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MIDDLE DISTILLATE FLOW IMPROVER

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ABSTRACT OF THE DISCLOSURE

Hydrocarbon distillate fuel improved in its low temperature flow properties by a mixture of one part by weight of copolymer comprising 60–99 weight percent ethylene and 1–40 weight percent vinyl acetate having molecular weights of 1000–3000 and about ½ to 2 parts by weight of a petroleum resin.

The present invention is broadly concerned with improving the flow of oils, particularly middle distillates, at low temperatures. The flow and other characteristics are improved by incorporating in these oils a synergistic mixture of a copolymer of ethylene and vinyl acetate and a particular extracted resin.

The resin is one which is extracted from a residuum of A Schoonegeek (Dutch) crude or a Pennsylvania crude. With the increase in the use of hydrocarbon fuels of all kinds, a serious problem has arisen in areas frequently subjected to low temperatures with respect to the cold flow characteristics of fuels. Particularly, serious problems have been encountered with heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional or operating difficulties or both. For example, the distribution of heating oils by pumping or syphoning is rendered difficult or impossible at temperatures around or below the pour points of the oils. Furthermore, the flow of the oils at such temperatures through the filters cannot be maintained, resulting in the failure of the operating equipment.

Also, the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 750° F. have attracted increasing attention in recent years because of the growth of markets of such fuels in subarctic areas and because of the development of turbojet aircraft capable of operating at altitudes where temperatures of —50° F. or lower may be encountered.

It is, of course, well known to add pour depressants to lubricating oils to lower the pour point. These lube oil additives, mostly high molecular weight organic compositions formed by alkylation of benzene or naphthalene or derivatives thereof or by polymerization of lower molecular weight methacrylates, or by condensation polymerization of various kinds, are not satisfactory in service with middle distillate and lighter fuel. Poor performance of these additives might possibly result from the molecular weight and structural differences between waxes occurring in lubricating oils and constituents of so-called middle distillates.

It is, therefore, the one object of the present invention to produce an improved pour depressant mixture for

middle distillate and lighter fuels. In general, these oils boil in the range from about 250° to 750° F. It is a still further object of the present invention to improve heating oils, diesel fuel oils, kerosenes and jet fuels with respect to their pour points. Such fuels include aviation turbo-jet fuels, kerosenes, diesel fuels, and heating oils. Aviation turbo-jet fuels in which the polymers may be used normally boil between about 250° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL–F–5624C, MIL–F–25554A, MIL–F–25558A, and amendments thereto. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D–396–48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D–975–35T and later versions of the same specification.

Thus the use of pour depressants in lubricating oils and middle distillate fuel oils is well known. However, it has become evident recently that the depression of the pour point of middle distillate fuel oil does not itself insure the good operability or flowability of a fuel oil at low temperatures.

Thus the present invention is concerned with a synergistic mixture of a copolymer of ethylene and vinyl acetate used in conjunction with an extracted petroleum resin.

The copolymer of the present invention is one described in U.S. Patent No. 3,048,479 issued Aug. 7, 1962, entitled, "Ethylene-Vinyl Ester Pour Depressant for Middle Distillates"; inventors: Stephan Ilnyckyj and Charles B. Rupar. In general, the pour depressant comprises an ethylene-vinyl acetate copolymer. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 60 to 99%, as compared to parts by weight of vinyl acetate in the range from about 40 to about 1%. A very desirable ethylene-vinyl acetate copolymer contains about 15 to 25% by weight of vinyl acetate, as for example about 20% by weight of vinyl acetate.

The molecular weights of the ethylene-vinyl acetate copolymer are critical and should be in the range from about 1000 to 3000, preferably in the range from about 1500 to 2200. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)).

The resin is one which is extracted from a residuum of a Schoonebeek (Dutch) crude or a Pennsylvania crude. These crudes are highly paraffinic in nature. Thus, certain crude oils are well-known as containing natural petroleum resins, and include paraffinic non-asphaltic crudes, for instance Pennsylvania and Schoonebeek crudes, or mixed-base crudes, for example Kuwait crudes. An example of a crude oil which does not contain natural petroleum resins is Quiri-quiri.

The resins themselves have previously been concentrated from such resin-containing crude oils, and have been found to consist of resinous matter characterized by low Holde asphalt contents (less than 0.2%) and a high proportion of acetone-insoluble matter. The residuum is one which boils above about 700° F.

The resin is extracted using a low boiling hydrocarbon

solvent, as for example propane or butane or a mixture of the same. The resin is recovered from the solvent after the solvent is removed from the residuum. A typical inspection of the resin is as follows:

TABLE I.—CHARACTERIZATION OF RESINS

Mol. wt.	1000–2000
CH_2/CH_3 ratio	5.5
Aromatic content by UV ——percent—	<1
Percent C	86.48
Percent H	11.68
Percent N	0.13
Percent S	0.22

The synergistic mixture is used in a concentration in the range from about .001 to .5% by weight, preferably in a concentration of about .005 to .1% by weight, based upon the base oil. It is preferred that the amount of copolymer present as compared to the resin present be in the range from about ½ to 2 parts by weight of the copolymer per part by weight of the resin. A particularly desirable synergistic mixture is one wherein the parts by weight of the copolymer to the resin is about 1:1.

The present invention may be more fully understood by the following examples illustrating the same.

Example 1

A base fuel having inspections as listed in Table II had a pour point of +5° F. (ASTM Test for Cloud and Pour Points, D–97–57).

TABLE II.—FUEL A

Gravity, °API at 60°	35
Color: Tag Robinson	[1] 18
Flash (Pensky-Martens)	130
Sulfur, wt. percent	0.05
Aniline point ——° F—	148
ASTM distillation range:	
IBP ——° F—	358
10%	430
50%	528
90%	595
FBP	625
Conradson carbon residue ——percent—	<0.2

[1] Light yellow.

When 0.04 weight percent of the copolymer of ethylene and vinyl acetate was added, the pour point was decreased from +5° F. to −55° F. This fuel, however, containing 0.04 weight percent copolymer in a winter field test* of an outdoor heating oil tank installation failed at +4° F., +6° F., and +8° F.

The cause of the fuel failure at relatively high temperatures was traced to the presence of non-normal hydrocarbons in the wax precipitating near the pour point. The copolymer apparently interacts with normal hydrocarbons which precipitate near the pour point and prevents their forming a gel except at low temperatures. The copolymer is not capable of interacting with non-normal hydrocarbons.

*Winter field test for middle distillate fuels—The winter field test is designed to simulate field flow conditions corresponding to the most critical type of home heating oil installations; namely, the outside storage tank. A typical test unit consists of a 275 gallon heating oil tank mounted outside and above ground. The test involves withdrawing the fuel through a gate valve and approximately six feet of copper tubing (⅜" O.D., 0.03" wall) using an ordinary domestic oil burner pump located inside the test site building. The fuel is not burned. Failures occur when wax plugs form in the gate valve or the copper line and are defined by a persistent increase in vacuum ranging up to 25 inches of mercury (vacuum side of pump) accompanied by a drop in pressure on the pressure side from the preset 100 p.s.i.g. to 75 p.s.i.g. or lower. Ambient and fuel temperatures are recorded not only at the fail points but continuously throughout the natural temperature cycling. Fuels are compared on the basis of their average failure temperatures.

Example 2

A second base fuel B having inspections as listed in Table III was tested in the standardized microscope test**.

TABLE III.—FUEL B

Gravity, ° API at 60°	38.5
Color: Tag Robinson	22.0
Flash (Pensky-Martens) ——° F—	156
Sulfur, wt. percent	0.11
Aniline point ——° F—	161.6
Conradson carbon residue ——percent—	0.01
ASTM distillation range:	
IBP ——° F—	338
10%	416
50%	523
90%	584
FBP ——° F—	613

In one test, .045 weight percent of the copolymer was added. In a second test, 04% of the copolymer was added plus .05 weight percent of the resin. In a third test, no additive was added. It was observed that in the absence of a pour depressant, large crystals were produced. The addition of the copolymer did not reduce the wax crystal size significantly. On the other hand, when the synergistic mixture was used, the size of the wax crystals was greatly reduced.

Example 3

Other tests were conducted using as the base fuel A. The results of these tests are as follows:

TABLE IV.—PLUGGING TEST[1]

	Flow Rate in ml./min.	
	Fuel+0,04% Copolymer	Fuel+0.04% Copolymer+0.05% Schoonebeek Resin
Temperature:		
+8° F	140	160
−1° F	80	70
−8° F	Plugged	70
−20° F	Plugged	40

[1] Plugging test—In the plugging test a sample of the cold, waxy fuel contained in a gallon can is drawn under vacuum through a length of copper tubing. At the end of the copper tubing is a conical inlet which accentuates the plugging tendency of the fuel. For a good fuel, a large percentage of the sample flows through the copper tube in each of a number of tests run over the temperature range of interest. Poor fuels may exhibit poor flow or plugging (1) over a fairly narrow temperature range, or (2) at all temperatures below a certain value.

From the above it is apparent that unexpected desirable results were secured when using the synergistic mixture of the present invention.

Example 4

Other plugging tests were conducted using as the base fuel B. The results of these tests are shown in Table V.

TABLE V.—PLUGGING TEST—FUEL B

	Percent of Fuel Removed by 5 lbs. Vacuum		
	Fuel—no Additive	Fuel+0.05% Copolymer	Fuel+0.05% Copolymer +0.05% Resin
Temperature, ° F.:			
−10	0	0	80
−5	0	0	95
0	0	0	100
+10	100	100	100

**Microscope test—Three drops of a fuel under investigation are placed in a depression in an aluminum plate and covered with a cover glass. The aluminum plate is placed on a cold stage microscope. The temperature of the fuel sample is lowered at less than ½° F./min. to within 2° F. of the cloud point. The temperature is followed by means of a thermocouple placed in the fuel sample. The temperature of the fuel is lowered from 2° F. above the cloud point to 2° F. below the cloud point over a period of 3 hours. The wax crystals appear either at this temperature or shortly thereafter.

The tests cited were carried out using an aluminum plate with three depressions. Three fuel samples were examined simultaneously, one the fuel oil without additive, the second the fuel containing only the copolymer and the third the fuel containing the copolymer and the Schoonebeek or Pennzoil resin. Thus the temperature and the cooling rate were exactly the same for all three samples.

Previous experience has shown that there is an excellent correlation between the size of the wax crystals formed under these cooling conditions and the field performance of the fuel. The smaller the wax crystals, the better the field performance.

From the above it is apparent that the synergistic mixture of the present invention gives unexpected desirable results with respect to the flowability of the fuel under field conditions.

While the synergistic mixture of the present invention is desirable for use in any type of base fuel hereinbefore described, it is particularly effective in base fuels wherein the wax which precipitates near the pour point has a higher isoparaffinic content as compared to normal paraffins. If the wax which precipitates near or about the pour point contains more than about 3% isoparaffins, the effectiveness of the copolymer in controlling flowability under field conditions is materially impaired. Thus, it is essential that if the wax which precipitates near the pour point contains in excess of 5% isoparaffins as compared to total wax precipitation, it is essential that the synergistic mixture of the present invention be utilized as described if flowability under field conditions is to be secured.

What is claimed is:

1. A hydrocarbon composition comprising, a major amount of a hydrocarbon distillate fuel boiling in the range from about 250°–750° F. and containing above 3% isoparaffins based on the total wax which precipitates about the pour point of said oil; and as a low temperature flow improver .001 to 0.5 weight percent of a mixture comprising one part by weight of a pour depressing copolymer comprising 60 to 99 weight percent ethylene and 1 to 40 weight percent vinyl acetate, said copolymer having a molecular weight of about 1,000 to 3,000; and ½ to 2 parts by weight of a petroleum resin having a Holde asphalt content of less than 0.2%, and a molecular weight in the range of about 1,000 to 2,000, said resin being obtained by extraction from a residuum boiling above 700° F. of a highly paraffinic crude with a hydrocarbon solvent selected from the group consisting of propane and butane, followed by recovering said resin from said solvent after the solvent is removed from the residuum.

2. A composition according to claim **1**, wherein the amount of said mixture is about .005 to .1 wt. percent, and wherein said resin is extracted from a residuum selected from the group consisting of residuums of Schoonebeek crude and Pennsylvania crude.

3. Composition as defined by claim **1** wherein the the amount of isoparaffins present in the wax which precipitates near the pour point is in excess of 5 weight percent, and wherein the molecular weight of the copolymer is in the range from about 1500 to 2200, and wherein the amount of vinyl acetate present in the copolymer is in the range from about 15 to 25 weight percent.

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