United States Patent Office 3,250,599 Patented May 10, 1966

3,250,599

FUELS OF IMPROVED LOW TEMPERATURE PUMPABILITY

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No Drawing. Filed Dec. 3, 1962, Ser. No. 241,493
9 Claims. (Cl. 44—62)

This invention relates to a distillate fuel oil composition having improved pumpability characteristics at low temperatures. More particularly, the present invention is directed to a distillate fuel oil boiling above the gasoline range containing a novel combination of additives that endows the fuel oil with improved pumpability properties over a wide low temperature range.

When fuels are to be used or stored under low temperatures such as from the cloud point of the fuels to —15° F. or below, it has become common practice to incorporate small amounts of a pour depressor. Although pour depressor additives assist in lowering the temperature at which the fuel will flow under standard conditions, we have found, in confirmation of the work of other researchers in this art, that ASTM pour points do not correlate with the actual pumpability characterics of the fuel. For example, the addition to distillate fuels boiling above the gasoline range of small, economically feasible concentrations of a copolymer of ethylene and vinyl acetate, a commonly employed pour point depressor, generally provides a significant reduction in the pour point of the fuels yet at temperatures near or slightly below the natural pour point of the fuel, the additive frequently has a highly detrimental effect on the pumpability of the fuel. To further complicate matters, it is not unusual at much lower temperatures, say —15° F. or lower, for the same concentration of this pour depressor to improve pumpability. It is apparent, therefore, that pour depressors such as the copolymers of ethylene and vinyl acetate, in economically feasible concentrations, will not provide a fuel with satisfactory pumpability characteristics over a wide range of low temperatures. Since low temperature climatic conditions to which fuels may be subjected vary from day to day over a wide range and cannot be controlled without the use of additional expensive equipment, the desirability of a distillate fuel possessing excellent pumpability throughout the wide range of low temperatures becomes quite evident.

A small degree of success has been experienced in alleviating this pumpability problem by employing relatively high concentrations of pour depressors including the aforementioned copolymer of ethylene and vinyl acetate, but the satisfactory results appear limited to certain fuels since the same or higher concentrations are not adequate in many other fuels. In any event, concentrations of the pour depressor required to provide the desired pumpability even in the fuels where they are effective, are so high as to mitigate their use for economic reasons.

It has now been found that a petroleum distillate fuel composition having excellent pumpability over a wide range of low temperatures, say from the cloud point of

the fuel to —15° F. or below, can be obtained by adding to the fuel at least about 0.001, often about 0.002 to 0.5, volume percent of a fuel oil-soluble copolymer of ethylene and a vinyl fatty acid ester having from about 3 to 5 carbon atoms, and about 0.05 to 0.4, preferably about 0.1 to 0.3 volume percent of petroleum microcrystalline wax, for instance petrolatum. Preferably the amount of copolymer used is about 0.005 to 0.02 volume percent. That the addition of petrolatum to a distillate fuel containing small amounts of the ethylene-vinyl fatty acid ester copolymer will provide the desired pumpability over the wide range of low temperatures is surprising in that petrolatum, first of all, is not a pour point depressor and in fact may even raise the pour point of the fuels. Secondly, when petrolatum is added to the fuel in the absence of other additives at low temperature, e.g. at —15° F. the pumpability of the fuel is frequently degraded. In addition to the advantageous low temperature pumpability properties exhibited by the fuel compositions of the present invention, they also have substantially improved pour properties.

The copolymers of ethylene and vinyl fatty acid esters of about 3 to 5 carbon atoms employed in the additive combination of the present invention are well-known distillate fuel oil pour point depressors and can be prepared by various methods. The copolymers are preferably composed of about 60 to 99%, preferably about 90 to 70%, by weight of ethylene and about 1 to 40%, preferably about 10 to 30%, by weight of the vinyl fatty acid ester and have a molecular weight, as determined by the K. Rast's method (Ber. 55, 1051, 3727 (1922)), usually ranging from about 1,000 to 3,000, preferably about 1,500 to 2,200. An especially useful copolymer is ethylene-vinyl acetate, particularly the copolymer containing about 15 to 25% by weight vinyl acetate, for example 20% by weight vinyl acetate. Copolymers of this type are described in U.S. Patents 3,037,850 and 3,048,-479, herein incorporated by reference.

The petroleum microcrystalline wax of the present invention includes those hydrocarbon waxes which are normally derived from heavy lubricating oil fractions obtained from paraffin and mixed base crude oils and which waxes have a fine, less apparent crystalline structure than paraffin wax. The wax can be in the form of petrolatum wax which generally contains up to 40% oil, more often about 5 to 25%, or the wax may be in the more refined or deoiled form. In the derivation of the microcrystalline waxes the heavy lubricating oil stocks, preferably those stocks non-distillable from petroleum by normal means, i.e. residual stocks, may first be subjected to solvent deasphalting, solvent refining with phenol or other solvents selective for aromatics or hydrotreating, and then to the normal dewaxing and deoiling procedures to produce the wax. Dewaxing may be accomplished by any one of a number of suitable processes including solvent extraction at low temperatures followed by crystallization and separation by centrifugation or by solvent dewaxing with methyl-ethylketone solutions. The resulting petrolatum wax may, if desired, be further deoiled as by methylethyleketone treatment to give a variety of microcrystalline waxes. The wax may also be obtained as foots waxes or foots oils during the manufacture of other microcrystalline waxes.

The hydrocarbon fuel oils which are improved in accordance with this invention are the normally liquid petroleum distillates boiling primarily above the gasoline range and include, for example, diesel fuels, heating oils, etc. These oils are usually petroleum middle distillates, which generally boil primarily in the range of about 250° to 750° F., and commonly have relatively high pour points, for instance, at least at −10° F. or higher. The oils can be in their relatively crude state or they can be treated in accordance with well-known commercial methods such as acid or caustic treatment, solvent refining, hydrotreating etc. The fuel oils can contain straight run distillate fuel oils, catalytically or thermally cracked fuel oils or mixtures of straight run fuel oils, naphthas and the like with cracked distillate stocks. The cracked materials will frequently be about 15 to 70 volume percent of the fuel.

The additives of the present invention can be added as such to the distillate fuels or if desired as an additive concentrate of the petroleum microcrystalline wax and copolymer of ethylene and vinyl fatty acid ester in a ratio of about 1 to 50 volume parts of the wax to 1 volume part to the copolymer, preferably about 5 to 30 parts of the wax to 1 part of the copolymer. The additive mixture per se can be added to the distillate fuel or as a solution in a normally liquid petroleum hydrocarbon, for example, distillate fuels such as kerosene in concentrations of say about 20 to 60 volume percent, preferably up to about 50% of the combined additives.

The following examples are included to further illustrate the present invention.

EXAMPLES

No. 2 fuel oil compositions containing small concentrations of either a copolymer of ethylene and vinyl acetate, a petroleum microcrystalline wax or a combination of the two additives were subjected to a pumpability test over a temperature range of +10° F. to −15° F. For comparison the neat fuel oil was also subjected to the test. The No. 2 fuel oil employed in all the runs analyzed as follows.

Table I

Composition:	
Naphtha	13
Water white distillate plus gas 0.1	63
Light cycle oil	22
Paraffinic hydrocarbons (C_8–C_9)	2
Laboratory tests:	
Gravity, ° API	34.4
Flash, ° F., PM	138
Viscosity at 100° F., cs.	2.622
Cloud point, ° F.	+16
Pour point, ° F.	+5
Olefins, FIA, percent	0.2
Aromatics, FIA, percent	31.7
Distillation, ° F.:	
I.B.P.	322
5 percent	348

Distillation, ° F.—*Continued*	
10	370
20	410
30	449
40	486
50	514
60	542
70	569
80	596
90	626
E.P.	652
Res.	2.0

Various commercially available petrolatums designated A, B and C were employed in the testing as the microcrystalline wax component. The physical properties of the waxes are shown in Table II below. Another microcrystalline wax component that may also be used is the foots oil also identified in Table II.

Table II

WAX ADDITIVES

	Petrolatum A	Petrolatum B	Petrolatum C	Foots oil from deoiling microcrystalline wax
Gravity (API)	31.7	32.9	32.7	31.1
ASTM M.P., ° F.	96	162.8	129	98.9
Cone penetration	187	39	76	173
Vis 210° F. (Saybolt)	121	91	85.6	104.7
Percent oil	7.6	5.9	20	7.4
Open cup flash	565	580	540	580
Closed cup flash				
Fire	630	640	590	640
Color	8	8	6	
RI at 80° C.		1.45350		1.45780
M.W.				800–850
Type	(1)	(2)	(1)	(2)

[1] Pennsylvania. [2] Midcontinent.

The pumpability test employed comprises the following:

40 gallons of the fuel composition tested was placed in a 275-gallon fuel storage tank in a cold room, maintained at a constant temperature of either +10° F., 0° F., −8° F. or −15° F., and the tank was manifolded to a home burner pump located in an adjacent warm room at normal temperatures. Immediately preceding the pump in the warm room was a filter. The test fuel was routed from the pump under a pressure of 100 p.s.i. through a total gallonage meter to a .75 g.p.h. nozzle, thence to discard. The pump was operated on a 20-minutes on, 10-minutes off basis, starting immediately after charging the fuel to the tank. Pumpability failure was taken as the point when fuel ceased to be pumped over a time period of at least 30 minutes, and the percentage of initial fuel oil charge removed from the tank was determined. The results of the tests, the concentration of additives utilized and the pour and cloud points of the compositions are shown in Table III.

Table III

Vol. percent pour depressant [1]	Vol. percent petrolatum	Cloud/pour, ° F.	Percent fuel removed		
			+10° F.	0° F.	−15° F.
		+16/+5	21.8	71.5	40.0
0.002		+18/+5		8.8	
0.01		+17/−18		23.7	88.0
0.02		+17/−23	44.2	48.5	99.2
0.06		+18/−50		100.0	
	0.2 A	+16/+10	98.8		27.5
	0.3 B	+14/+10			1.5
	0.2 C	+16/+5	97.5		
	0.3 B	+16/+5		98.5	
0.01	0.05 A	+16/−10	40.6, 30.0		
0.01	0.1 A	+16/0	69.8	100	56.5
0.02	0.1 A	+17/−20	96.0	100	99.7
0.02	0.3 B	+16/−5		100	

[1] 50% kerosene solution of the ethylene-vinyl acetate copolymer characterized by containing about 20% ethylene and having a molecular weight of about 1800.

Concentrates of a combination of the additives can be prepared for instance by adding to this solution petroleum microcrystalline wax in amounts and ratios to the copolymer as indicated in Table III above.

Examination of the data of Table III reveals that small concentrations of the ethylene-vinyl acetate copolymer alone do not provide improved pumpability over the entire low temperature range. Note that at 0° F., for example, small concentrations of copolymer were actually detrimental to pumpability. Also that data demonstrate that microcrystalline wax is not a pour point improver and does not provide improved pumpability over the entire range of low temperatures. The fuel oil containing small concentrations of a combination of the copolymer and microcrystalline wax are shown to exhibit surprising pumpability characteristics throughout the range of low temperature conditions.

We claim:

1. A fuel oil composition having improved pumpability over a wide range of low temperatures consisting essentially of a petroleum distillate fuel boiling above the gasoline range having incorporated therein about 0.001 to 0.5 volume percent of a copolymer of about 60 to 99% by weight ethylene and about 1 to 40% by weight of a vinyl fatty acid ester of about 3 to 5 carbon atoms, said copolymer having a molecular weight of about 1,000 to 3,000, and about 0.05 to 0.4 volume percent of a petroleum microcrystalline wax, said amounts improving the low temperature pumpability of the fuel.

2. The composition of claim 1 wherein the copolymer consists essentially of about 70 to 90% of ethylene and about 10 to 30% of the vinyl fatty acid ester.

3. The composition of claim 2 wherein the amount of the copolymer is about 0.005 to 0.02 volume percent.

4. The composition of claim 3 wherein the vinyl fatty acid ester is vinyl acetate and is about 15 to 25% of the copolymer.

5. The composition of claim 4 wherein the amount of petroleum microcrystalline wax is about 0.1 to 0.3 volume percent.

6. A composition consisting essentially of petroleum microcrystalline wax and a copolymer of about 60 to 99% by weight ethylene and about 1 to 40% by weight of a vinyl fatty acid ester of about 3 to 5 carbon atoms, said copolymer having a molecular weight of about 1,000 to 3,000, and the ratio of said wax to said copolymer being about 1 to 50 volume parts to 1 volume part.

7. The composition of claim 6 wherein the ratio of petroleum microcrystalline wax to said copolymer is about 5 to 30 volume parts to 1 volume part.

8. The composition of claim 7 wherein the copolymer consists essentially of about 70 to 90% of ethylene and about 10 to 30% of the vinyl fatty acid ester.

9. The composition of claim 8 wherein the vinyl fatty acid ester is vinyl acetate and is about 15 to 25% of the copolymer.

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