

- [54] MIDDLE DISTILLATE FUEL HAVING
INCREASED LOW TEMPERATURE
FLOWABILITY
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- [58] Field of Search 44/62, 70; 252/56; 208/45,
208/33, 15

[56] References Cited
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FOREIGN PATENTS OR APPLICATIONS

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[57] ABSTRACT

The low temperature flowability of a middle distillate petroleum fuel oil boiling within the range of about 250° to about 700°F. at atmospheric pressure is improved by adding to the fuel oil from about 0.1 to about 3 weight percent of an essentially saturated hydrocarbon fraction which is substantially free of normal paraffinic hydrocarbons and which has a number average molecular weight in the range of about 600 to about 3,000, together with a flow-improving additive such as a copolymer of ethylene and an unsaturated ester, wherein said copolymer has less than six methyl terminating side branches per 100 methylene groups, the weight ratio of said saturated hydrocarbon fraction to said copolymer flow-improving additive being in the range of about 25:1 to 1:1.

5 Claims, No Drawings

MIDDLE DISTILLATE FUEL HAVING INCREASED LOW TEMPERATURE FLOWABILITY

FIELD OF THE INVENTION

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

DESCRIPTION OF THE PRIOR ART

It is known in the prior art to employ 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 oxysubstituted hydrocarbon groups of up to 16 carbon atoms. The use of copolymers of ethylene and other 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 temperature 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.

REFERENCE TO COPENDING APPLICATION

It is taught in the application of Nicholas Feldman and Wladimir Philippoff, Ser. No. 807,953, having the same filing date as the present application, and subsequently issued on May 2, 1972 as U.S. Pat. 3,660,058 that an amorphous, normally solid, essentially saturated hydrocarbon fraction, obtained from a residual petroleum oil, said fraction being substantially free of normal paraffinic hydrocarbons and having a number average molecular weight within the range of about 600 to 3,000, when added to a middle distillate petroleum fuel oil in a concentration of about 0.01 to about 3 weight percent, will depress the pour point of the fuel oil to some extent and will also improve the low temperature flowability of the said petroleum fuel oil. It is

that type of hydrocarbon that is used as one component of the additive combination of the present invention.

DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has been found that the low temperature flow properties of the petroleum middle distillate fuel oil can be improved by incorporating into the fuel oil a small concentration of an ethylene copolymer type pour point depressant and a small concentration of an essentially saturated hydrocarbon fraction that is substantially free of normal paraffinic hydrocarbons, the hydrocarbon fraction having a number average molecular weight in the range of about 600 to about 3,000. The ethylene copolymer is further characterized by being a random copolymer of from 3 to 40 moles of ethylene and 1 mole of an unsaturated ester, wherein the copolymer has less than 6 methyl-terminating side branches per 100 methylene groups, and the copolymer has a number average molecular weight of about 1000 to 50,000. More specifically, there are added to a waxy middle distillate petroleum fuel, from about 0.1 to about 3 weight percent, preferably about 0.2 to 1 weight percent, of the said high molecular weight hydrocarbon fraction, together with from about 0.005 to about 1 weight percent, generally about 0.01 to 0.1 weight percent, of the ethylene copolymer pour depressant. The weight ratios of the two types of additives can vary from equal parts to as little as 1/25th as much of the ethylene copolymer pour depressant as the high molecular weight hydrocarbon fraction.

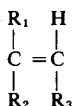
The distillate fuel oils that can be improved by this invention include those having boiling ranges within the limits of about 250°F. to about 700°F. The distillate fuel oil can comprise straight run or virgin gas oil or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates.

The most common petroleum middle distillate fuels are kerosene, diesel fuels, jet fuels and heating oils. Since jet fuels are normally refined to very low pour points, there will be generally no need to apply the present invention to such fuels. The low temperature flow problem is most usually encountered with diesel fuels and with heating oils. A representative 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°F. to 650°F., although some specifications set the 90 percent point as high as 675°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. A representative specification for a diesel fuel includes a minimum flash point of 100°F. and a 90 percent distillation point between 540°F. and 640°F. (See ASTM Designations D-396 and D-975.)

The copolymer flow-improving additive that is used in this invention is a copolymer formed from about 3 to about 40 molar proportions of ethylene, and one mole of at least one second unsaturated monomer. The polymer is oil-soluble and is characterized by having less than six methyl terminating side branches on the polyethylene backbone per 100 methylene groups of the said backbone. Such polymers are prepared by free radical catalysis in a solvent at temperatures of less than 130°C. in order to minimize ethylene branching,

preferably using free radical catalysts or initiators that have a half-life of no greater than about one hour. The polymers have number average molecular weights in the range of about 1,000 to 50,000, preferably about 1,000 to about 2,900, and most preferably about 1,500 to 2,500 as measured by Vapor Phase Osmometry, for example, by using a Mechrolab Vapor Phase Osmometer Model 310A. The preparation of this type of copolymer is taught in co-pending application Ser. No. 717,902, filed Apr. 1, 1968, for Max J. Wisotsky and Norman Tunkel.

The unsaturated monomers, copolymerizable with ethylene, include unsaturated 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 and R_3 are hydrogen and R_2 is $-OOCR_4$ includes vinyl alcohol esters of C_2 to C_{17} monocarboxylic acids, preferably C_2 to C_5 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 methyl acrylate, methyl methacrylate, lauryl acrylate, 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 $-COOR_4$ groups, include mono- and diesters of unsaturated dicarboxylic acids such as: mono- C_{13} Oxo fumarate, di- C_{13} Oxo fumarate, diisopropyl maleate; di-lauryl fumarate; ethyl methyl fumarate; etc.

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 $400^\circ F.$, under pressures of about 1000 to 3000 psi, 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.

As previously mentioned, about 3 to 40 moles of ethylene will be used per mole of other monomer, which other monomer is preferably an ester as hereinbefore defined, or a mixture of about 30 to 99 mole percent ester and 70 to 1 mole percent of a C_3 to C_{16} , preferably C_4 to C_{14} , branched or straight chain alpha monoolefin. Examples of such olefins include propylene, n-octene-1, n-decene-1, etc.

In general, the polymerizations can be carried out as follows: Solvent and a portion of the unsaturated ester, e.g., 0-50, preferably 10 to 30 weight percent, of the total amount of unsaturated ester used in the batch, are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to the desired reaction temperature and pressured to the desired pressure with ethylene. Then catalyst, preferably dissolved in solvent

so that it can be pumped, and additional amounts of unsaturated ester are added to the vessel continuously, or at least periodically, during the reaction time, which continuous addition gives a more homogeneous copolymer product as compared to adding all the unsaturated ester at the beginning of the reaction. Also during this reaction time, as ethylene is consumed in the polymerization reaction, 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 in the pressure vessel is distilled to remove the solvent and other volatile constituents of the reacted mixture, leaving the polymer as residue.

Usually, based upon 100 parts by weight of copolymer to be produced, about 100 to 600 parts by weight of solvent, and about 1 to 20 parts by weight of catalyst or initiator will be used.

The solvent can be any non-reactive organic solvent for furnishing a liquid phase reaction which will not poison the catalyst or otherwise interfere with the reaction, and preferably is a hydrocarbon solvent such as benzene, hexane, cyclohexane, dioxane, or tert-butyl alcohol.

The temperature used during the reaction will be in the range of 70° to $130^\circ C.$, preferably 80° to $125^\circ C.$ Preferred free radical catalysts or initiators are those which decompose rather rapidly at the prior noted reaction temperatures, for example, those that have a half-life of about an hour or less at $130^\circ C.$ preferably. In general, this will include the acyl peroxides of C_2 to C_{18} , branched or unbranched, carboxylic acids such as di-acetyl peroxide (half-life of 1.1 hours at $85^\circ C.$); di-propionyl peroxide (half-life of 0.7 hour at $85^\circ C.$); di-pelargonyl peroxide (half-life of 0.25 hour at $80^\circ C.$); di-lauroyl peroxide (half-life of 0.1 hour at $100^\circ C.$), etc. The lower peroxides such as di-acetyl and di-propionyl peroxide are less preferred because they are shock sensitive, and as a result the higher peroxides such as di-lauroyl peroxide are especially preferred. The short half-life catalysts also include various azo free radical initiators such as azodiisobutyronitrile (half-life, 0.12 hour at $100^\circ C.$); azobis-2-methylheptonitrile and azobis-2-methyl-valeronitrile. In contrast to the preceding, di-tert. butyl peroxide, which has been used extensively in the prior art, has a half-life of about 180 hours at $100^\circ C.$ and a half-life of about 7 hours at $130^\circ C.$, and does not produce the desired low degree of branching. For example, nuclear magnetic resonance studies indicate that a copolymer of 6 to 6.5 moles of ethylene per mole of vinyl acetate has an average of about 3.5 methyl-terminating side branches on the polyethylene backbone per 100 methylene groups of the backbone if the copolymer is prepared at $105^\circ C.$ and 900-950 psig pressure using lauroyl peroxide catalyst or initiator, but has an average of about 10 to 11 such branches if prepared at $150^\circ C.$ and 900-950 psig and using tert.butyl peroxide catalyst or initiator.

The pressures employed can range between 500 and 30,000 psig. However, relatively moderate pressures of 700 to about 3,000 psig will generally suffice with vinyl esters such as vinyl acetate. In the case of esters having a lower reactivity to ethylene, such as methyl methacrylate, then somewhat higher pressures, such as 3,000 to 10,000 psi have been found to give more optimum results than lower pressures. In general, the pressure

should be at least sufficient to maintain a liquid phase medium under the reaction conditions, and to maintain the desired concentration of ethylene in solution in the solvent.

The time of reaction will depend upon, and is interrelated to, the temperature of the reaction, the choice of catalyst, and the pressure employed. In general, however, 0.5 to 10, usually 2 to 5 hours will complete the desired reaction.

The fractions of essentially saturated hydrocarbons that are used in accordance with the present invention in conjunction with the copolymer pour point depressants, are generally amorphous solid materials having melting points within the range of about 80° to 140°F. and having number average molecular weights within the range of about 600 to about 3,000. This molecular weight range is above the highest molecular weight of any hydrocarbons that are naturally present in the fuel oil.

An amorphous hydrocarbon fraction that is useful in accordance with this invention can be obtained by deasphalting a residual petroleum fraction and then adding a solvent such as propane to the deasphalted residuum, lowering the temperature of the solvent-diluted residuum, and recovering the desired solid or semi-solid amorphous material by precipitation at a low temperature followed by filtration. The residual oil fractions from which the desired hydrocarbons are obtained will have viscosities of at least 125 SUS at 210°F. Most of these residual oils are commonly referred to as bright stocks.

In some instances products obtained by this procedure will be naturally low in normal paraffin hydrocarbons and can be used in the present invention without further treatment. For example, by low temperature propane treatment of a deasphalted residual oil from certain Texas coastal crudes, a precipitated high molecular weight amorphous fraction can be obtained which has only a trace of normal paraffins, about 5 percent of isoparaffins, about 73 percent of cycloparaffins and about 22 percent of aromatic hydrocarbons. In other instances it is necessary to treat the high molecular weight fraction in some manner to reduce its content of normal paraffins. Removal of normal paraffins from an amorphous hydrocarbon mixture can be effected by complexing with urea, as will be illustrated hereinafter in one of the examples. Solvent extraction procedures can also be used, but in many instances they are not as effective as complexing techniques. Thus the amorphous hydrocarbon mixture can be dissolved in a ketone, e.g., methyl ethyl ketone, at its boiling point and then when the solution is cooled to room temperature the normal paraffins will be predominantly precipitated and the resultant supernatant solution will give a mixture containing some normal paraffins but predominating in cycloparaffins and isoparaffins.

Vacuum distillation can also be used for the removal of normal paraffin hydrocarbons from a high molecular weight paraffinic fraction, but such a procedure requires a very high vacuum, i.e., less than 5 mm Hg. absolute pressure, preferably a pressure below 3 mm Hg,

absolute, e.g., 2 mm. or 120 microns. If the pressure used is 5 mm or higher, the necessary temperature for the distillation is high enough to cause cracking of the constituents, which is undesirable.

In the following examples, the essentially saturated hydrocarbon fraction that was used was an amorphous solid hydrocarbon fraction having a melting point of 111°F., that had been obtained by propane precipitation from a deasphalted residual stock from a Texas coastal crude oil. This hydrocarbon fraction was found by mass spectrographic analysis and gas chromatography to contain 5 weight percent of isoparaffins, 22 weight percent of aromatic hydrocarbons, 73 weight percent of cycloparaffins, and no more than a trace of normal paraffin hydrocarbons. The number average molecular weight of this material was about 775 as determined by osmometry. The distillation characteristics of this solid amorphous hydrocarbon fraction were as follows:

(ASTM D-1160)	Vapbr Temp. at 5 mm Hg.	Vapor Temp. Converted to Atmospheric Pressure
Initial BP	442°F.	754°F.
5%	590	926
10%	636	978
20%	686	1034
24%	689	1037

Only 24% would distill over. There wee 75 percent bottoms, and 1 percent loss.

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

EXAMPLE 1

Fuel oil blends were prepared using a middle distillate fuel oil consisting of 85 volume percent of cracked distillates having a final boiling point of 660°F. and 15 volume percent of heavy virgin naphtha, the fuel oil having a cloud point of +12°F. and a pour point of -5°F. To separate portions of this fuel oil there were added various percentage concentrations of the amorphous solid hydrocarbon fraction, essentially free of normal paraffin hydrocarbons, described above. To other portions of the fuel oil there were added various concentrations of the copolymer of ethylene and vinyl acetate described above. To still other portions of the fuel oil there were added both the solid hydrocarbon fraction and the pour point depressant. Each of the resulting fuel oil blends was subjected to a low temperature filterability test which is run as follows:

A 200 milliliter sample of the oil is cooled at a controlled rate of 2°F. per hour until a temperature of 0°F. is reached, this being the temperature at which the flow test is conducted. The oil is then filtered through a U.S. 40 mesh screen at the test temperature, and 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.

TABLE I

EFFECT OF SOLID AMORPHOUS
HYDROCARBON AND COPOLYMER POUR
DEPRESSANT ON LOW TEMPERATURE
PROPERTIES OF FUEL OIL

Additive Solid Hydrocarbon	Copolymer	% Recovery in Filterability Test	ASTM Pour Point of Blend °F
0.4%	None	100	-10
0.3%	None	15	-5
None	0.02	3	-50
None	0.05	30	
None	0.06	36	-75
0.4	0.02	100	-20
0.3	0.015	100	-20
0.2	0.01	100	-25
0.1	0.015	100	-40

Percentages are by weight.

The data in Table I demonstrate that the combination of the amorphous solid hydrocarbon fraction and the ethylene-vinyl acetate copolymer more effectively improved low temperature flow properties of the fuel than did either additive alone. Thus while it required 0.4 weight percent of the solid hydrocarbon to attain 100 percent recovery in the flow test, only 0.1 weight percent of the added hydrocarbon was needed for 100 percent when 0.015 weight percent of the copolymer was present, and yet even four times as much of the copolymer when used alone was not highly effective in improving filterability.

The copolymer flow improver that was used in this example was a copolymer of ethylene and vinyl acetate having a mole ratio of ethylene to vinyl acetate of about 4.2 and having an average molecular weight as determined by vapor phase osmometry of about 1740. A typical preparation of this pour depressant is as follows:

A three-liter stirred autoclave was charged with 850 ml. of benzene as solvent and 40 ml. of vinyl acetate. The vapor space of the autoclave was first purged with a stream of nitrogen and then with a stream of ethylene. The autoclave was then heated to 180°F. while ethylene was pressured into the autoclave until the pressure was raised to 750 psig. Then, while maintaining a temperature of 180°F. and said 750 psig pressure, 100 ml./hour of vinyl acetate and 160 ml./hour of solution consisting of 12 parts by weight of di-lauroyl peroxide dissolved in 88 parts by weight of benzene, were continuously pumped into the autoclave at an even rate. A total of 250 ml. of vinyl acetate was injected over 2 hours and 30 minutes, while 440 ml. of the peroxide solution (or about 55 grams of peroxide) were injected into the reactor over a period of two hours and 45 minutes from the start of the injection. After the last of said peroxide was injected, the batch was maintained at 180°F. for an additional 15 minutes. Then, the temperature of the reactor contents was lowered to about 140°F., the reactor was depressurized, and the contents were discharged from the autoclave. The emptied reactor was rinsed with one liter of warm benzene (about 120°F.) which was added to the product. The product mixture was then stripped of the solvent and unreacted monomers by blowing nitrogen through it while it was heated on a steam bath. This final stripped product consisted of about 325 grams of copolymer of ethylene and vinyl acetate.

EXAMPLE 2

A copolymer of ethylene, vinyl acetate, and di-C₁₃ Oxo alcohol fumarate ester is prepared at 900 psig and 105°C. reaction temperature, using the general proce-

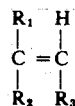
cedure as in the preparation of the vinyl acetate and ethylene copolymer of Example 1. The initial charge is 670 ml. of benzene and 32 ml. of vinyl acetate. A mixture of 80 weight percent of vinyl acetate and 20 weight percent of fumarate esters is injected at the rate of 80 ml. per hour for 145 minutes along with 64 ml. per hour of a solution of 23 weight percent lauroyl peroxide in 77 weight percent of benzene for a total of 155 minutes. A yield of 200 grams of polymer is obtained. A 47 10 percent solution of the polymer in kerosene has a kinematic viscosity at 100°F. of 42 centistokes. The base fuel oil of Example 1 is improved in low temperature properties by adding thereto 0.02 weight percent of the terpolymer and 0.2 weight percent of the amorphous solid, substantially normal-paraffin-hydrocarbon-free fraction used in Example 1.

What is claimed is:

1. A wax-containing petroleum distillate fuel having a boiling range within the limits of about 250°F. and 700°F. which has been improved with respect to its low temperature flow properties by adding thereto:

from about 0.1 to about 3 weight per cent of a flow-improving, amorphous, normally solid essentially saturated hydrocarbon fraction that is substantially free of normal paraffin hydrocarbons, said fraction having a number average molecular weight of from about 600 to about 3000 and having been obtained from a residual petroleum oil, and

from about 0.005 to about 1 weight per cent of a wax-modifying random copolymer of ethylene and an unsaturated ester, said random copolymer having an average molecular weight of from about 1,000 to 50,000 and comprising from about 3 to 40 molar proportions of ethylene per molar proportions of other monomers, said copolymer having less than 6 methyl-terminating side branches on the polyethylene backbone per 100 methylene groups of the said backbone, unsaturated ester having the general formula:



wherein:

- R_1 is selected from the group consisting of hydrogen and methyl radicals;
- R_2 is selected from the group consisting of $-OOCR_4$ and $COOR_4$ groups.
- R_3 is selected from the group consisting of hydrogen and $-COOR_4$, and
- R_4 is selected from the group consisting of hydrogen and $C_1 - C_{16}$ alkyl groups.

2. Fuel composition as defined by claim 1 wherein the weight ratio of said substantially normal-paraffin-hydrocarbon-free hydrocarbon fraction to said random copolymer is from about 1:1 to about 25:1.

3. Fuel composition as defined by claim 1 wherein said copolymer has been prepared in an inert solvent by free radical catalysis at a temperature of about 70° to 130°C. using a catalyst having a half life at 130°C. under 1 hour.

4. Fuel composition as defined by claim 1 wherein said copolymer is a copolymer of ethylene and vinyl acetate.

5. Fuel composition as defined by claim 1 wherein said copolymer is a terpolymer of ethylene, vinyl acetate, and aliphatic alcohol diester of fumaric acid.

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