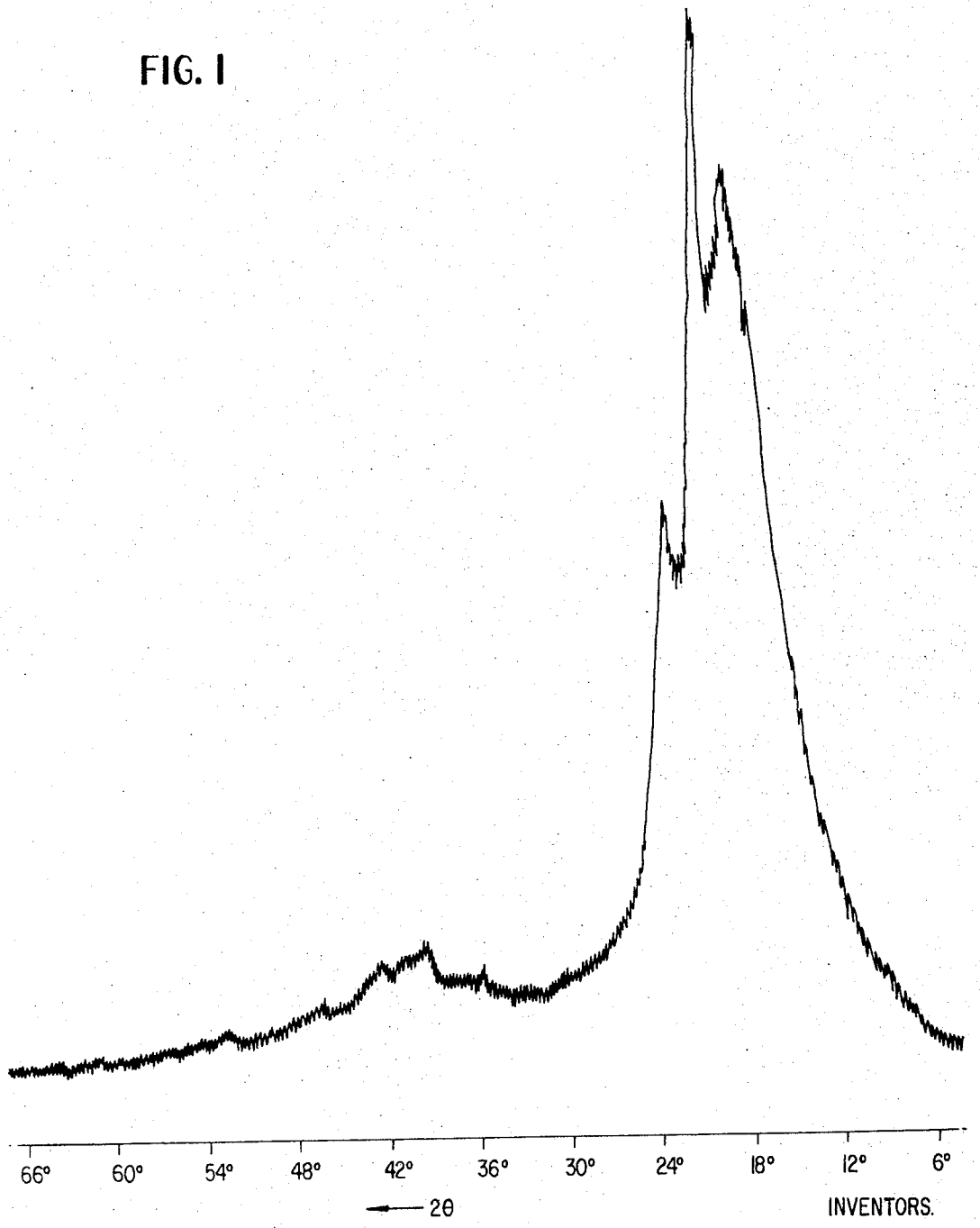
July 8, 1969 H. V. ISAACSON ET AL 3,454,379

HYDROCARBON OIL COMPOSITION HAVING IMPROVED LOW TEMPERATURE PUMPABILITY

Filed Oct. 23, 1964 Sheet 1 of 4

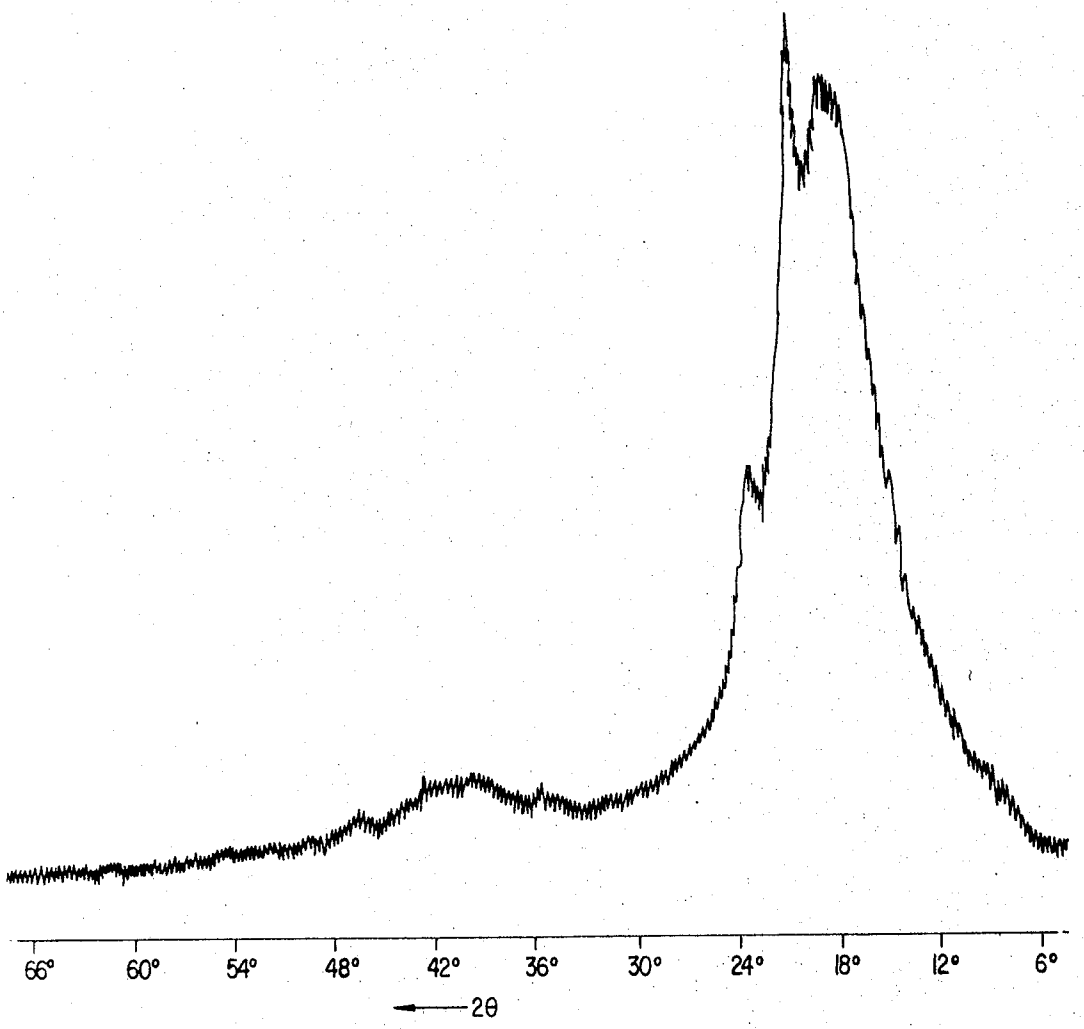
FIG. 1



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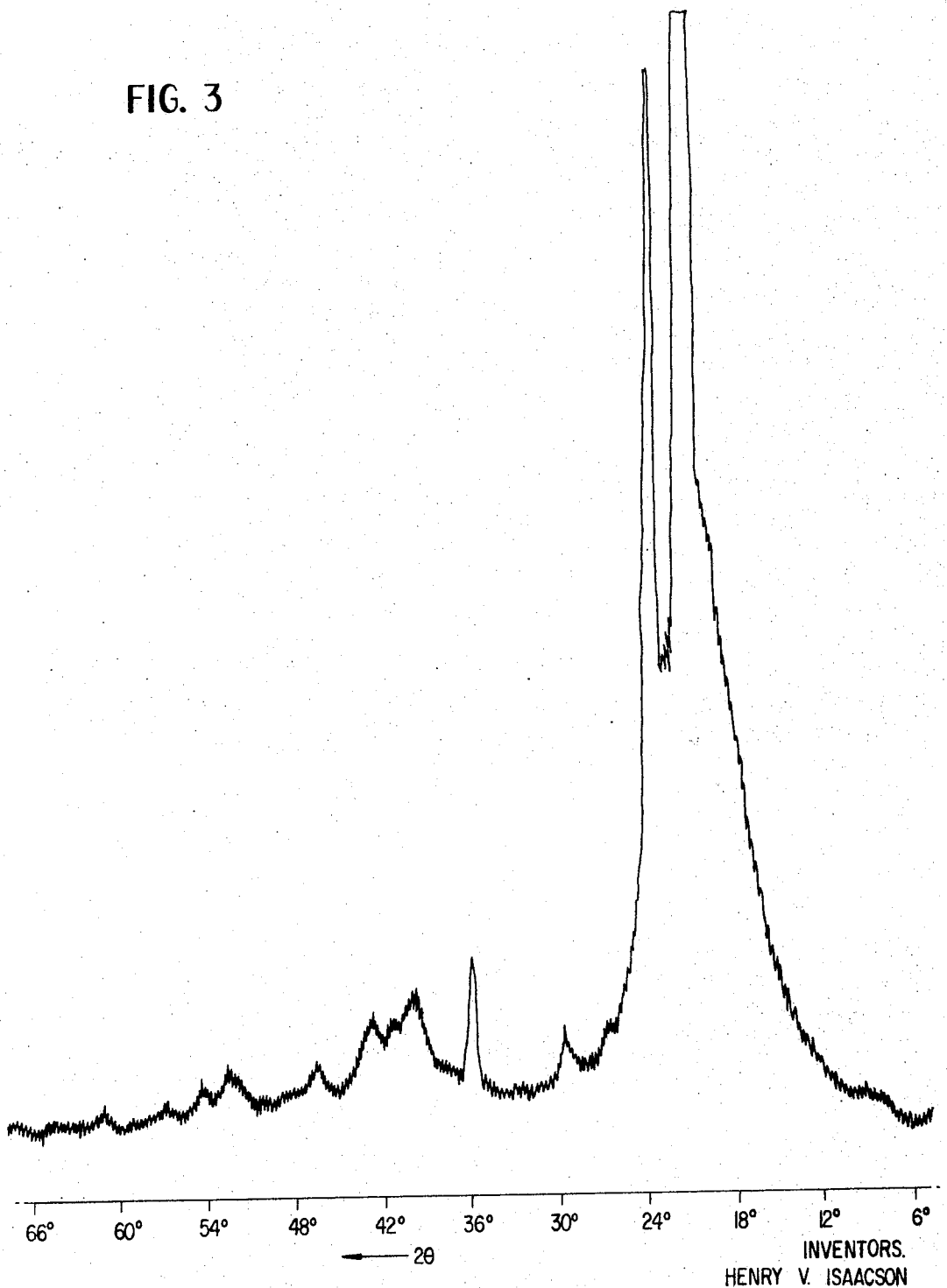
FIG. 2



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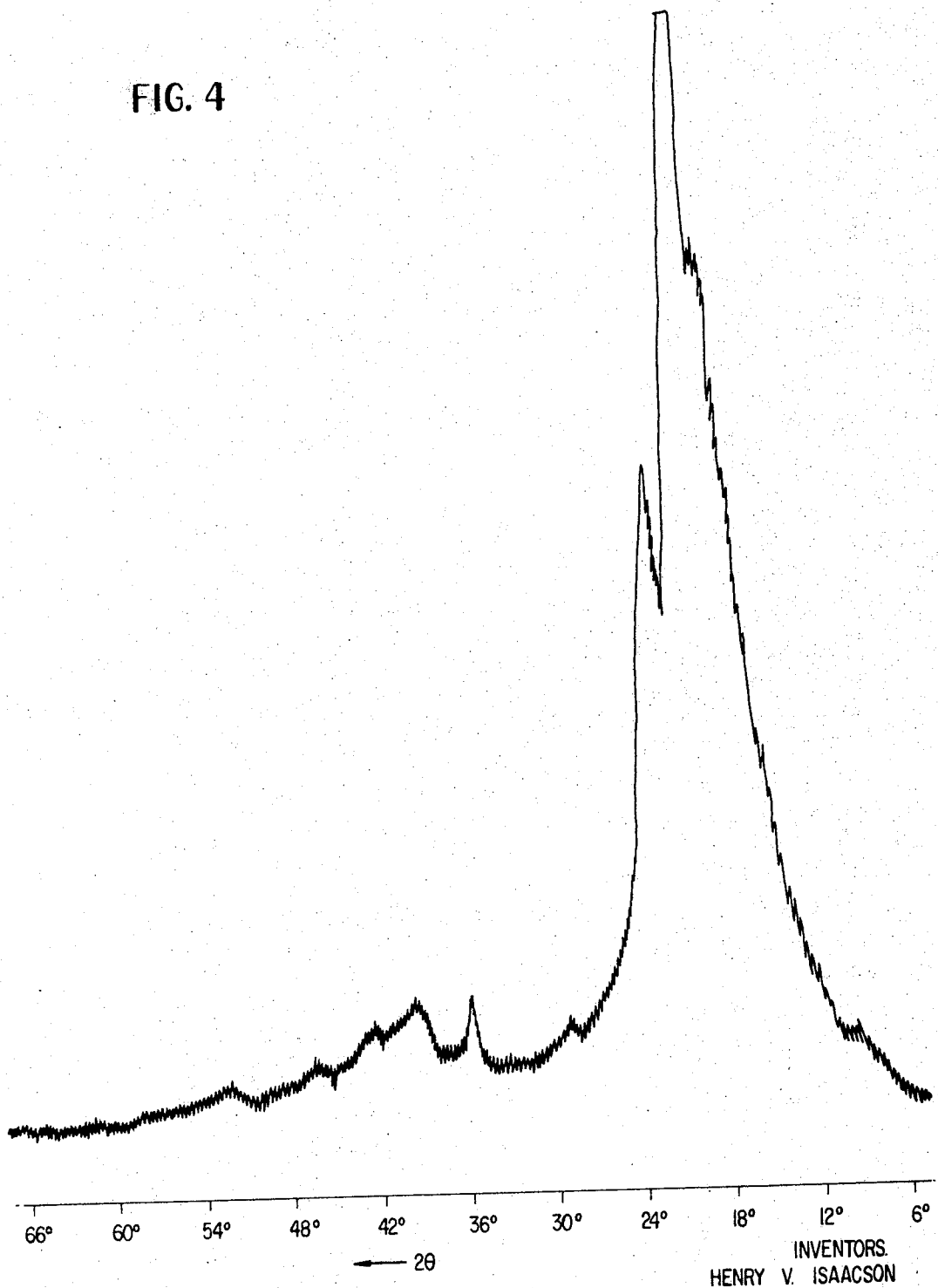
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FIG. 3



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FIG. 4



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HYDROCARBON OIL COMPOSITION HAVING IMPROVED LOW TEMPERATURE PUMPABILITY

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Int. Cl. C10l 1/16
U.S. Cl. 44—62 4 Claims

ABSTRACT OF THE DISCLOSURE

A distillate hydrocarbon fuel oil composition which is improved with respect to pumpability by incorporating polyethylene having a molecular weight in the range of from about 1500–3500.

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 additive 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, it has been 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 0.01 to 0.5, preferably about 0.04 to 0.2 weight percent of an oil-soluble, essentially amorphous, low molecular weight polymer of ethylene produced by the peroxide catalyzed polymerization of ethylene. The amount may vary depending, for instance, on the nature of the fuel, etc., but in any event is sufficient to give improved pumpability at low temperatures.

That the addition of a small amount of essentially amorphous, low molecular weight polyethylene produced by peroxide catalyzed polymerization of ethylene to a distillate fuel provides the desired low temperature characteristics, e.g. pumpability over a wide range of low temperatures, is surprising in that higher molecular weight polyethylene produced by peroxide catalysis and low molecular weight polymers produced by, for example, aluminum chloride catalyzed polymerization of ethylene do not provide the desired low temperature characteristics. Applicants are aware, for example, that it has been suggested, see U.S. Patent No. 2,379,728, to polymerize olefins, including ethylene, using an aluminum chloride catalyst and prepare a low molecular weight polymeric material for use as a pour point depressant. A polymeric produce made from technical ethylene and using the process of the patent does not, however, produce the desired low temperature characteristics when added to fuel oils, and, in fact, does not depress the pour point in fuel oil.

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. When used as a pour depressant, the additives of the present invention can often be used in amounts of from about 0.01 to 0.05 weight percent, preferably 0.04 to 0.2 weight percent.

The polyethylene additives of the present invention can be produced by heating ethylene in the presence of a peroxide catalyst under a high pressure. The pressures are often at least about 7500 p.s.i., preferably above 10,000 p.s.i., and up to about 45,000 p.s.i. or more, particularly in the range of from about 25,000 to about 27,000 p.s.i. The other conditions of the process such as temperature and period of time, are often sufficient to polymerize the ethylene until a yield of from about 8%, preferably 10%, up to about 15 weight percent by weight of polymer based on the ethylene reacted, is produced. Generally, a temperature of from about 60 to 300° C. is sufficient although the specific temperature and time are dependent upon the degree of polymerization desired, catalyst used, and reaction pressure. The catalyst may be any conventional peroxide catalyst such as for example, benzoyl peroxide, di-tert-butyl peroxide, etc. The magnitude of the action pressure may determine whether a linear or a branched polymer is produced, with linear polymers often being produced at pressures in excess of 30,000 p.s.i. and branched polymers being produced at lower pressure. The additives of the instant invention are formed in the production of either type of polymer.

When, for example, a 10% yield of polymer on ethylene is reached, the reaction product may be cooled down and the normally desired polymer product is extracted with the mother liquor in situ. Thereafter, the unreacted ethylene is flashed off the mother liquor, after extracting the polymer, and the remaining mother liquor is filtered. The filtrate so recovered forms the additive of the present invention.

The additive of the present invention often amounts to about 0.2% of the total polymer and comprises the soluble ends dissolved during extraction of the desired polymer and is a wax-like, polyethylene composition having a molecular weight, generally of from about 1500 to 3500, preferably 2000 to 3000, as determined by the

vapor phase osmotic pressure method. The polyethylene additives of the present invention are further characterized by their essentially amorphous structure and they often have a heat softening point of about 100° F. A typical analysis of the composition is as follows:

Carbon (percent)	85.44
Hydrogen (percent)	14.36
Spec. gravity 60/60	0.851
Iodine no.	5.1
Peroxide no.	11.5

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, naphtha and the like with cracked distillate stocks. The cracked materials will frequently be about 15 to 70 volume percent of the fuel.

The polymeric pumpability aids can, in accordance with the invention, 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 pour depressants, 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.

The following examples serve to further illustrate the invention without, however, limiting the same.

EXAMPLE I

To illustrate the improvement in pumpability characteristics upon the addition of the polyethylene composition of the present invention, varying amounts of Polymer A prepared by peroxide catalyzed polymerization of ethylene and described in Table I below were added to two fuel oils identified in Table II as Fuels A and B and the pumpability thereof tested.

TABLE I

Iodine No.	5.1
Peroxide No.	11.5
Molecular wt.	2526
Spec. gravity 60/60 (0.8476)	0.8517
Carbon (percent)	85.44
Hydrogen (percent)	11.36
IR ratio CH_2/CH_3	3.06

TABLE II

Laboratory tests	Fuel A	Fuel B
Gravity, ° API	37.6	34.2
Flash, ° F. P.M.	144	140
Viscosity at 100° F., cs.	2.586	2.625
Cloud point, ° F.	+10	+16
Pour point, ° F.	0	+10
Olefins, FIA percent		0.60
Aromatics, FIA percent		30.7
Distillation	**Fuel A**	**Fuel B**
IBP, ° F.	336	326
10%	382	374
50%	522	520
90%	590	628
E.P.	620	664
Recovery, percent	98	98

The pumpability test employed comprises the following:

40 gallons of the fuel composition tested while still at room temperature, 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 and concentration of additives utilized are shown in Table III.

TABLE III

Wt. percent polymer	Pumpability score	
	Fuel A	Fuel B
0.000	29	67
0.025	43	90
0.100	64	99

EXAMPLE II

Various amounts of the Polymer A described in Example I and Polymer B described below, also produced by peroxide catalyzed polymerization of ethylene, were added to two different No. 2 Fuel Oils identified in Table IV as Fuels C and D. Pour point depression results for Polymers A and B are set forth in Table V.

TABLE IV

	Fuel C	Fuel D
Composition:		
Naphtha		
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., P.M.	150	136
Viscosity at 100° F., cs.	2.183	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	406
50%	552	514
90%	584	594
E.P.	618	632
Recovery, percent	98	98

TABLE V

Polymer A

Amount added to fuel A, percent wt.:	Pour point, ° F.
0.100	−65
0.050	−40
0.025	−20
0.000	−5
0.100	−25
0.050	−15
0.025	−15
0.000	−5

Polymer B

Description:	
Iodine No.	10.4
Peroxide No.	4.0
Molecular Wt.	2240
Spec. Gravity	0.8644
Carbon (percent)	85.72
Hydrogen (percent)	14.40
IR ratio CH_2/CH_3	3.08

Polymer B—Continued

Amount added to fuel A, percent wt.:	Pour point, ° F.
0.100	—80
0.050	—50
0.025	—20
0.000	—5
Amount added to fuel B, percent wt.:	Pour point, ° F.
0.100	—35
0.050	—20
0.025	—15
0.000	—5

EXAMPLE III

Polymer A of Example I and Polymer B of Example II were compared with two commercial polyethylene compositions, Epolene N–10 which has a molecular weight of about 12,000 and Bakelite DYDT which has a molecular weight of about 4000 as an additive in fuel oils. Neither commercial polyethylene composition gave the desired low temperature characteristics. Epolene N–10 was not soluble in fuel oil. Bakelite DYDT was soluble in fuel oil. All samples tested with Bakelite DYDT indicated no change in pour point.

Polymers A and B, Epolene N–10 and Bakelite DYDT were examined by X-ray diffraction techniques using a Phillips X-ray diffractometer with CuK_2 radiation at 40 kv. and 20 ma. The samples were pressed into or melted into standard square aluminum powder diffractometer sample holders. The data were obtained by scanning the sample at one degree per minute with a chart speed of 7.5 inches per hour. The instrumental scale factor was 1000 with a time constant of two seconds.

Crystallinity was determined by comparing diffraction maxima at 20 angles of 21.2°, 23.4°, and 36.1°, the samples with the greater degree of crystallinity having the more intense maxima. FIGURES 1, 2, 3 and 4 are

curves obtained for, respectively, Polymers A and B, Epolene N–10 and Bakelite DYDT. The curves demonstrate that the polymer of the present invention has little, if any, crystallinity, whereas the commercial products have substantially more crystallinity.

It is claimed:

1. A hydrocarbon oil composition having improved pumpability over a wide range of low temperatures consisting essentially of a petroleum distillate boiling above the gasoline range which has been improved with respect to pumpability by the incorporation therein of from about 0.01 to 0.5 weight percent of an oil-soluble, essentially amorphous polyethylene having a molecular weight in the range of from about 1500 to 3500, said polyethylene being further characterized by having been produced by peroxide catalyzed polymerization of ethylene.

2. The composition of claim 1 wherein said amount is from about 0.04 to about 0.2% by weight based on the oil.

3. The composition of claims 1 wherein said molecular weight is from about 2000 to 3000.

4. The composition of claim 1 wherein the petroleum distillate oil is a petroleum distillate fuel oil boiling primarily in the range of about 250° to 750° F.

References Cited

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U.S. Cl. X.R.

44—80