distribution of not greater than 4.0, and contains not more than 6 methyl terminated side chains per 100 main chain methylene units in addition to methyl groups contained in the acetyl groups thereof.

Patentansprüche

1. Verfahren zur Verbesserung der Kältefließfähigkeit, gemessen als erniedrigter Kaltfließstockpunkt, von Grundbrennöl, das in der Hauptsache aus mittleren oder schweren Rohödestillaten besteht, wobei das Verfahren die folgenden Schritte umfaßt:
 - a) die Menge von n-Paraffin mit zumindest 25 Kohlenstoffatomen und die Menge von Wachs, das bei einer Temperatur von 10 °C unter dem Trübungspunkt ausfällt, werden bestimmt,
 - b) erforderlichenfalls werden die Menge von n-Paraffin mit zumindest 25 Kohlenstoffatomen im Grundbrennöl auf eine Menge von nicht weniger als 0,1 Gew.-% und weniger als 0,6 Gew.-% und die Menge des Wachses auf weniger als 4 Gew.-% eingestellt und
 - c) ein Kaltfließverbesserungsmittel wird zugesetzt, das aus einem Copolymeren von Ethylen und einem Vinylester von ungesättigter Carbonsäure besteht, wobei das Copolymer einen Ethylengehalt von 60 bis 80 Gew.-% und eine mittlere Molekülmasse von 1000 - 5000 in einer Menge von 30 bis 1500 ppm besitzt.

2. Verfahren nach Anspruch 1, bei dem die Bestimmung der Menge von n-Paraffin nach a) unter Verwendung eines programmierten Temperatur-Gaschromatographie-Gerätes durchgeführt wird.
3. Verfahren nach Anspruch 2, bei dem die Einstellung von b) dadurch durchgeführt wird, daß das Öl mit einem anderen Öl mit mehr oder weniger n-Paraffin in zweckgerechter Weise gemischt wird, so daß die Menge von n-Paraffin in den Zwischenbereich zwischen 0,1 und 0,6 Gew.-% gebracht wird.
4. Verfahren nach Anspruch 1, bei dem die Menge von n-Paraffin nicht kleiner als 0,2 Gew.-% und kleiner als 0,5 Gew.-% ist.
5. Verfahren nach Anspruch 1, bei dem das Vinylester der ungesättigten Carbonsäure Vinylacetat ist.
6. Verfahren nach Anspruch 5, bei dem das Copolymere von Ethylen und Vinylacetat einen Ethylengehalt von 60 bis 75 Gew.-%, ein Molekulargewicht-Zahlenmittel von 1000 bis 4000 und eine Molekulargewichtsverteilung von nicht größer als 4,0 besitzt und nicht mehr als 6 methylbeendete Seitenketten pro 100 Hauptketten-Methyleneinheiten zusätzlich zu Methylgruppen enthält, die in deren Acetylgruppen enthalten sind.

Revendications

1. Procédé d'amélioration des propriétés d'écoulement au froid, mesurée par la baisse du point d'écoulement à froid, d'huile combustible de base composée principalement de distillats moyens ou lourds de pétrole brut, le procédé comprenant les étapes suivantes:
 - (a) déterminer la quantité de n-paraffine comportant au moins 25 atomes de carbone et la quantité de cire qui se sépare par précipitation à une température inférieure de 10 ° C au point de trouble,
 - (b) si nécessaire, régler la quantité de n-paraffine comportant au moins 25 atomes de carbone dans ladite huile combustible de base à une quantité non inférieure à 0,1% en poids et inférieure à 0,6% en poids, et régler la quantité de cire à moins de 4% en poids, et
 - (c) ajouter, dans une proportion de 30 à 1500 ppm, un additif pour l'amélioration de l'écoulement au froid, composé d'un copolymère d'éthylène et d'un ester vinylique d'acide carboxylique insaturé, le copolymère ayant une teneur en éthylène de 60 à 80% en poids et un poids moléculaire moyen de 1000 à 5000.
2. Procédé selon la revendication 1, dans lequel la détermination de la quantité de n-paraffine dans l'étape (a) est effectuée au moyen d'un appareil de chromatographie en phase gazeuse à température programmée.
3. Procédé selon la revendication 2, dans lequel le réglage dans l'étape (b) est effectué par mélange de l'huile avec une autre huile qui contient, suivant le cas, plus ou moins de n-paraffine, pour amener la quantité de n-paraffine dans l'intervalle entre 0,1 et 0,6% en poids
4. Procédé selon la revendication 1, dans lequel la quantité de n-paraffine n'est pas inférieure à 0,2% en poids et est inférieure à 0,5% en poids.
5. Procédé selon la revendication 1, dans lequel l'ester vinylique de l'acide carboxylique insaturé est l'acétate de vinyle.
6. Procédé selon la revendication 5, dans lequel le copolymère d'éthylène et d'acétate de vinyle a une teneur en éthylène de 60 à 75% en poids, un poids moléculaire en moyenne numérique de 1000 à 4000 et une distribution du poids moléculaire ne dépassant pas 4,0, et il ne contient pas plus de 6 chaînes latérales terminées par un groupement méthyle pour 100 motifs méthylène de la chaîne principale, en plus des groupements méthyle contenus dans les groupements acétyle de cette dernière.

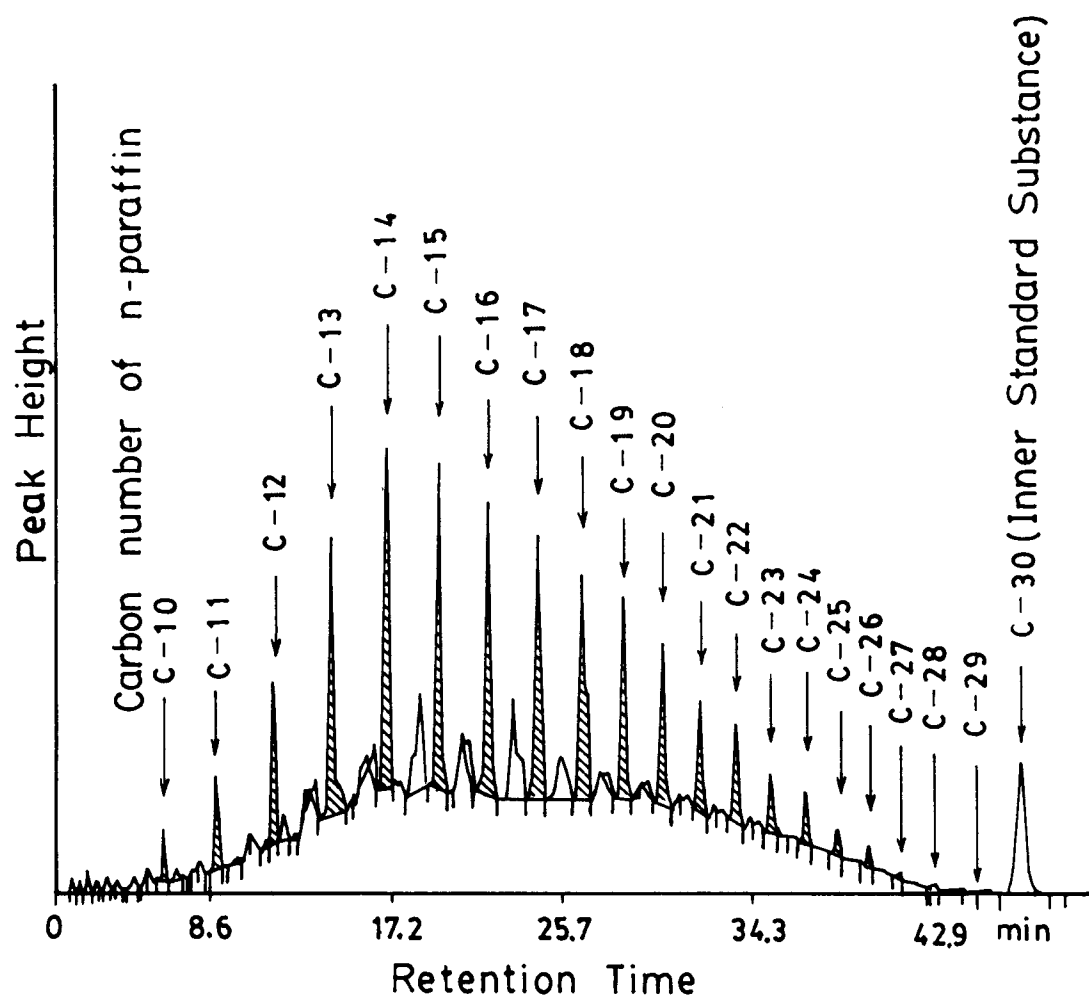
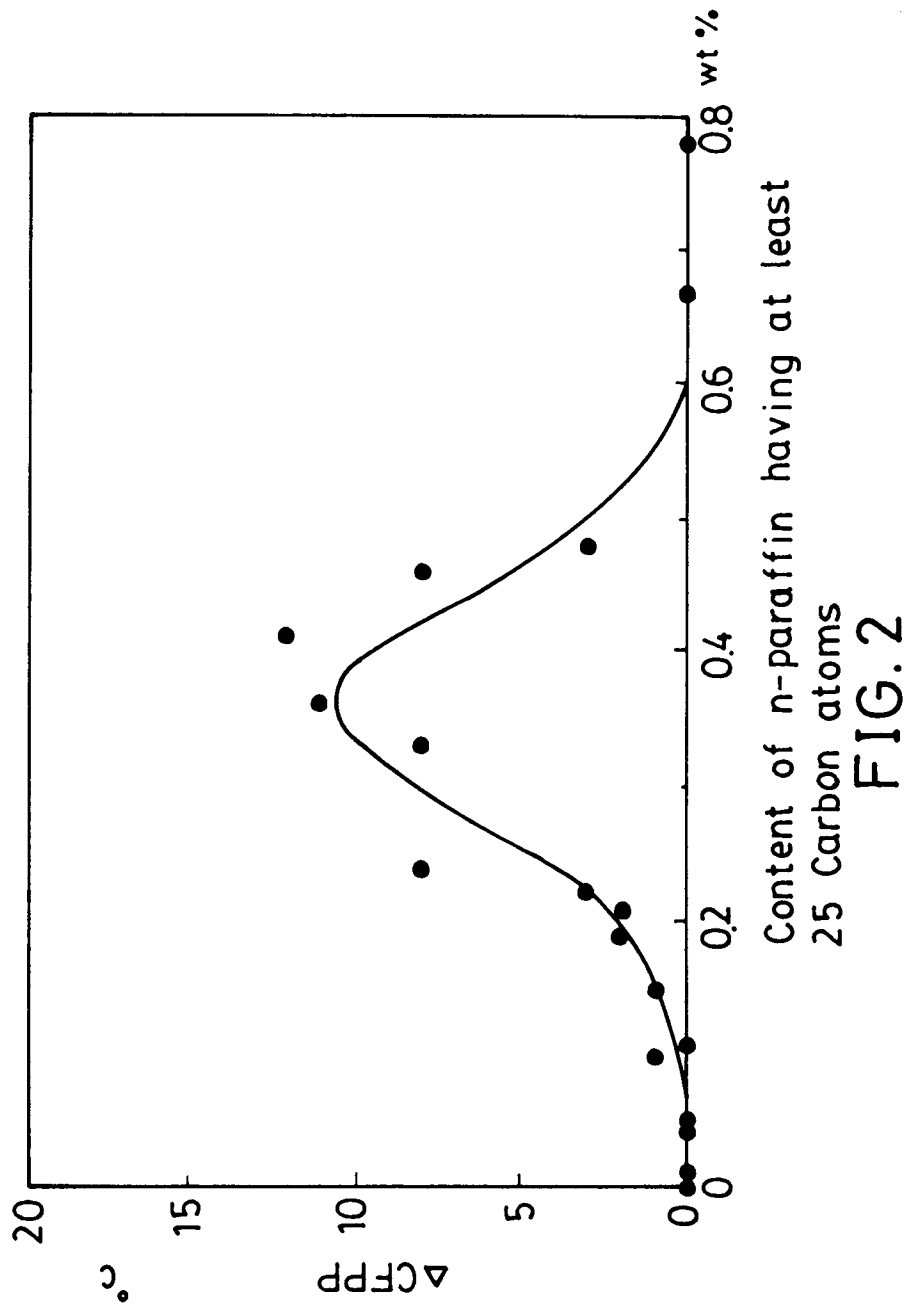


FIG. 1



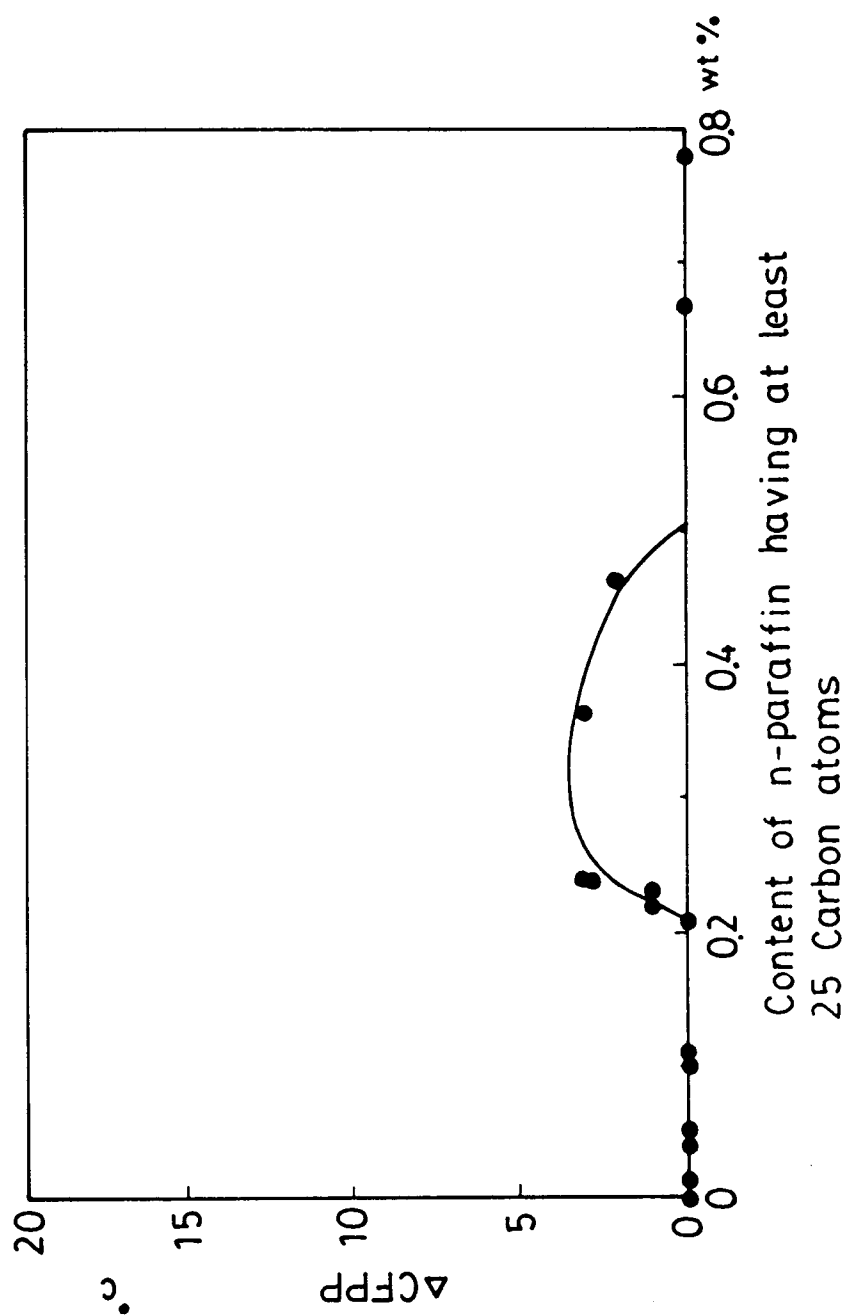


FIG. 3

