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[54] ENHANCING LOW-TEMPERATURE FLOW PROPERTIES OF FUEL OIL

[72] Inventors: **Stephan Ilnyckyj,** Islington, Ontario; **John Charles O. Cole,** Sarnia, Ontario, both of Canada; **Nicholas Feldman,** Woodbridge; **Barney R. Strickland,** Westfield, both of N.J.

[73] Assignee: **Esso Research and Engineering Company**

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[58] **Field of Search** 44/62, 70, 80; 252/56, 59; 208/15, 17, 28, 33

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Primary Examiner—Daniel E. Wyman
Assistant Examiner—W. J. Shine
Attorney—Pearlman & Stahl and Byron O. Dimmick

[57] **ABSTRACT**

The response of a middle distillate petroleum fuel oil, boiling within the range of about 250° to about 670° F. at atmospheric pressure and containing normal paraffinic hydrocarbons within the range of about n-decane and n-hexacosane to the addition of a flow-improving additive such as a copolymer of ethylene, is improved by adding to the fuel oil a paraffinic distillate fraction, obtained from a crude petroleum, the said fraction boiling at atmospheric pressure within the range of about 450° to about 950° F. and containing normal paraffins higher than n-hexacosane and as high as n-tetracontane, $C_{40}H_{82}$.

7 Claims, No Drawings

ENHANCING LOW-TEMPERATURE FLOW PROPERTIES OF FUEL OIL

FIELD OF THE INVENTION

This invention concerns an improvement in the low-temperature flowability of a waxy-cloudy middle distillate petroleum fuel through flow lines and filters wherein there is utilized a copolymer pour point depressant or flow improver of the type comprising a copolymer of ethylene with another ethylenically unsaturated monomer, such as an unsaturated ester or another alpha olefin, wherein the ethylene forms a backbone along which there are randomly distributed side chains consisting of hydrocarbon groups or of oxy-substituted hydrocarbon groups of up to 16 carbon atoms. It has been found in accordance with this invention that the response of a middle distillate fuel oil that contains constituents derived from a paraffinic crude oil, to the addition of a flow improver of the types mentioned will be greatly improved if there is incorporated into the fuel oil a minor proportion of a paraffinic distillate fraction that contains normal paraffinic hydrocarbons within the range of C_{24} up to C_{40}, provided there are present in the paraffinic distillate fraction at least normal paraffinic hydrocarbons of from 24 to 28 carbon atoms, inclusive.

DESCRIPTION OF THE PRIOR ART

The use of copolymers of ethylene and other polar monomers such as vinyl esters, acrylate esters or methacrylate esters, and the like to lower the pour point and improve the flowability of middle distillate fuels at low temperatures is well known in the art. See for example U.S. Pat. Nos. 3,037,850, 3,048,079, 3,069,245, 3,093,623 and 3,236,612.

The petroleum refinery products which are included in the category known as middle distillate fuels, are aviation turbojet fuels, fuel oils and diesel fuels. They are more fully described in such specifications as MIL-F-25558B (USAF) for turbojet fuels, ASTM D-396-67 for fuel oils and ASTM D-975-67 for diesel fuel oils. The quality of these products is defined by a number of specification tests. Of interest to this invention are those specifications which are related to the low-temperature performance of the above products. They are the ASTM freezing point, and the ASTM cloud and pour points. These tests define the temperature at which either the separation of wax from the oil is first observed, or the temperature at which sufficient amounts of wax separate from the oil to cause its gelation. The wax which separates when paraffinic petroleum products are being cooled, consists almost exclusively of hydrocarbon-type compounds known as n-paraffins. The lowest temperature at which the oil will still flow is generally known as the pour point. When the fuel temperature 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 interlock and set into a gel. It is believed that the pour depressant additive functions not only by arresting wax crystal growth but also by destroying cohesive forces between the crystals. Even though a pour point depressant may lower the temperature at which the oil will no longer flow, wax crystallization occurs at a point above the pour point, i.e., at the cloud point, at which point the oil becomes cloudy because of wax crystallization. Usually, the cloud point is not affected by the flow improver. Small size wax crystals are desirable so that the precipitated wax will not clog the fine mesh screens that are provided in fuel transportation, storage, and dispensing equipment. Pour point depressants that function by changing the wax crystals to a more advantageous size and shape can thus also be referred to as flow improvers. It is desirable to obtain not only fuel oils with low pour 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.

The upper limit for the temperature at which wax crystals can separate from middle distillate petroleum fuels, ranges from −50° F. for turbine-jet fuels to 30° F. for summer grade No. 2 fuel oils. The refiner manufactures these products by blending suitable refinery streams in appropriate ratios. These streams are heavy naphtha, which is wax-free at temperatures as low as −70° F. and has an end boiling point of about 460° F. (ASTM D-86), kerosene which usually has an ASTM freezing point lower than −40° F. and an end boiling point of about 530° to 560° F. (ASTM D-86), and gas oil which has an ASTM cloud point of about 30° F. and an end boiling point of about 650° to 670° F. (ASTM D-86). These are so-called straight run products, i.e., the products of distillation of petroleum crude oils. Also used as blending components in the preparation of middle distillate fuels are products boiling in about the same similar ranges as those discussed above but obtained by thermal or catalytic cracking of heavier petroleum fractions which boil in the range of about 600° to about 1,100° F.

It is highly unlikely that wax would separate even under the most severe winter conditions possible in the civilized areas of the earth, from the middle distillate blending components other than gas oils, either of straight run or cracked type. Thus, for all practical purposes, gas oils are the only wax-bearing middle distillate streams. The low-temperature quality of the fuel blends has customarily been improved in the past either by reducing the amount of a typical gas oil (FBP up to 670° F.) in the blend or by the undercutting of such gas oils to final boiling points of 625° F. or even lower. Regardless of which one of the two methods is employed the overall volume of the middle distillate pool is reduced, resulting ultimately in a shortage of the product, higher production costs to the refiner, and higher prices to the consumer. Neither of these methods could satisfactorily meet the demand for middle distillate fuel oils suitable for extremely low temperatures, which has become particularly high in the second half of this century because of the development of jet aircraft engines as well as the high level of industrial and military activity in the arctic regions. In recent years pour depressant or flow improving additives have become of great assistance in fulfilling this objective. Although they did not prevent wax separation at lower temperatures, they modified the structure of the crystals to such degree that wax-cloudy fuels could be used to perform satisfactorily.

DESCRIPTION OF THE INVENTION

In accordance with the present invention it has been found that the response of a middle distillate petroleum fuel oil blend to a flow improver is greatly improved if there is incorporated in that middle distillate fuel oil a higher boiling fraction having a final boiling point as high as 950° F. so that the final fuel oil blend will also contain normal paraffin hydrocarbons higher than n-hexacosane (n-C_{26}), and as high as n-tetracontane ($C_{40}H_{82}$). This improvement in the fuel oil blend is manifested not so much in the enhanced depression of the ASTM pour point as in the increased capability of a wax-cloudy fuel oil to pass through the screens and filters of fuel oil distribution equipment.

More particularly the response of a petroleum middle distillate fuel oil to a flow improver particularly of the type comprising a copolymer of ethylene and another unsaturated monomer, is increased if there is incorporated into that fuel oil from about 0.4 to about 20 weight percent of a paraffinic distillate fraction boiling within the range of about 450° and 950° F. and containing paraffinic hydrocarbons, provided that the amount of the distillate fraction added is such as to incor-

porate into the fuel oil from about 0.1 to about 2 weight percent of normal paraffinic hydrocarbons of n-C_{24} and higher, there being at least normal paraffins of C_{24} to C_{28} inclusive. Preferably, the resulting blend contains a spread of at least 16 carbon atoms from the lowest to the highest n-paraffin. A particularly effective range of C_{24} and higher normal paraffin hydrocarbon addition to the fuel in many cases will be from about 0.2 to about 1 weight percent. These weight percents are based on the total fuel composition.

The distillate fuel oils that can be improved by this invention include those having boiling ranges within the limits of about 250° to about 670° F. The distillate fuel oil can comprise straight run or virgin gas oil or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. These distillate fuels, before they are improved by the present invention, will contain normal paraffins within the range of about 10 and about 26 carbon atoms, although not necessarily all of the normal paraffins in that range.

The most common petroleum middle distillate fuels are kerosene, diesel fuels, jet fuels and heating oils. The low-temperature flow problem is most usually encountered with diesel fuels and heating oils. A representative Number 2 heating oil specification calls for a 10 percent distillation point no higher than about 440° F., a 50 percent point no higher than about 520° F., and a 90 percent point of at least 540° F. and no higher than about 640° to 650° F. Heating oils are preferably made of a blend of virgin distillate, e.g., gas oil, naphtha, etc., and cracked distillates, e.g., catalytic cycle stock.

The paraffinic distillate that is added to the distillate fuel oil to improve its response to a flow improver, in accordance with this invention, can be almost any virgin distillate fraction from a petroleum refinery distillation, provided the distillate meets the requirements outlined above. Thus the distillate fraction will have originated from a wax-bearing crude oil. The amount of the paraffin distillate that will be used will depend largely on its content of C_{24} and higher normal paraffin hydrocarbons.

It is not intended that this invention be limited by any theory regarding its operation. In any event, by adding the paraffinic distillate to the fuel oil, the higher members of the n-paraffinic homologous series are introduced. Unexpectedly, the presence of the higher homologues that were not originally present in the fuel oil brings about the desired modification of the wax crystals as the fuel oil is cooled in the presence of the flow improver. It is believed that it is the presence of a greater number of individual normal paraffins in the fuel oil that makes the fuel oil more responsive to the flow improver.

The pour point depressants or flow improvers that are employed in this invention are of the type comprising a copolymer of ethylene and at least one second unsaturated monomer. The second unsaturated monomer can be another mono alpha olefin, e.g., a C_3 to C_{16} 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. (See Canadian Pat. Nos. 676,875 and 695,679). Other monomers include N-vinyl pyrrolidone. (See Canadian Pat. No. 658,216). 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 (see U.S. Pat. Nos. 3,037,850 and 3,069,245).

Stated more generally, a copolymer pour depressant useful in this invention will consist essentially of about 3 to 40, and 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 1,500 to about 5,000 molecular weight. Molecular weights can be measured by vapor phase osmometry, for example by using a Mechrolab Vapor Phase Osmometer Model 310A. Cryoscopic methods of molecular weight determination can also be used.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated acids, acid anhydrides, and mono and diesters of the general formula:

wherein R_1 is hydrogen or methyl; R_2 is a $-OOCR_4$ or $-COOR_4$ group wherein R_4 is hydrogen or a C_1 to C_{16}, preferably a C_1 to C_4, straight or branched chain alkyl group and R_3 is hydrogen or $-COOR_4$. The monomer, when R_1 to R_3 are hydrogen and R_2 is $-OOCR_4$ includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R_2 is $-COOR_4$ such esters include C_8 Oxo alcohol acrylate, methyl acrylate, methyl methacrylate, lauryl acrylate, isobutyl methacrylate, palmityl alcohol ester of alpha-methyl-acrylic acid, C_{13} Oxo alcohol esters of methacrylic acid, etc. Examples of monomers where R_1 is hydrogen and R_2 and R_3 are $-OOCR_4$ groups, include mono C_{13} Oxo alcohol fumarate, di—C_{13} Oxo alcohol fumarate, diisopropyl maleate; di-lauryl fumarate; ethyl methyl fumarate, fumaric acid, maleic acid, etc.

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_3 to C_{16} branched or straight chain alpha monoolefin, e.g., propylene, n-octene-1, n-decene-1, etc.

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 Oxo 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° to 400° F., under pressures of about 1,000 to 3,000 p.s.i., to form aldehydes. The resulting aldehyde product is then hydrogenated to form the Oxo alcohol, the latter being recovered by distillation from the hydrogenated product.

Any of the known methods for polymer preparation can be used in preparing the copolymer flow improver or pour depressants, including the techniques taught for ethylene-vinyl ester polymerizations in U.S. Pat. Nos. 3,048,479, 3,131,168, 3,093,623 and 3,254,063. However, a particularly useful technique is as follows: Solvent and a portion (e.g., 5 to 50 percent of the total amount to be reacted) of each of the unsaturated monomers, that is to be copolymerized with the ethylene are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to reaction temperature and pressured to the desired pressure with ethylene. Then a catalyst, which can be dissolved in a solvent to aid in handling, and additional amounts of the comonomer or comonomers are added to the vessel periodically or continuously during the reaction time. Also during this reaction time, as ethylene is consumed in the polymerization, additional ethylene is supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, the liquid phase of the contents of the pressure vessel is distilled to remove the solvent and other

volatile constituents of the reacted mixture, leaving the polymer as residue. In general, based upon 100 parts by weight of polymer to be produced, about 100 to 600 parts by weight of solvent, and about 1 to 20 parts by weight of catalyst, will be used.

The catalyst, or promoter, will generally be of the free radical type, including organic peroxide types such as benzoyl peroxide, diacetyl peroxide, ditertiary butyl peroxide, dicumyl peroxide, tertiary butyl perbenzoate, di-lauroyl peroxide, t-butyl hydroperoxide, and also such nonperoxy compounds as azo-bis-isobutyronitrile, and the like.

The solvent can be any nonreactive organic solvent for furnishing a liquid phase reaction, preferably a hydrocarbon solvent such as benzene, hexane, or the like. The solvent should, of course, be one that will not poison the catalyst or otherwise interfere with the reaction.

Temperatures and pressures employed may vary widely. For example, depending primarily on the half life time of the promoter, the temperature can range from 100° to 450° F., with pressures of 500 to 30,000 p.s.i.g. However, usually the temperature will range between about 160° F. and about 350° F. Relatively moderate pressures of 700 to about 3,000 p.s.i.g. will be used with vinyl esters such as vinyl acetate, whereas with esters that have a lower reactivity to ethylene, such as methyl methacrylate, somewhat higher pressures, e.g., 3,000 to 10,000 p.s.i.g. are more satisfactory. A superatmospheric pressure is employed which is sufficient to maintain the desired concentration of ethylene in solution in the solvent. In general, this pressure is attained by maintaining a continuous pressure on the reaction chamber through controlling the inlet feed of ethylene. The time of reaction will generally be within 1 to 10 hours, the reaction time being usually interrelated with the reaction temperature and pressure, and will also vary with the particular catalyst used.

The pour point depressant or flow improver can be used in a concentration in the range of from about 0.001 to about 2 weight percent but is preferably used in a concentration of from about 0.005 to about 0.5 percent by weight, based on the weight of the fuel oil being treated.

The specific copolymer of ethylene and vinyl ester used in the working examples of the invention, and referred to as flow improver A, consisted of about 65 weight percent of ethylene and about 35 weight percent of vinyl acetate, and the copolymer had a number average molecular weight of about 2,000 as measured by vapor phase osmometry. The copolymer was prepared by copolymerizing ethylene and vinyl acetate, using di-tertiary-butyl peroxide catalyst etc. (See Belgium Pat. No. 673,566, and French Pat. No. 1,461,008).

A typical preparation of this copolymer is as follows:

A 3-liter stirred autoclave is charged with 1,150 ml. of benzene as solvent and 40 ml. of vinyl acetate. The vapor space of the autoclave is first purged with a stream of nitrogen, followed by a stream of ethylene. The autoclave is heated to about 300° F. while ethylene is pressured into the autoclave until a pressure of 950 p.s.i.g. is reached. Then, while maintaining a temperature of about 300° F. and 950 p.s.i.g. pressure, 90 ml./hour of vinyl acetate and 30 ml./hour of a solution consisting of 23 volume percent t-butyl peroxide dissolved in 77 volume percent of benzene, are continuously pumped into the autoclave at an even rate. Vinyl acetate is injected over about 135 minutes, while the peroxide solution is injected into the reactor over a period of about 150 minutes from the start of the injection. After the last of the peroxide solution is injected, the batch is maintained at 300° F. for an additional 15 minutes. Then, the temperature of the reactor contents is lowered to about 140° F., the reactor is depressured, and the contents are discharged from the autoclave. The emptied reactor is rinsed with 1 liter of warm benzene (at about 120° F.) which is added to the product. The product mixture is then stripped of the solvent and unreacted monomers by blowing nitrogen through it while it is heated on a steam bath.

Flow improver B is a copolymer of 22 weight percent vinyl acetate, 8 weight percent of C_{13} Oxo alcohol diesters of fumaric acid, and 70 weight percent of ethylene, the copolymer having a number average molecular weight of 2,400 as measured by vapor phase osmometry.

The copolymer pour point depressants or flow improvers may constitute the sole additive in the fuel oil composition, or they can be employed in conjunction with other additives commonly used in distillate fuels, including rust inhibitors, antioxidants, sludge dispersants, demulsifying agents, haze inhibitors, dyes, etc.

The invention will be further understood when reference is made to the following examples, which include preferred embodiments of the invention.

EXAMPLE 1

Two separate paraffinic distillates obtained from the same crude petroleum oil were selected for comparative tests. These two distillates differed from each other in their final boiling points as determined by high-efficiency gas chromotography, and in their content of normal paraffin hydrocarbons, as determined by urea extraction. The distillate with the lower final boiling point is designated distillate L and the other is designated distillate H. The data were as follows:

GAS CHROMATOGRAPHIC DISTILLATION DATA BOILING POINTS IN ° F.

	Distillate L	Distillate H
5%----------	456	455
10%----------	506	521
50%----------	607	654
95%----------	685	751
F.B.P.--------	765	839

n-PARAFFIN DISTRIBUTION, WT. PERCENT

n-Paraffin	Distillate L	Distillate H
C_{13}----------	0.8	0.7
C_{14}----------	1.7	1.7
C_{15}----------	4.0	3.1
C_{16}----------	9.2	6.2
C_{17}----------	17.7	12.8
C_{18}----------	20.8	16.9
C_{19}----------	17.6	15.7
C_{20}----------	13.3	12.8
C_{21}----------	8.1	10.1
C_{22}----------	3.9	6.9
C_{23}----------	1.6	4.6
C_{24}----------	0.7	3.4
C_{25}----------	0.3	2.0
C_{26}----------	0.1	1.6
C_{27}----------	----	0.7
C_{28}----------	----	0.4
C_{29}----------	----	0.1
C_{30}----------	----	0.1

Three fuel oil blends were prepared, using a heavy virgin naphtha (final ASTM boiling point 366° F.), a light gas oil fraction (final ASTM boiling point 594° F.) and either distillate L or distillate H, together with 0.025 weight percent of flow improver A, described above. Each of these blends was subjected to a low-temperature filterability test which was run as follows:

A 200-milliliter sample of the oil is cooled at a controlled rate of 2° F. per hour until a temperature is reached that is 5° F. below the ASTM freezing point of the oil, this being the temperature at which the flow test is conducted. The cooling rate of 2° F. per hour is the rate that is frequently encountered under natural climatic conditions. The oil is then filtered under vacuum (12 inches of water below atmospheric) through a U.S. 40-mesh screen at the test temperature. The volume percentage of oil that passes through the screen at the end of 25 seconds is then measured. If at least 90 percent of the oil has gone through the screen in no more than 25 seconds, the oil is considered to pass the test.

The composition of each blend and the low-temperature filterability test results are given in Table I which follows. The table also shows the average size of the wax crystals in each oil blend just before the filterability test was run. This information was obtained by placing a drop of the cloudy oil under phase contrast microscope and photographing the crystals.

ASTM pour points were determined by ASTM Method D 97-66.

TABLE I

	Blend 1	Blend 2	Blend 3
Composition, wt. percent:			
Light gas oil	58	49	73
Heavy naphtha	17	11	17
Distillate:			
L		40	10
H	15		
Filterability test:			
Percent flow improver added	0.025	0.025	0.025
Percent recovery in test	100	8	8
Average length of wax crystals, mm.	0.07	2	2
Cloud and pour point data:			
ASTM cloud of blend, ° F.	20	20	0
Depression of ASTM pour point by addition of flow improver, ° F.	45	25	30

The above Blends 1 and 2 were prepared according to refinery practice to an ASTM cloud-point specification, in this case +20° F. In order to meet this specification, Blend 1 contained 15 percent of distillate H and Blend 2 contained 40 percent of distillate L. Blend 1 was found to be of excellent low-temperature flow characteristics as shown by the data in Table I. Blend 2, in contrast, had extremely poor low-temperature characteristics even though it contained the same amount of the flow improver as was used in Blend 1. The purpose of testing Blend 3 was to establish whether it was the composition of the normal paraffins in the blend or the lower concentration of paraffins in the blend which rendered Blend 1 more responsive to the flow improver. Blend 3 contained even less paraffinic distillate than did Blend 1 (10 percent versus 15 percent). Nevertheless the low-temperature qualities of Blend 3 were essentially as poor as those of Blend 2. It is thus established that the better quality of Blend 1 as compared with Blend 2 was not related to the lower percentage of the respective paraffinic distillate fractions that were used in making the blend, but rather was a result of the particular normal paraffin hydrocarbons that were present in the blend. The data in Table I show that the paraffinic distillate that contained no appreciable quantity of normal paraffins higher than C_{26} was not effective in improving the low-temperature properties of a fuel oil blend when incorporated therein along with the flow improver additive.

COMPARATIVE TESTS

The influence of the distribution of normal paraffin hydrocarbons in a fuel oil blend after the paraffinic distillate has been added to the fuel oil is shown by the following tests:

A fuel oil was prepared by blending together 40 weight percent of a gas oil having a final boiling point of 594° F., 35 weight percent of a heavy petroleum naphtha having a final boiling point of 366° F. and 25 percent of the above-described distillate H from which the normal paraffins had been removed prior to the blending operation by treating the distillate H with urea, using well-known procedures. The wax that was recovered from distillate H by this procedure is hereinafter referred to as wax A. A separate portion of distillate H was distilled so as to take overhead in the still 80 volume percent of the oil fed to the still. The product obtained overhead in the distillation was also treated with urea to separate therefrom the wax content, and this wax was recovered as wax B. Wax A was found to consist of normal paraffins ranging from C_{12} to C_{31}, whereas wax B contained C_{12} to C_{23} normal paraffins.

The blend of gas oil and heavy naphtha and dewaxed distillate H was found to be substantially wax free, being essentially free of any cloudiness at −80° F. This blend is referred to as the fuel base. To separate portions of this fuel base were added various quantities of wax A and wax B respectively, and these blends were subjected to the low-temperature filterability test described in Example 1. The results obtained are shown in Table II which follows:

TABLE II.—EFFECT OF NORMAL PARAFFINS ON FUEL RESPONSE TO FLOW IMPROVER

Wt. percent of wax added to fuel base	Cloud point, ° F.	Result of filterability test
2.8 percent of—		
Wax B	−6	Fail.
Wax A	+15	Pass.
9.5 percent of—		
Wax B	+15	Fail.
Wax A	+35	Pass.

NOTE.—Wax A contained C_{12}–C_{31} n-paraffins; Wax B contained C_{12}–C_{23} n-paraffins.

It will be noted from Table II that the test blends which contained wax A had very satisfactory low-temperature properties. On the other hand blends that contained similar concentrations of wax B did not pass the filterability test even though their cloud points were lower than the cloud points containing wax A. It is to be noted that wax B contained normal paraffins no higher than C_{23}.

EXAMPLE 2

Fuel oil blends were prepared by adding various weight percentages of Flow Improver A, i.e., the above-described copolymer of ethylene and vinyl acetate, to the following respective fuel oils.

Oil A: heating oil	of 29.5° API gravity containing 80% cat cracked fuel of 654° F. FBP and 20% of 290°/430° F. heavy virgin naphtha
Oil B: heating oil	of 30.3° API gravity containing 85% cat cracked fuel, 660° F. FBP and 15% heavy virgin naphtha, 290°/430°<Σ F.
Oil C: heating oil	of 29.9° API gravity containing 85% cat cracked fuel, 600° F. FBP and 15% heavy virgin naphtha, 290°/430°<Σ F.

Comparative blends were prepared, using each of the fuel oils to which had been added 1 weight percent of a paraffinic petroleum distillate having the following characteristics:

Distillation	vapor temp. at 10 mm. Hg pressure	Vapor temp. converted to atmospheric pressure
(D-1160)		
Initial	240° F.	477° F.
10%	401	671
30%	435	710
50%	466	747
70%	498	784
90%	520	809
FBP	534	825

The normal paraffin hydrocarbon content of this paraffinic distillate in the range of 17 to 32 carbon atoms was as follows, in weight percent.

n-Paraffin	% Present	n-Paraffin	% Present
C_{17}	0.25	C_{25}	5.71
C_{18}	0.46	C_{26}	4.72
C_{19}	0.98	C_{27}	3.45
C_{20}	1.56	C_{28}	1.98
C_{21}	2.44	C_{29}	0.99
C_{22}	3.49	C_{30}	0.39
C_{23}	4.71	C_{31}	0.13
C_{24}	5.85	C_{32}	0.14

Each blend was subjected to a fluidity test which is a laboratory test that has been found to give results which correlate with field tests that have been run to measure the low-temperature operability of fuel oils. This test is referred to as the programmed fluidity test (PFT test). Briefly described this test consists of allowing the test oil to flow by gravity through a standard-sized opening for a period of 3 minutes and then

measuring the percent of the volume of oil which will flow through the opening during this period of time.

Specifically this fluidity test was carried out in the following manner. The test instrument is essentially an hourglass-shaped device having upper and lower chambers connected by a passageway having a diameter of about 2.25 mm. (0.10 inch). The lower section is covered by a thin aluminum disc. The lower chamber of the test instrument is filled with 40 milliliters of the fuel to be tested and then the fuel is cooled to a temperature which is 10° F. above the predetermined cloud point of the fuel. Then the sample is cooled evenly at a rate of either 2° F. or 4° F. per hour until a temperature of −10° F. is reached, the latter being the temperature at which the test is run. At this time a reading is taken of the volume of fuel in the test instrument and then the sample container is inverted. After 1 minute of settling time, the disc is punctured so that oil is permitted to drain through the flow opening. The percentage of oil that drains through the opening in a period of 3 minutes is referred to as percent recovery. Less than 80 percent recovery is considered to be a failure of the test. Each test is run in quadruplicate.

If the test is a failure with the particular concentration of the flow improver used, a new blend is prepared using a higher concentration of the flow improver until a pass of the test is obtained. The results obtained in these tests are shown in Table III which follows:

TABLE III

	% Flow Improver Needed to Pass at −10° F.	
	Cooling at 4°/hr.	Cooling At 2°/hr.
Oil A Alone	0.10	0.12
1% Paraffinic Dist. in Oil A	0.03	0.06
Oil B Alone	0.07	0.10
1% Paraffinic Dist. in Oil B	0.03	0.06
Oil C Alone	—	0.08
1% Paraffinic Dist. in Oil C	—	0.02

The data in Table III show that in each instance the amount of pour depressant or flow improver that must be added to the fuel oil in order to pass the fluidity test is greatly reduced by incorporation of 1 percent of the paraffinic distillate.

EXAMPLE 3

Blends were prepared by adding to portions of oil A and oil B described in Example 2, 3 weight percent of a paraffinic raffinate obtained upon phenol extraction of an overhead distillate of 75 SUS viscosity at 100° F. The raffinate had the following characteristics.

Atmospheric Distillation	Data for Raffinate
Initial BP	656° F.
10%	689
30%	722
50%	740
70%	763
90%	800
FBP	859

n-Paraffin Hydrocarbon Distribution			in Raffinate
C_{17}	0.32	C_{25}	2.14
C_{18}	0.42	C_{26}	1.65
C_{19}	0.74	C_{27}	0.93
C_{20}	1.31	C_{28}	0.55
C_{21}	1.51	C_{29}	0.28
C_{22}	2.24	C_{30}	0.14
C_{23}	2.62	C_{31}	0.08
C_{24}	2.57		

To these blended fuel oils there were added various weight percentages of flow improver A described above, and a determination was made of the amount of flow improver needed to pass the PFT test described in Example 2, the cooling rate being 2° F. per hour. The results obtained are shown in Table IV.

TABLE IV

	% Flow Improver Needed to Pass PFT Test
Oil A Alone	0.12
Oil A and 3% Raffinate	0.06
Oil B Alone	0.10
Oil B and 3% Raffinate	0.05

Incorporation of the 3 weight percent of the paraffinic raffinate into oil A and into oil B in each instance reduced, by half, the amount of flow improver required for the fuel oil to pass the PFT test.

Additional test blends were prepared by adding 2 weight percent, 3 weight percent and 4 weight percent of the raffinate described to separate portions of oil B. Then into each of these respective blends there was incorporated 0.05 weight percent of flow improver A described above. To other portions of oil B to which none of the raffinate had been added there were incorporated, respectively, 0.1 and 0.15 weight percent of the same flow improver. All five of these resulting blends were then subjected to a low-temperature filterability test which was run as follows:

A 200-milliliter sample of the oil is cooled at a controlled rate of 4° F. per hour until a temperature of −5° F. is reached, this being the temperature at which the flow test is conducted. The oil is then permitted to flow by gravity at the test temperature through a 30-mesh screen of 9 millimeters diameter for 25 seconds. The volume percentage of oil that has flowed through the screen at the end of this time is then measured. If more than 85 percent of the oil has gone through the screen at the end of the 25 seconds, the oil is considered to pass the test.

The compositions of the various oil blends tested and the test results obtained in the low-temperature flow test are given in Table V, which follows.

TABLE V

Oil Tested	% Flow Improver Added	% Recovery In Test
B	0.10	0
B	0.15	100
B+2% Raffinate	0.05	0
B+3% Raffinate	0.05	100
B+4% Raffinate	0.05	100

The results in Table V show that the addition of the paraffinic distillate to fuel oil B reduced significantly the amount of flow improver needed to improve the low-temperature flowability of the fuel oil.

EXAMPLE 4

The low-temperature flow properties of fuel oil A, described above, are improved by adding thereto 0.07 weight percent of a 2,400 number average molecular weight copolymer of vinyl acetate, C_{13} Oxo alcohol diesters of fumaric acid, and ethylene (flow improver B, described above) and 4 weight percent of a heavy gas oil having an atmospheric pressure distillation range of 567° to 917° F. and containing 12.45 weight percent of C_{24} to C_{33} normal paraffinic hydrocarbons.

EXAMPLE 5

Fuel oil C of Example 1 is improved with respect to its low-temperature flow properties by adding thereto 4 percent of the raffinate of Example 2 and 0.1 percent of flow improver B, described above.

EXAMPLE 6

A petroleum distillate fuel oil comprising a blend of straight run and cracked distillate stocks and having an initial boiling point of 310° F. and a final boiling point of 665° F. is improved in low-temperature flowability by incorporating therein 0.14 weight percent of a copolymer of 75 weight percent ethylene and 25 weight percent propylene, the copolymer having a number average molecular weight of about 3,200 and having been prepared as described in British Pat. No. 993,744, and 1.5 weight percent of a paraffinic distillate having an initial boiling point of 500° F. and a final boiling point of 895° F. and containing 10.2 weight percent of C_{24} to C_{31} n-paraffin hydrocarbons.

The scope of this invention is defined by the appended claims. There is no intention to limit the invention to the specific examples, which have been presented by way of illustration.

What is claimed is:

1. A petroleum distillate fuel initially having a boiling range within the limits of about 250° and 670° F., which has been improved with respect to its low-temperature flow properties by adding thereto from about 0.4 to about 20 weight percent of a petroleum distillate fraction boiling within the range of about 450° F. and about 950° F. and from about 0.001 to about 2.0 weight percent of an oil-soluble, wax modifying random copolymer of ethylene and an additional ethylenically unsaturated polymerizable monomer, said copolymer having an average molecular weight of from 1,000 to 50,000 and comprising about 3 to 40 molar proportions of ethylene per molar proportion of other monomers, said copolymer consisting primarily of an ethylene polymer backbone along which are distributed side chains of hydrocarbon or oxy-substituted hydrocarbon, said other monomers being selected from the group consisting of an alpha mono-olefin of three to 16 carbon atoms; N-vinyl pyrrolidone; and an unsaturated acid, unsaturated acid anhydride, unsaturated monoester, or unsaturated diester, of the general formula:

wherein R_1 is hydrogen or methyl; R_2 is a $-OOCR_4$ or $-COOR_4$ group wherein R_4 is hydrogen or a C_1 to C_{16} straight or branched chain alkyl group and R_3 is hydrogen or $-COOR_4$, said petroleum distillate fraction containing normal paraffinic hydrocarbons within the range of C_{24} to C_{40}, there being present at least C_{24} to C_{28} normal paraffin hydrocarbons, inclusive, the amount of said added distillate fraction being such as to incorporate into the fuel oil from about 0.1 to about 2.0 weight percent of said C_{24} and higher normal paraffinic hydrocarbons, said weight percents being based on the total fuel composition.

2. A petroleum distillate fuel as defined by claim 1 wherein the resulting blend containing the added distillate fraction contains a spread of at least 16 carbon atoms from the lowest to the highest normal paraffin hydrocarbon present in the blend.

3. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a copolymer of ethylene and an unsaturated ester.

4. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a copolymer of ethylene and another olefin.

5. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a copolymer of ethylene and vinyl acetate.

6. Improved petroleum distillate fuel as defined by claim 1 wherein said copolymer is a terpolymer of ethylene, vinyl acetate and aliphatic alcohol diester of fumaric acid.

7. Improved petroleum distillate fuel as defined by claim 1 wherein said paraffin-hydrocarbon-containing distillate fraction is a raffinate obtained by solvent extraction of a petroleum distillate.

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