

1

3,288,577

FUEL OIL COMPOSITION OF IMPROVED PUMPABILITY

Seymour H. Patinkin, Chicago, and William L. Steinhoff, South Holland, Ill., and James H. Kirk, Dyer, Ind., assignors to Sinclair Research, Inc., New York, N.Y., a corporation of Delaware
 No Drawing. Filed July 6, 1964, Ser. No. 380,622
 5 Claims. (Cl. 44-62)

This application is a continuation-in-part of application Serial No. 241,493 to James H. Kirk, Seymour H. Patinkin and William L. Steinhoff, filed December 3, 1962, now U.S. Patent No. 3,250,599.

This invention relates to a distillate hydrocarbon 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 characteristics 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 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.

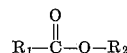
It has now been found that a hydrocarbon distillate fuel composition having excellent pumpability over a wide range of low temperatures, say from the cloud point of the fuel to -15° F. or below, can be obtained by adding to the fuel about 0.05 to 0.5, preferably about 0.1 to 0.4 volume percent of petroleum microcrystalline wax, for instance, petrolatum and at least about 0.001, often about 0.002 to 0.5 volume percent of an additive selected from the group consisting of:

2

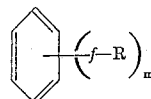
(A) A fuel oil-soluble polymer of ethylene and a vinyl fatty acid ester having from about 3 to 5 carbon atoms;

(B) A fuel oil-soluble polymer of styrene and a normal alpha-olefin of 10 to 24, preferably 14 to 20, carbon atoms having at least about 60% of normal alpha-olefins of 16 to 18 carbon atoms, which polymer is normally liquid and has a kinematic viscosity at 210° F. of at least about 20 or at least about 35 centistokes; and

(C) A fuel oil-soluble, normally liquid, condensation product of a polyunsaturated monoester having the general formula:



wherein R_1 is an olefinic hydrocarbon radical of about 11 to 25 carbon atoms and R_2 is an olefinic hydrocarbon radical of 12 to 26 carbon atoms and an aromatic hydrocarbon having the general formula:



wherein R forms an aromatic hydrocarbon ring, $-f-$ indicates the fused ring relationship and m is 0 to 2, the molar ratio of the aromatic hydrocarbon to the monoester being about 0.2 to 2:1, said condensation product boiling above about 200° F. at 1 mm. Hg.

That the addition of petrolatum to a distillate fuel containing small amounts of the aforementioned additives provides the desired pumpability over the wide range of low temperatures is surprising in that petrolatum is not a significant pour depressor. Secondly, when the petrolatum is added to the fuel in the absence of other additives at low temperatures, 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 frequently have substantially improved pour properties.

The additives designated respectively as A, B and C above will now be more fully described.

A.—Polymer of ethylene and vinyl fatty acid esters

These polymers are well-known distillate fuel oil pour point depressors and can be prepared by various methods. The polymers are composed of about 60 to 99%, preferably about 10 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 polymer is ethylene-vinyl acetate, 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 Nos. 3,037,850 and 3,048,479, herein incorporated by reference.

B.—Polymer of styrene and normal C_{16} – C_{18} alpha-olefins

Although a normal alpha olefin of 16 to 18 carbon atoms per se can be employed in the preparation of the polymer, mixtures of normal alpha-olefins having 10 to 24 carbon atoms, preferably 14 to 20 carbon atoms, can also be used in the polymerization provided they contain at least 60% by weight, preferably at least about 70% by weight, C_{16} to C_{18} normal alpha-olefins in the total alpha-olefin mixture. Polymers of styrene and alpha-olefin mixtures which contain less than about 60% C_{16} to C_{18} alpha-olefins fail to provide an effective mineral oil pour depressor. The alpha-olefin mixture can also contain small minor amounts, preferably less than 10% by weight, of branched

chain alpha-olefins and small amounts of other hydrocarbons such as other olefins, saturated hydrocarbons and aromatics.

The polymer can be prepared by subjecting a mixture of styrene and the alpha-olefin to a polymerization temperature of about 0 to 50° C., preferably 0 to 25° C., in the presence of the Friedel-Crafts catalyst such as aluminum chloride, aluminum bromide, titanium tetrachloride, boron trifluoride etherate, etc. The preferred catalysts are the metal halides, especially aluminum chloride. It is preferred that an inert diluent for the catalyst be also employed and when used will generally be present in an amount of about 0.5 to 5 volumes of diluent per volume of the styrene-alpha-olefin feed. Suitable inert normally liquid diluents are, for instance, the non-polymerizable alkanes of say up to 10 carbon atoms or the lower alkyl halides of 1 to 3 carbon atoms as, for example, methyl chloride, ethyl chloride, propyl chloride and the like. The Friedel-Crafts catalyst will generally be present in the catalyst solution in a concentration of about .5 to 5%, preferably about 2 to 5%, by weight, and the total amount of the catalyst employed is generally about 0.1 to 15% by weight, preferably about 2 to 10% by weight, of the polymer formed.

The styrene in the reactant mixture of the present pour depressor constitutes about 2.5 to 35%, preferably about 5 to 25%, by weight of the reactant mixture, while the long chain normal alpha-olefins constitute the essential balance, e.g., about 65 to 97.5%, preferably 75 to 95%, by weight. The proportions of styrene-alpha-olefin mixtures to catalyst solution employed may be about 0.5 to 1 part of the mixture to 2.0 to 2.5 parts of the catalyst solution.

It is preferred to form the polymer by simultaneous addition of the catalyst solution and the mixture of styrene and alpha-olefin to a reaction vessel in order to avoid monomeric polymerization of styrene. The volumetric ratio of catalyst solution to the olefin reactant at a given unit of time is preferably about 2 to 1.

After the addition has been completed the polymerization may be permitted to continue for a short period of time generally about 5 to 45 minutes, to insure polymerization to a polymer product having a kinematic viscosity at 210° F. of say 25 or about 35 to 600 centistokes, preferably about 30 to 60 or even up to 300 centistokes. The polymerization reaction can then be quenched using for instance a lower alkane or lower alkanol, e.g., of 1 to 4 carbon atoms. The resulting polymer can be separated from residual catalyst as by washing with water, alcohol, dilute aqueous caustic soda or other suitable hydrolyzing and washing methods. The polymerization product is a light colored, viscous oil.

C.—Condensation product of polyunsaturated monoester and aromatic hydrocarbon

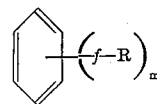
It is important that the ester reactant from which this condensation product is formed contain at least one double bond in each of the acid and alcohol residues. Esters in which either the acid or alcohol residue is saturated, as for instance glycerides or ester mixtures composed essentially of glycerides, on condensation with aromatic hydrocarbons do not form the effective pour depressors of the instant invention. Suitable aliphatic acids that may be used include the natural mono-unsaturated acids such as hypogeic, oleic, elaidic, erucic and brassidic and polyunsaturated acids such as linoleic acid, linolenic acid. Preferably the acid does not contain more than two olefinic bonds.

Suitable alcohols for use in preparing the monoesters are the monohydric, unsaturated aliphatic (including cycloaliphatic) alcohols. The alcohols may be primary, secondary or tertiary and may contain one or more carbon-to-carbon double bonds. The preferred class of alcohols are the primary and secondary monohydric, aliphatic unsaturated alcohols which contain about 12 to 26 carbon atoms. Examples of suitable alcohols include

octene-3-ol-8, decene-1-ol-10, oleyl alcohol, erucyl alcohol, linoleyl alcohol, cetenyl alcohol, eicosene-10-ol-1, citronellol, and the like. The preferred alcohol contains at least 12 carbon atoms and not over 22, and is mono- or diolefinic in character.

The following monoesters are typical and illustrative of the general class that are suitable in the condensation reaction: decylene oleate, dodecylene oleate, pentadecylene oleate, oleyl oleate, eicosylene linoleate, erucyl erucate, linolenyl erucate, etc. Naturally-occurring oils containing essentially a mixture of monoesters such as sperm oil, jojoba oil, etc., may also be used. It is known that sperm oil is a mixture of monoesters of unsaturated fatty acids of the oleic series and of monohydric alcohols of the ethylene series. The principal and characteristic components of sperm oil are monoesters which are unsaturated, i.e., contain double bonds, on each side of the ester (—COO—) group. If desired, the esters may be substituted with non-interfering substituents.

The aromatic hydrocarbon reacted with the monoester may be chosen from a wide variety of aromatic compounds including mono- and poly- cyclic aromatic hydrocarbon compounds which correspond to the general formula:



wherein R forms a fused aromatic hydrocarbon ring, preferably R is $\text{—C}_6\text{H}_4\text{—}$; —f— indicates the fused ring relationship (two carbon atoms common to two aromatic nuclei, e.g., as in naphthalene); and m is 0 to 2. The aromatic ring and R may be substituted with other radicals such as alkyl and phenyl groups which do not prevent the desired reaction. Particularly preferred aromatic hydrocarbons are benzene and naphthalene.

The condensation products of the present invention can be prepared, for example, by subjecting a mixture of about 0.2 to 2 moles of the aromatic hydrocarbon monoester per mole of the polyunsaturated ester, preferably about 0.5 to 1.5 moles of the aromatic hydrocarbon per mole of the ester, to a condensation temperature, usually about 25 to 125° C., preferably about 45 to 110° C., in the presence of a Friedel-Crafts catalyst such as aluminum chloride, aluminum bromide, titanium tetrachloride, boron trifluoride, etc. The preferred catalyst is aluminum chloride. The weight proportions of aromatic-unsaturated monoester mixture to catalyst employed may be about 1 to 10 parts of the mixture to 1 part of catalyst or preferably about 2 to 5 parts of the mixture to 1 part of catalyst. If desired, inert liquid hydrocarbon diluents, e.g., petroleum distillates, alkanes, and aromatics (if used under non-reactive conditions), preferably of 5 to 12 carbon atoms such as hexane, may also be employed. When used the liquid diluent or solvent is generally present in the range of about .05 to 10 or more, preferably about 0.5 to 3 volumes of diluent to 1 volume of the unsaturated monoester. The resulting solution of the additive may be used as such.

A preferred method of preparation comprises adding equimolar amounts of the polyunsaturated ester and aromatic compound to a reaction vessel and stirring the mixture until the aromatic compound is dispersed. With continued stirring the Friedel-Crafts catalyst is then added portionwise, the rate of addition being such that the desired reaction is attained and maintained. On completion of the reaction, a liquid $\text{C}_5\text{—C}_{12}$ hydrocarbon solvent or a mixture thereof is then added in an amount sufficient to reduce the viscosity of the reaction product mixture to the point where it can be readily withdrawn and further processed. The solution is then treated with an acid solution to decompose the catalyst complex formed and the resulting solution washed with water, dilute aqueous caustic soda, or by other suitable washing methods.

The solvent may or may not be removed but it is preferred to employ a solvent that need not be removed, that is, having chemical and physical properties compatible with those of the mineral oils into which it is to be added. In the latter case, the product is obtained as a concentrate solution, more conveniently usable. Solvents which in general need not be removed are, for example, C₅ to C₁₂ liquid alkanes, including cycloalkanes, or mixtures thereof. A process variation, which may be preferred in this method is the addition of an inert, low-boiling liquid hydrocarbon diluent, preferably one that need not be removed as aforesaid, to the ester-aromatic mixture before the addition of the aluminum halide catalyst.

The active reaction products from the condensation reaction are oil soluble, normally liquid reaction products boiling essentially above about 200° F. at 1 mm. Hg. If desired the product can be separated from the total reaction mixture as by vacuum distillation but it can conveniently be employed in admixture with any unreacted material and lighter products that may be present in the reaction mixture or otherwise diluted as with lighter hydrocarbons to form an additive concentrate.

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 apparently 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 methylethylketone solutions. The resulting petrolatum wax may, if desired, be further deoiled as by methylethylketone 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 distillates boiling primarily above the gasoline range and include, for example, diesel fuels, heating oils, etc. These oils are often 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 following examples are included to further illustrate the present invention.

EXAMPLE I

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 (approximate boiling range 300-400° F.)	13
Water white distillate plus gas oil	63
Light catalytic cycle oil	22
Paraffinic hydrocarbons (C ₈ -C ₉)	2

Laboratory tests:

Gravity ° API	34.4
Flash ° F. PM	138
Viscosity at 100° F., c.s.	2.622
Cloud point ° F.	+16
Pour point ° F.	+5
Olefins FIA %	0.2
Aromatics FIA %	31.7

Distillation:

IBP ° F.	322
5%	348
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, ° F.	565	580	540	580
Fire, ° F.	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 Mid-Continent.

The pumpability test employed comprises the following: 40 gallons of the fuel composition tested was placed while at room temperature 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 composition are shown in Table III:

line wax or a combination of the two were subjected to the pumpability test of Example I at temperatures of -5°

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.

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 the data demonstrate that microcrystalline wax was not a pour point improver and did 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.

EXAMPLE II

A 1-liter reaction flask was equipped with two dropping funnels and a Dry Ice trap to remove and condense from the polymerization system, the volatile ethyl chloride. One dropping funnel was charged with 140 ml. of a mixture of alpha-olefins from tallow of approximate composition:

- 4% C₁₄ alpha-olefin
- 32% C₁₆ alpha-olefin
- 64% C₁₈ alpha-olefin

to which was added 20% by weight styrene. To the other funnel was added 280 ml. of a saturated AlCl₃ in ethyl chloride solution at 12° C. Both olefin mixture and catalyst solution were introduced into the reaction flask simultaneously, the olefin mixture at a rate of 20 ml./minute, the catalyst solution at a rate of 40 ml./minute. The total time for addition was 7 minutes and the polymerization was continued for an additional 20 minutes. The reaction was quenched with 250 ml. of isopropyl alcohol. Hexane was added and the polymer washed with H₂O. The polymer after being stripped of solvents had a kinematic viscosity of 40.10 centistokes at 210° F. and an iodine number of 12.2.

No. 2 fuel oil compositions containing small amounts of the copolymer thus prepared, petroleum microcrystal-

F. and -15° F. For comparison, the neat fuel oils were also subjected to the test. No. 2 fuels from two different sources were utilized and analyzed as follows:

TABLE IV

Composition	No. 2 Fuel I	No. 2 Fuel II
Water White Distillate	-----	15
Gas Oil	65	55
Light Cycle Oil	30	30
Kerosene	5	-----
Laboratory Tests:		
Gravity, ° API	33.9	34.6
Flash, ° F. PM	150	136
Viscosity at 100° F., c.s.	2.813	2.548
Cloud Point, ° F.	+2	+4
Pour Point, ° F.	-5	-5
Olefins, FIA Percent	0.2	0.2
Aromatics, FIA Percent	30.1	33.2
Sulfur, Percent	0.34	0.39
Bromine Number	4.0	7.7
Distillation:		
IBP, ° F.	305	330
10%	380	400
50	522	514
90	584	594
E.P.	618	632
Rec.	98	98

The microcrystalline wax employed was a foots oil obtained from the deoiling of petrolatum. The foots oil analyzed as follows:

- Gravity, ° API 30.2
- ASTM M.P., ° F. <100
- Cone penetration 207
- Viscosity at 210° F. (Saybolt) 107.2
- Percent oil 8.6
- Flash, ° F. 588
- Crude source Mid-continent

The results of the pumpability test, the concentration of additives utilized and the pour and cloud points of the composition are shown in Table V:

TABLE V

Additives		No. 2 Fuel	Cloud/Pour, ° F.	Percent Pumped	
Vol. Percent Pour Depressor	Vol. Percent Wax			-5° F.	-15° F.
-----	0.2 Foots Oil	I	+2/-5	83	27
-----	0.2 Foots Oil	I	+7/0	89	44
0.015	0.2 Foots Oil	I	+8/-5	92	95
0.04	-----	I	-2/-10	22	-----
-----	0.2 Foots Oil	II	+4/-5	92	43
-----	0.2 Foots Oil	II	+6/-5	99	80
0.015	0.2 Foots Oil	II	+11/-8	100	38
0.04	-----	II	+2/-35	23	-----

The effect of the styrene-alpha-olefin polymer pour depressor and another petrolatum identified below in both No. 2 fuel I and No. 2 fuel II was also evaluated in a pumpability test herein designated Pumpability Test 3. This test comprises chilling the test oil sample to a point of clouding, that is, a point at which wax or other components crystallize, gels or sediments. The sample is then pumped through a zone of lower temperature and also of more resistance to flow and observations are made to determine the pumpability of the oil under the conditions imposed. The more detailed description of the test method and apparatus is given in copending application Serial No. 354,226 to Thomas J. Smollett and Seymour H. Patinkin, filed March 24, 1964.

The petrolatum employed, designated F, was obtained from a Pennsylvania crude source and analyzed as follows:

Gravity, ° API	32.4
ASTM M.P., ° F.	124
Cone penetration	91
Viscosity at 210° F. (SUS)	83.2
Percent oil	11.3
Flash, ° F.	495

The concentrations of the additives, pour points and pumpability results are shown below in Table VI:

TABLE VI

Fuel Additive.....			No. 2 Fuel I				
Pour Depressor, vol. percent.....			0.0	0.01	0.05	0.01	0.05
Petrolatum F, vol. percent.....			0.0	0.1	0.1	0.3	0.3
Pour Point, ° F. (ASTM D-97-57).....			-5	-5	-50	-3	-35
Pumpability (percent removal of fuel at failure), Temp., ° F.							
Reservoir	Coil	Differential					
1/4	-11 1/4	2					
-1 1/4	-3 1/4	2	142 P	29 P	24 P	64 P	95+R
-3 1/4	-5 1/4	2		64 P	23 P	95+R	51 P
-5 1/4	-7 1/4	2	55 P & R	76 R	28 P	95+R	76 P
-10 1/4	-12 1/4	2	49 P & R	77 R	17 P	92 R	52 P
-15 1/4	-17 1/4	2	0 P	51 R	25 P	78 R	95+R
Fuel (Additive Concentrations as above)...			No. 2 Fuel II				
Pour Point, ° F. (ASTM D-97-57).....			-5	-10	-10	-50	-70
Pumpability (percent removal of fuel at failure), Temp., ° F.							
Reservoir	Coil	Differential					
-1 1/4	-3 1/4	2	76 R	43 P	20 P	95+R	95+R
-6 1/4	-8 1/4	2	70 R	90 R	23 P		95+R
-10 1/4	-12 1/4	2	53 R	78 R	20 P	95+R	95+R
-14 1/4	-16 1/4	2	35 R	61 R	47 P	95+R	95+R
-2 1/2	-6 1/2	4		22 P	41 P	51 P	95+R
-11 1/4	-15 1/4	4		73 R	20 P	95+R	95+R
-16 1/4	-20 1/4	4		51 R	20 P	95+R	95+R

¹ Type of failure: R=Reservoir failure; P=Line plug failure.

² 95+ is considered complete removal of fuel.

The data of Tables V and VI show the improved pumpability provided by the combination of the styrene-alpha-olefin polymer and microcrystalline wax.

EXAMPLE III

966 grams of sperm oil and 245 grams of naphthalene were placed in a reaction vessel and the mixture stirred until the naphthalene dissolved. The stirring was continued while 278 grams of anhydrous aluminum chloride catalyst was added in increments, the addition being such that a temperature of 45 to 50° C. was attained. The stirring was continued until the reaction was substantially complete and hexane was added to reduce the viscosity of the reaction mixture to the point where it could be readily withdrawn. The resulting solution was then treated with an excess of aqueous 20% HCl to decompose the aluminum chloride complex and the treated solution was washed with water until neutral.

Employing the No. 2 fuel oils of Example II, compositions of these fuels containing small concentrations of the condensation product thus prepared, the microcrystalline wax of Example II or a combination of the two were subjected to the pumpability test of Example I at -5° F. and -15° F. For comparison, the neat fuel oils were also subjected to the pumpability test. The concentrations of the condensation product, microcrystal-

line wax and pumpability results are shown in Table VII below:

TABLE VII

Additives		No. 2 Fuel	Cloud/Pour, ° F.	Percent Pumped	
Vol. Percent Pour Depressor	Vol. Percent Wax			-5° F.	-15° F.
0	0	I	+2/-5	83	27
0.015	0.2 Foots Oil	I	+7/-3	100	44
0.04	0.2 Foots Oil	I	-2/-40	7	3
	0.2 Foots Oil	I	+7/0	89	44
0	0	II	+4/-5	92	43
0.015	0.2 Foots Oil	II	+6/-15	100	100
0.04	0.2 Foots Oil	II	-2/-60	6	4
	0.2 Foots Oil	II	+6/-5	99	80

Combinations of the sperm oil-naphthalene additive with the petrolatum F was also evaluated in the same fuels in accordance with the Pumpability Test 3 of Example II. The concentrations of additives, the pour points and pumpability results are shown in Table VIII below:

radical of 12 to 26 carbon atoms and an aromatic hydrocarbon having the general formula:

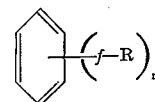


TABLE VIII.—THE EFFECT OF ADDITIVES ON PUMPABILITY
[Bench scale test]

Fuel Additive.....			No. 2 Fuel I				
Pour Depressor, vol. percent.....			0.0	0.01	0.05	0.01	0.05
Petrolatum F, vol. percent.....			0.0	0.1	0.1	0.3	0.3
Pour Point, ° F. (ASTM, D-97-57).....			-5	-5	-60	-25	-75
Pumpability (Percent removal of fuel at failure), Temperature, ° F.							
Reservoir	Coil	Differential					
1/2	-1 1/4	2	144 P	48 R	60 P	93 P	95+R
-1 1/4	-3 1/4	2		44 P	25 P	70 P	95+R
-3 1/4	-5 1/4	2		68 R	70 R & P	95+R	95+R
-5 1/4	-7 1/4	2	55 P & R	54 P	85 P	92 R	95+R
-10 1/4	-12 1/4	2	49 P & R	43 R	77 P	80 R	95+R
-15 1/4	-17 1/4	2	0 P				95+R
Fuel (Additive Conc. as above).....			No. 2 Fuel II				
Pour Point, ° F. (ASTM, D-97-57).....			-5	-10	B-80	-50	B-80
Pumpability (Percent removal of fuel at failure), Temperature, ° F.							
Reservoir	Coil	Differential					
-1 1/4	-3 1/4	2	76 R	36 P	95+P	95+R	95+R
-6 1/4	-8 1/4	2	70 R	92 R	95+R	95+R	95+R
-10 1/4	-12 1/4	2	53 R	82 R	95+R	95+R	95+R
-15 1/4	-16 1/4	2	35 R	64 R	95+R	95+R	95+R
-2 1/4	-6 1/4	4		24 P	88 P	68 P	95+R
-11 1/4	-15 1/4	4		77 R	62 P	95+R	95+R
-16 1/4	-20 1/4	4		64 R	52 P	95+R	95+R

¹ Type of failure: R=Reservoir failure; P=Line plug failure.

² 95+ is considered complete removal of fuel.

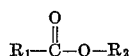
The data of Tables VII and VIII show that significantly improved fuel pumpability was obtained when combination of the sperm oil-naphthalene product and petrolatum were employed. The data also show that there is little, if any, correlation between pumpability and pour point. For instance, fuel compositions containing only the sperm oil-naphthalene additive exhibited excellent pour point but poor pumpability.

It is claimed:

1. A fuel oil composition having improved pumpability over a wide range of low temperatures consisting essentially of a distillate hydrocarbon fuel boiling above the gasoline range having incorporated therein about 0.05 to 0.5 volume percent of a petroleum microcrystalline wax and about 0.002 to 0.5 volume percent of an additive selected from the group consisting of:

A. A fuel oil-soluble polymer of about 65 to 97.5 percent by weight normal alpha-olefin of 10 to 24 carbon atoms having at least 60% normal alpha-olefins of 16 to 18 carbon atoms and about 2.5 to 35 percent by weight of styrene, said polymer having a kinematic viscosity at 210° F. of about 20 to 600 centistokes;

B. A fuel oil-soluble normally liquid condensation product of a polyunsaturated monoester having the general formula:



wherein R₁ is an olefinic hydrocarbon radical of about 11 to 25 carbon atoms and R₂ is an olefinic hydrocarbon

wherein R forms an aromatic hydrocarbon ring, —f— indicates the fused ring relationship and m is 0 to 2, the molar ratio of the aromatic hydrocarbon to the monoester being about 0.2 to 2:1, said condensation product boiling above about 200° F. at 1 mm. Hg, said amounts of wax and additive being sufficient to improve the low temperature pumpability of the fuel.

2. The composition of claim 1 wherein the amount of the additive selected is about .005 to .02 volume percent.

3. The composition of claim 2 wherein the amount of microcrystalline wax is about 0.1 to 0.3 volume percent.

4. The composition of claim 1 wherein the additive selected is the polymer of about 5 to 25% styrene and 75 to 95% by weight normal alpha-olefins of 14 to 20 carbon atoms with at least 70% being in the 16 to 18 carbon atom range.

5. The composition of claim 1 wherein the additive selected is the condensation product of sperm oil and naphthalene.

References Cited by the Examiner

UNITED STATES PATENTS

1,286,091	11/1918	Phillip	44—80
2,917,375	12/1959	Hudson	44—62
3,037,850	6/1962	Wythe et al.	44—62
3,048,479	8/1962	Ilnyckyj et al.	44—62

DANIEL E. WYMAN, *Primary Examiner*.

Y. H. SMITH, *Assistant Examiner*.