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MIDDLE DISTILLATE COMPOSITION OF IMPROVED POUR CHARACTERISTICS

Stephan Ilnyckyj, Sarnia, Ontario, Canada, assignor to Esso Research and Engineering Company, a corporation of Delaware

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The present application is a continuation-in-part of U.S. Serial No. 26,407 filed May 3, 1960, entitled, "A Copolymer Pour Point Depressant for Middle Distillates," inventor: Stephan Ilnyckyj, and now abandoned.

The present invention is concerned with improving the flow at low temperatures and the pour point characteristics of middle distillates. More particularly, the present invention relates to the preparation of improved low cold test hydrocarbon fuels, in particular heating oils and diesel fuels, kerosene, aviation turbo-jet fuels and other fuels that are subject to low temperatures. In accordance with the present invention, improved middle distillate fuel compositions of improved pour points are produced by using in conjunction with middle distillates a pour depressant comprising a copolymer of ethylene and a vinyl fatty acid ester wherein the vinyl ester contains from 7 to 14 carbon atoms per molecule. Particularly desirable compounds are copolymers of ethylene with vinyl octanoate, ethylene with vinyl valerate, ethylene with vinyl laurate, ethylene with vinyl hexanoate, ethylene with vinyl nonanoate, and ethylene with vinyl decanoate.

With the increase in the use of hydrocarbon fuels of all kinds, a serious problem has arisen in areas frequently subjected to low temperatures in the cold test characteristics of fuels. Particularly, serious problems have been encountered by 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 synphoning is rendered difficult or impossible at temperatures around or below the pour point of the oil. Furthermore, the flow of the oil at such temperatures through the filters cannot be maintained, leading to the failure of the equipment to operate.

Also the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 800° F. have attracted increasing attention in recent years because of the growth of markets for such fuels in subarctic areas and because of the development of turbo-jet 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 lubricting 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 fuels. Poor performance of these additives might possibly result from the structural differences between waxes occurring in lubricating oils and so-called middle distillates.

A wide variety of compounds have been found to be effective as pour point depressants for lubricating oil. Among the best known are "Paraflow," "Santopour" and "Acryloid" and their modifications. They are prepared either by condensing aromatic compounds with long chain paraffins, such as wax, or by condensing olefinic esters. It is generally considered that these pour depressants are effective in that in cooling an additive-containing oil, the hydrocarbon chain of the additive becomes incorporated into the crystal lattice of the separated wax, while the other part of the pour depressant molecule prevents the crystals from adhering together to form a gel structure. The failure of these additives to be effective in middle distillates may at least in part be due to the basic difference in the composition between the wax in lubricating oils and that in middle distillate fuels.

It is, therefore, the principal object of the present invention to set forth an improved pour depressant 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 provide heating oils, diesel fuel oils, kerosenes and jet fuels having low 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–975–53T and later versions of the same specification.

The polymeric pour depressants may, in accordance with the invetion, be employed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitors, antistatic agents and the like. It will frequently be found convenient to prepare additive concentrates for use in the various types of fuels and thus add all of the additives simultaneously.

Other and further objects of the present invention will appear more clearly hereinafter.

The pour point depressants of the present invention comprise a copolymer of ethylene and a vinyl fatty acid ester. The vinyl ester is secured preferably by reacting acetylene and a fatty acid which contains from 5 to 12 carbon atoms in the fatty acid molecule. Thus, the fatty acid ester will contain from 7 to 14 carbon atoms in the molecule. It is preferred that the parts by weight of ethylene in the copolymer be in the range from about 70% to 50% and that the parts by weight of the vinyl fatty acid ester be in the range from about 30% to 50%.

The molecular weights of the ethylene-vinyl fatty acid ester copolymer are critical and should be in the range from about 1000 to 3500, preferably in the range from 1500 to 3000. The molecular weights are determined by K. Rast's method (Ber., 55, 1051, 3727 (1922)).

The ethylene-vinyl fatty acid ester copolymer as described above is used in a concentration in the range from about .002 to .5% by weight. It is preferred that the maximum amount used not exceed about .2% by weight, and a particularly desirable concentration is in the range from about .01 to .05% by weight.

With respect to the above, if the copolymer is a copolymer of ethylene and vinyl octanoate, the amount of vinyl ester is preferably in the range from about 42% to 48% by weight and the molecular weight is in the range from about 1800 to 2600. If the copolymer is a copolymer of ethylene and vinyl valerate, it is preferred that the amount of vinyl ester present in the copolymer be in the range from about 30% to 35% and the molecular weight range from about 1900 to 2400. If the copolymer is a copolymer of ethylene and vinyl laurate, it is preferred that the weight percent of ester present in the molecule

range from about 35% to 45% and that the molecular weight be in the range from about 1000 to 1500. On the other hand, if the ester is a copolymer of ethylene and vinyl hexanoate, it is preferred that the concentration of the ester present in the molecule range from about 40 to 50 weight percent and that the molecular weight be in the range from about 1000 to 1500.

Surprisingly, these low molecular weight copolymers have no effect upon the pour points of lubricating oils, thus emphasizing the difference in structure between the wax associated on the one hand with lube oils and on the other with middle distillates. The low molecular weight copolymers may be prepared by any peroxide process. In some instances, it may be desirable to first prepare a higher average molecular weight copolymerization product and then recover from that product material having a molecular weight within the range between about 1000 and about 3500. Since such copolymerization products normally consist of a smear of copolymers whose molecular weights vary over a wide range, an effective method for recovering the 1500 to 3000 molecular weight portion therefrom is to extract the product with a solvent such as normal heptane or methyl-ethyl ketone. Other methods for obtaining the low molecular weight materials include thermal degradation of the high molecular weight polymer or treatment of the high molecular weight copolymer with ozone in order to break the polymer chains. Still other methods also useful will be apparent to those skilled in the art.

A very desirable method is to conduct copolymerization in a benzene solution using di-tertiary-butyl-peroxide as an initiator at a temperature in the range from about 260° to 400° F. The preferred temperature is in the range from 290° F. to 325° F. as for example about 300° F. The pressure is in the range from about 600 to 1500 pounds, preferably 800 to 1000 pounds such as 900 pounds. The autoclave or similar equipment containing the solvent, initiator and vinyl octanoate is purged about three times with nitrogen, twice with ethylene and then charged with a sufficient amount of ethylene to yield the desired pressure when heated to the reaction temperature. During the copolymerization, additional ethylene is added whenever the pressure drops by about 100 p.s.i.g. Copolymerization is considered complete when it is less than 50 p.s.i.g. pressure drop per hour. The product is stripped free of solvent and unreacted vinyl octanoate under vacuum.

In general the class of depressants comprise a copolymer of ethylene and a vinyl fatty acid ester wherein the ester group contains from 7 to 14 carbon atoms in the molecule and wherein the weight percent of the ester present in the copolymer is in the range from 30 to 50%. Satisfactory fatty acid esters are, for example, vinyl n-octanoate, vinyl 2-ethyl-hexanoate, vinyl nonanoate, vinyl decanoate, vinyl butyrate, vinyl laurate, and vinyl valerate.

A typical distillate fuel boiling in the range from 250° to 750°F. to which the present additives may be added are middle distillate heating oils. These fuels are of commercial grade and have typical properties as follows:

Composition:	
Straight run gas oil	40
Cat. Cracked gas oil	60
Inspections:	
Gravity, ° API	29.1
ASTM pour, ° F., no additive	20
Flash Pensky-Martin, ° F.	192
Distillation ASTM, ° F.:	
I.B.P.	398
10%	492
50%	566
90%	612
F.B.P.	644

The improvements obtained by adding the additives in accordance with the present invention are set forth in the following table. All pour points quoted hereafter were obtained by ASTM Method D-97-47.

A number of tests were conducted using various copolymers in a 50–50 blend of virgin gas oil and cracked gas oil. The virgin gas oil boiled in the range from about 350° to 700° F., and the cracked gas oil boiled in the range from about 350° to 650° F. The blend had a pour of 20° F. The various copolymers were prepared under varying pressure and other varying operating conditions. As pointed out theretofore, the critical factors with respect to desirable copolymers are molecular weights and the concentration of the vinyl octanoate in the copolymer. The results of these tests are shown in the following table:

TABLE I.—SYNTHESIS AND POUR DEPRESSING POTENCY OF COPOLYMERS OF ETHYLENE AND VINYL OCTANOATES

[Synthesis conditions: 900 p.s.i.g., 300° F., in 655 ml. of benzene, one gallon reactor]

Operation	1	2[1]	3	4
Vinyl ester	(2)	(3)	(3)	(3)
Vinyl ester, g.	200	200	200	277
Vinyl ester, g./min.	1.66	1.66	1.66	2.3
Di-t-butyl peroxide, g.	11.9	11.9	11.9	11.9
Di-t-butyl peroxide, g./min.	0.066	0.066	0.066	0.066
Copolymerization time, hr.	3.5	3.5	3.5	3.5
Product:				
Yield, g.	423	573	461	548
Copolymer g./peroxide, g.	35.5	48.2	38.7	46.0
Vinyl octanoate, wt. percent	47.3	50.5	43.0	34.9
Molecular weight	1,780	3,570	2,657	3,030
Depression of ASTM pour point,[4] ° F.:				
0.015% copolymer	−15	−5	−5	+10
0.025% copolymer	−50	−15	−45	−25

[1] 1,200 p.s.i.g.
[2] n-Octanoate.
[3] 2-ethyl-hexanoate.
[4] 50/50 blend of straight run and cracked gas oils, ASTM pour point +20° F.

From the above it is apparent that the most potent pour depressants were the copolymers 1 and 3. In a concentration of 0.025 wt. percent copolymer 1 which contained 47.3 wt. percent of vinyl n-octanoate depressed the pour point of the reference oil from +20° F. to −50° F. A similar potency was shown by copolymer 3 containing 43 wt. percent of vinyl 2-ethyl-hexanoate. It will be noted that the copolymer of ester of the branched acid had a molecular weight of 2650 and prepared under similar conditions the copolymer of ester of the straight chain acid had a molecular weight of 1780. The copolymer 2 containing 50.5 wt. percent of vinyl 2-ethyl-hexanoate respectively showed for lower potency in depressing the pour point of the reference oil.

TABLE II.—POUR DEPRESSING POTENCY OF COPOLYMERS OF ETHYLENE WITH VINYL VALERATE

[Synthesis conditions: 900 p.s.i.g., 300° F., in 655 ml. of benzene, one gallon reactor]

Operation:	
Vinyl ester	Vinyl valerate
Vinyl ester, g.	200
Vinyl ester, g./min.	1.67
Di-t-butyl peroxide, g.	11.9
Di-t-butyl peroxide, g./min.	0.066
Copolymerization time, hr.	3.5
Product:	
Yield, g.	407
Copolymer g./peroxide g.	34.2
Vinyl ester, wt. percent	29.7
Molecular weight	2300
ASTM pour point (1), ° F.:	
0.015 wt. percent copolymer	−10
0.025 wt. percent copolymer	−65

[1] 50/50 blend of straight run and cracked gas oils, ASTM pour point +20° F.

Thus, from the above, a potent copolymer contained 29.7 wt. percent of vinyl valerate. In 0.025 wt. percent concentration, it lowered the pour point of the same refer-

ence fuel to −65° F. The copolymers had a molecular weight of about 2,300.

TABLE III.—SYNTHESIS AND POUR DEPRESSING POTENCY OF COPOLYMERS OF ETHYLENE AND VINYL LAURATE

[Conditions of copolymerization: 900 p.s.i.g., 300° F., in 655 mls. of benzene, one gallon reactor]

Operation	A	B
Vinyl laurate, g.	100	250
Vinyl laurate, g./min.	0.84	2.08
Di-t-butylperoxide, g.	11.9	11.9
Di-t-butylperoxide, g./min.	0.066	0.066
Copolymerization time, hr.	3.5	3.5
Product:		
Yield, g.	364	491
Copolymer, g./peroxide, g.	30.6	41.3
Vinyl ester, wt. percent	24.0	39.0
Molecular weight	1,630	1,360
ASTM pour point,[1] ° F.:		
0.015 wt. percent copolymer	+5	−35
0.025 wt. percent copolymer	−10	−70

[1] Reference oil: 50/50 blend of straight run and cracked gas oils, ASTM pour +20° F.

From the above, it is apparent that the copolymers of the present invention are very effective pour depressants for middle distillates. It is also apparent that the weight percent of vinyl laurate present is critical, for example, with 24 wt. percent of the vinyl laurate present and when utilizing 0.025 wt. percent of the copolymer, the pour was reduced from +20° F. to −10° F. On the other hand, when the concentration wt. percent of the vinyl laurate was 39% when utilizing only .015 wt. percent, the pour was reduced to −35 and when utilizing .025 wt. percent, the pour is reduced to below −70° F.

TABLE IV.—SYNTHESIS AND POUR DEPRESSING POTENCY OF COPOLYMERS OF ETHYLENE WITH VINYL ESTERS

[Conditions of copolymerization: 900 p.s.i.g., 300° F., in 655 mls. of benzene, one gallon reactor]

Operation	A	B	C	D
Vinyl ester	(1)	(1)	(1)	(2)
Vinyl ester, g.	50	150	300	88
Vinyl ester, g./min.	0.42	1.25	2.5	0.73
Di-t-butylperoxide, g.	11.9	11.9	11.9	11.9
Di-t-butylperoxide, g./min.	0.066	0.066	0.066	0.066
Copolymerization time, hr.	3.5	3.5	3.5	3.5
Product:				
Yield, g.	306	373	459	301
Copolymer, g./peroxide, g.	25.7	31.3	38.6	25.3
Vinyl ester, wt. percent	9.9	25.4	45.6	15.6
Molecular weight	1,740	1,620	1,155	1,390
ASTM pour point,[3] ° F.:				
0.015 wt. percent copolymer	+10	0	0	+5
0.025 wt. percent copolymer	+5	−20	−50	−10

[1] Hexanote.
[2] *n*=Decanoate.
[3] Reference oil: 50/50 blend of straight run and cracked gas oils, ASTM pour point, 20° F.

From the above, it is apparent that excellent pour depressant results are secured by the copolymers of the present invention having the molecular weights and molecular structure as set forth hereinbefore.

What is claimed is:

1. A petroleum distillate composition having an improved pour which comprises a distillate fuel boiling in the range between about 250° F. and about 800° F. which has been improved with respect to pour point by the incorporation therein of a pour depressing effective amount in the range from about .01 to .5% by weight of an oil soluble copolymer of ethylene and a vinyl fatty acid ester having from about 7 to about 14 carbon atoms in the ester, said copolymer having a molecular weight in the range from about 1000 to 3500, said copolymer being further characterized by containing from about 30% to about 50% by weight of said vinyl fatty acid ester.

2. Composition defined by claim **1** wherein the distillate fuel contains from about .01 to about .1% by weight of said copolymer.

3. Composition as defined by claim **1** wherein said distillate fuel contains from about .01 to about .05% by weight of said copolymer.

4. Composition as defined by claim **1** wherein said vinyl fatty acid ester comprises vinyl octanoate present in said distillate fuel in a concentration in the range from about .01 to about .05% by weight.

5. Composition as defined by claim **1** wherein said fatty acid ester comprises vinyl valerate present in a concentration in said distillate fuel in the range from about .01 to .05% by weight and wherein the molecular weight of said copolymer is in the range from about 1500 to 2500.

6. Composition as defined by claim **3** wherein said fatty acid ester comprises vinyl laurate and wherein the molecular weight is in the range from about 1000 to 2000.

7. Composition as defined by claim **3** wherein said fatty acid ester comprises vinyl nonanoate.

8. Composition as defined by claim **3** wherein said fatty acid ester comprises vinyl decanoate.

9. Composition as defined by claim **3** wherein said fatty acid ester comprises vinyl hexanoate.

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DANIEL E. WYMAN, *Primary Examiner.*