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POUR POINT DEPRESSANT FOR MIDDLE DISTILLATES

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ABSTRACT OF THE DISCLOSURE

The low temperature flow characteristics of petroleum distillate fuels boiling from 300° F. to 750° F. are improved by incorporating therein, from 0.01% to about 1% by weight of such fuel, of a copolymer of ethylene and ethoxy-ethyl acrylate. The copolymer has a molecular weight of from 1000 to 3000 and the ethoxy-ethyl acrylate constitutes from about 5% to about 20% by weight of the copolymer.

The present invention relates to improving the low temperature flow characteristics of middle distillate petroleum products. More particularly, this invention is concerned with the lowering of the pour point of middle distillate petroleum fuels.

The petroleum products which are referred to as middle distillates are those which boil within the range of about 300° F. to about 750° F., and include, for example, heating oils, diesel fuel, kerosene, and aviation jet fuels. The pour point is defined to be the lowest temperature at which the petroleum product will pour or flow when chilled without disturbance under specified conditions.

With the increase in use of hydrocarbon fuels of all kinds difficulties have arisen in the utilization of these fuels in areas which are subject to low temperatures. Problems have been encountered in the low temperature storage and use of those middle distillate fuels having a high pour point, since distribution and filtration is rendered difficult or impossible at temperatures around or below the pour point of the fuel. The problems and difficulties encountered in the use of middle distillate fuels at low temperatures have become more acute in recent years due to an increased demand for these fuels in arctic areas of the world, and also the development of jet aircraft capable of operating at altitudes where temperatures in the neighbourhood of —40° to —50° F. can be encountered.

The difficulties associated with low temperature use of middle distillate petroleum products arise through the formation of solid or semi-solid wax particles within the petroleum composition when its temperature drops to around or below its pour point. As an example, if a furnace oil having a pour point near or just below 0° F. is stored at temperatures as low as —20° to —40° F., these low temperatures can result in crystallization and solidification of wax in the furnace oil which interfere with its utilization.

Problems which arise with the use of petroleum products at low temperatures below their pour point have long been recognized in the storage and use of heavy oils, such as lubricating oils, which have higher boiling and solidification temperatures than middle distillate petroleum products. The use of additives which will depress the pour point in lubricating oils is well known, but compounds which have been effective as pour point depressants for lubricating oils have not been found to be satisfactory in service with middle distillates or lighter petroleum products. The ineffectiveness of these additives may at least in part be due to differences in the structure and composition of the waxes which occur in lubricating oils and in the waxes which appear in middle distillate petroleum products.

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In the past, the problem of lowering the pour point temperature in middle distillates has been overcome in part by urea-dewaxing, but such an operation is expensive. Another approach for solving the problem of pour point depression of middle distillate petroleum products has been to find a substance which will satisfactorily decrease the pour point temperature of such products. Recently, a number of polymeric materials which will lower the pour point of middle distillates have been discovered. United States Patent 3,007,784, issued November 1961, discloses the use of amine oxides as pour point depressants in middle distillate fuels. British Patent 848,777, granted September 1960, describes the utilization of branched polyethylene. More recently, Canadian Patents 646,421 and 646,456 (issued Aug. 7, 1962) disclose the use of copolymers of ethylene and vinyl esters. A more recent Canadian Patent 676,875 (issued Dec. 24, 1963, to Esso Research and Engineering Company) describes the utilization of copolymers of ethylene with alkyl acrylate as pour point depressants. A number of other mixed polymers also have been proposed, but very few have proved to have a high efficiency for pour point lowering.

It is among the objects of this invention to provide a compound with satisfactory pour point depressant properties for middle distillate petroleum products, and to provide middle distillate petroleum products having pour points which are lower than normal.

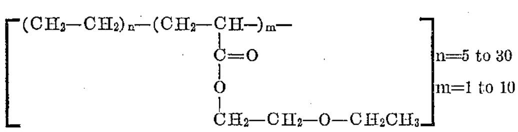
According to the present invention, it has been found that the addition of an oil soluble copolymer of ethylene and ethoxy-ethyl acrylate having a molecular weight of between about 1,000 to 3,000 and containing about 5% to 20% (by weight) of ethoxy-ethyl acrylate can lower the pour point of middle distillate petroleum products. The copolymer is preferably included in the petroleum middle distillate in an amount ranging from about 0.01% to about 1% by weight of the petroleum distillate. The pour point depressant can be employed in conjunction with other additives commonly used in the petroleum products. Typical of such additives are rust and corrosion inhibitors, anti-emulsifying agents, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitors, antistatic agents, and the like. It may be found convenient to prepare additive concentrates which can be used to add several desired additives simultaneously.

The ethoxy-ethyl acrylate component of the copolymer is also known under the name "Cellosolve" acrylate; "Cellosolve" being a registered trademark for 2-ethoxy-ethanol-1, which can be described as the monoethyl ether of ethylene glycol.

The structure of the copolymers useful in practicing this invention is characterized by the following infra-red stretching frequencies:

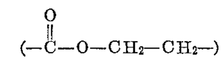
2800 to 3000 cm.$^{-1}$	(C—H) stretch)
1735 cm.$^{-1}$	(ester carbonyl)
1400 to 1300 cm.$^{-1}$	(—CH_2— stretch)
1200 cm.$^{-1}$	(C—O—C stretch of the ester linkage)
1110 to 1150 cm.$^{-1}$	(C—O—C stretch of the ether linkage)
730 to 750 cm.$^{-1}$	(—(CH_2—CH_2)-type of long chain polyethylene)

These copolymers of ethylene and ethoxy-ethyl acrylate can be considered to be represented by the following partial structural formula:



The above described structure for the copolymers is also supported by its typical nuclear magnetic resonance spectrum in which the following chemical-shifts are observed:

(1) A broad multiplet at $\tau=5.5$ to 6.1



(2) A broad multiplet at $\tau=6.5$ to 6.8

$$(—O—CH_2—CH_3)$$

(3) An unresolved peak at $\tau=9$ to 9.3 (polyethylene chain)

(The chemical-shifts are measured with reference to tetramethylsilane at $\tau=10.0$)

The above indications as to the structure of the copolymers useful in practicing this invention show how it differs from the structure of the ethylene and alkyl acrylate copolymers described in Canadian Patent 676,875 (mentioned previously).

The copolymers according to this invention can be prepared under conditions of elevated temperature and pressure utilizing a peroxide catalyst. The copolymers utilized in the examples which follow were prepared by copolymerization conducted in a 3/32" (internal diameter) high pressure, continuous tubular reactor. As a typical example, ethoxy-ethyl acrylate (20 weight percent based on ethylene) and dipropionyl peroxide (1050 p.p.m. based on ethylene) were charged into the reactor. Ethylene was passed at a rate of 1 lb./hr. and having a space velocity of 2500 lb./hr./cf. The polymerization temperature was maintained at 200° C. and the reactor was pressurized to 12,000 p.s.i. At the end of 30 minutes, the product was collected, washed with acetone, and dried. A typical conversion amounted to 20%, based on ethylene. The following Table I gives the details of several runs for the synthesis of copolymers of ethylene and ethoxy-ethyl acrylate. The oily products resulting from Runs 1, 2, and 3 were found to include homopolymers of ethoxy-ethyl acrylate, and were not utilized in subsequent tests shown in Table II.

utilizing a typical middle distillate furnace oil composed of about 50% virgin gas oil and about 50% cracked gas oil. The pour points were determined by dissolving known concentrations of the copolymer in the furnace fuel oil, and measuring the pour point of the latter, thereby determining the effect of the copolymer at different concentrations upon the pour point of the fuel oil. The pour points were measured according to ASTM procedure D–97. The results of five experiments are set forth in Table II.

TABLE II.—RESPONSE OF FURNACE FUEL OIL TO ETHYLENE ETHOXY-ETHYL ACRYLATE COPOLYMER POUR DEPRESSANTS

Experiment No.	Copolymer, wt. percent	ASTM pour, ° F.	Molecular weight	Wt. percent ethoxy-ethyl acrylate in copolymer
1	Nil	+5		
2	.025	−20	1,780	11
	.05	−35	1,780	11
	.1	−50	1,780	11
3	.025	−25	2,400	13
	.05	−40	2,400	13
	.1	−60	2,400	13
4	.05	−40	1,000	15
	.1	−65	1,000	15
5	.05	−5	≈5,000	
	.1	−10	≈5,000	

NOTE.—The copolymers used in experiments 4 and 5 were obtained by fractional precipitation of the sample used in experiment 3.

It is apparent from a consideration of Table II that a copolymer having the preferred properties of a molecular weight of about 1,000 to 2,400 and containing about 13 to 15% (by weight) of ethoxy-ethyl acrylate is an excellent pour point depressant when added to middle distillate petroleum products. The low molecular weight copolymers appear to be more efficient than the higher molecular weight copolymers.

It is also apparent that a copolymer of ethylene and ethoxy-ethyl acrylate according to this invention is efficient in lowering the pour point of middle distillate petroleum products when compared to a copolymer of ethylene and simple alkyl acrylate as disclosed in Canadian Patent 676,875. The data disclosed in the patent shows that a copolymer of ethylene and alkyl acrylate lowers the pour point of furnace fuel oil to about —20° F. at 0.05 weight percent concentration, whereas a similar concentration of an ethylene ethoxy-alkyl acrylate copolymer according to this invention in similar furnace oil lowers the pour point to about —40° F.

TABLE I.—SYNTHESIS OF COPOLYMERS OF ETHYLENE AND ETHOXY-ETHYL ACRYLATE

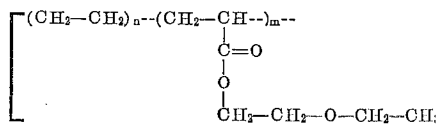
Run No.	Temp., ° C.	Pressure, p.s.i.	Ethoxy-ethyl acrylate, wt. percent	Ethylene: Flow s.c.f.h.	Ethylene: Flow, lb./hr.	Space velocity, lb./hr./c.f.	Catalyst dipropionyl peroxide (p.p.m.)	Time (min.)	Wt. of dry product	Mol wt. product	Ethoxy-ethyl acrylate in copolymer (wt. percent)
1	180	6,500	20	14	1	2,500	1,050	30	Oily product		
2	200	9,000	20	14	1	2,500	525	10	do		
3	210	12,000	20	14	1	2,500	525	10	do		
4	200	15,000	20	14	1	2,500	1,050	15	24.5 gm	1,785	10
5	200	12,000	20	14	1	2,500	1,050	20	16.2 gm	2,410	13

The approximate molecular weights of the copolymers used in the examples were determined by the Rast method of melting point lowering. The ester contents were determined by the standard procedure of hydrolysis and titration. The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrophotometer using a rock-salt prism; the spectra being run either in chloroform or carbon disulfide solvent. The nuclear magnetic resonance spectra were recorded on a Varian Model A–60, using deuterated chloroform as solvent and tetramethylsilane as an internal reference.

The pour point depressant properties of the copolymers of ethylene and ethoxy-ethyl acrylate were determined

What we claim is:

1. A petroleum distillate fuel boiling in the range from 300° F. to 750° F. having incorporated therein a copolymer of ethylene and ethoxy-ethyl acrylate in an amount of from 0.01% to about 1% by weight of the petroleum distillate, said copolymer having a molecular weight of from 1000 to 3000 and is represented by the partial structural formula



wherein n is an integer from 5 to 30 and m is an integer from 1 to 10, the ethoxy-ethyl acrylate constituting from about 5% to about 20% by weight of said copolymer.

2. A fuel as claimed in claim **1** wherein the ethoxy-ethyl acrylate constitutes from about 10% to about 20% by weight of said copolymer.

3. A fuel as claimed in claim **2** wherein the copolymer is incorporated in an amount of from 0.025% to about 0.1% by weight of petroleum distillate.

4. A fuel as claimed in claim **3** wherein the copolymer has a molecular weight of from 1000 to 2400 and the ethoxy-ethyl acrylate constitutes from about 13% to about 15% by weight of said copolymer.

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676,875 12/1963 Canada.

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U.S. Cl. X.R.

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