

United States Patent

Burkard et al.

[15] 3,645,704

[45] Feb. 29, 1972

[54] **MIDDLE DISTILLATE POUR
DEPRESSANT**

[72] Inventors: **Herbert G. Burkard**, Convent Station;
Harold N. Miller, Millington; **Edward N.
Kresge**, Elizabeth, all of N.J.

[73] Assignee: **Esso Research and Engineering Company**

[22] Filed: **Aug. 19, 1969**

[21] Appl. No.: **854,021**

Related U.S. Application Data

[63] Continuation of Ser. No. 637,334, May 10, 1967,
abandoned.

[52] U.S. Cl. **44/62, 44/79**

[51] Int. Cl. **C10I 1/20**

[58] **Field of Search** **44/62, 79; 252/58**

[56] **References Cited**

UNITED STATES PATENTS

3,337,313 8/1967 Otto **44/62**

Primary Examiner—**Daniel E. Wyman**

Assistant Examiner—**W. J. Shine**

Attorney—**Pearlman and Stahl and Frank T. Johmann**

[57] **ABSTRACT**

Middle distillate oils are improved with respect to flow and pour point by incorporating therein halogenated polymers comprised of ethylene and C₃–C₁₈ alpha-olefins.

12 Claims, No Drawings

MIDDLE DISTILLATE POUR DEPRESSANT

This application is a streamlined continuation of Ser. No. 637,334, filed May 10, 1967, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to improving the flow and pour point characteristics of middle distillates and lighter fuels. More particularly, the present invention relates to the preparation of improved low cold test hydrocarbon fuels, in particular heating oils, diesel fuels, aviation turbojet fuels, gas oils and other fuels that are subject to low temperatures, which fuels contain certain halogenated polymerization products of ethylene and alpha-olefins, especially propylene.

2. Description of the Prior Art

A serious problem has arisen in the cold characteristics of fuels with the increase in the use of hydrocarbon fuels of all kinds in areas frequently subjected to low temperatures. Particularly serious problems have been encountered by heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributing or operating difficulties or both. For example, the distribution of heating oils by pumping or siphoning 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 of such fuels in subarctic areas and because of the development of turbojet aircraft capable of operating at altitudes where temperatures of -50° F. or lower may be encountered.

It is well known in the art to use various mixtures and additives in order to lower the pour point of oils. For example, a wide variety of compounds has been found to be effective as pour point depressants for lubricating oils. Among the best known are those 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 point depressant molecule prevents the crystals from adhering together to form a gel structure. It has, however, been found that such known pour point depressants have little or no effect in oils of the middle distillate boiling range. 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.

SUMMARY OF THE INVENTION

It has now been found, in accordance with this invention, that the pour point of a middle distillate oil may be improved by incorporating therein halogenated copolymers of ethylene and C₃-C₁₈ alpha-olefins or terpolymers of ethylene, propylene and a third monomer which is a C₄-C₂₈ alpha-olefin and/or polyolefin, e.g., a C₆-C₂₈ bicyclic, alicyclic or aliphatic nonconjugated diolefin such as methylene-norbornene.

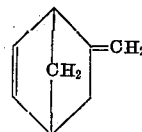
According to the invention, an improved pour depressant and flow improver is formed from an amorphous, random, oil-soluble ethylene-alpha olefin which has been halogenated to a halogen content ranging from about 0.25 to about 20 weight percent halogen, preferably 0.5 to 10 weight percent. The halogen-containing polymer of this invention may be a fluoride, iodide, bromide, or a chloride. It is preferred, however, that the polymer be a bromide or a chloride. The term "amorphous" is used herein to designate polymers which at room temperature have a degree of crystallinity which is less than about 8 percent, preferably less than 3 percent as is detectable by conventional X-ray measurements. By the term "random" is meant those polymers containing relatively small

regions of ethylene or alpha-olefin homopolymer sequences or blocks. In this connection, it is found that the aforescribed crystallinity range efficiently limits the amount of blocks of homopolymer which may be contained within the polymers.

5 Ethylene and a C₃-C₁₈ alpha-olefin can be copolymerized to prepare the additive of this invention. The alpha-olefin may be linear or branched where the branching occurs 3 or more carbon atoms from the double bond, and, while a single olefin is preferable, mixtures of these C₃-C₁₈ olefins may be employed. Suitable examples of C₃-C₁₈ alpha-olefins include: propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 4-methyl-1-pentene, 4-methyl-1-hexene, 5-methyl-1-hexene, 4,4-dimethyl-1-pentene, 4-methyl-1-heptene, 5-methyl-1-heptene, 6-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,6,5-trimethyl-1-heptene and mixtures thereof.

When propylene is employed as the comonomer, i.e., with ethylene, the present invention also contemplates the use of a C₄-C₂₈ alpha-olefin and/or diolefin, polyolefin and the like. These monomers are preferably linear, but may be branched where the branching occurs three or more carbon atoms from the double bond, and, while a single olefinic monomer is preferable, mixtures of these C₄-C₂₈ olefinic monomers may be employed.

25 The diolefins which are useful for copolymerization with ethylene and propylene include the bicyclic, alicyclic or aliphatic nonconjugated diolefins containing from about six to about 28 carbon atoms, preferably from about six to 12 carbon atoms. Nonlimiting examples of suitable monomers include 1,5-cyclooctadiene, 1,5-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-isopropyl-2-norbornene, 5-vinyl-2-norbornene, 1,5-cyclodecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl) cyclopentene, 1,5-octadecadiene, and the like. Especially preferred is methylene-norbornene, that is:



A preferred embodiment of the instant invention is an ethylene-propylene-methylene norbornene terpolymer containing from about 0.25 to about 10 weight percent chlorine.

There are many alternate methods that are available to obtain the copolymers and terpolymers of this invention. The present invention, therefore, is not known to be dependent on any particular method of preparing the aforescribed polymers. Methods for their preparation are well known to those skilled in the art. For example, the polymers of this invention may be conveniently prepared by the well-known Ziegler Process and improvements thereof. See, for example, U.S. Pat. Nos. 2,959,576; 2,996,459; 3,004,962; 3,051,690; 3,033,844; 3,105,066; 3,166,542; and 3,294,766, which patents are incorporated herein in their entirety by express reference.

Typically, the ethylene-alpha olefin polymer of this invention will have a viscosity average molecular weight (M_v), prior to halogenation, of about 10,000 to about 500,000, preferably 50,000 to 150,000. Unless otherwise specified, the term "molecular weight" as used herein means molecular weight based on viscosity measurement. The molecular weights indicated herein and in the claims hereof were estimated on the basis of viscosity measurement at 135° C. of solutions which contained 0.5 milligrams of polymer per milliliter of decalin. The polymers of this invention may be further described as containing (prior to halogenation) from about 20 to about 80, preferably 40 to 70, weight percent ethylene; from about 20 to about 80, preferably 30 to 60, weight percent of the aforescribed C₃-C₁₈ alpha-olefin, and from about 0 to about 15, preferably 0.5 to 10, weight percent of the aforescribed C₄-C₂₈ alpha-olefin and/or polyolefin.

Halogenation of the ethylene-alpha-olefin polymer may be carried out in accordance with well-known techniques. For example, chlorination or bromination can be effected in the liquid phase by photochemical or thermal initiation. In these methods, chlorine or bromine gas, either with or without nitrogen dilution, is introduced intimately into a solution of the aforescribed polymer and inert solvent until the desired amount of chlorination or bromination has been achieved. Suitable inert solvents include benzene, ethylene dichloride, carbon tetrachloride, chlorobenzene, etc. Typically, solutions containing from about 1 to about 20 weight percent of the polymer are exposed to ultraviolet light at a temperature within the range between about -20° to $+50^{\circ}$ C. Alternately, the chlorination or bromination may be carried out without photochemical initiation but at elevated temperatures, e.g., temperatures in excess of about 50° C. Chlorination or bromination of the terpolymers containing unsaturation, i.e., those polymers prepared from ethylene-propylene and polyolefins, may be conveniently carried out without photochemical initiation at temperatures within the range between about -40° and 50° C.

In general, the middle distillate fuels of this invention have atmospheric boiling points within the range between about 250° and 800° F. Specific examples of such materials include, among others, heating oils, virgin gas oils, cracked gas oils, diesel fuel oils, and turbojet fuels. Turbojet fuels in which the polymers may be used normally boil between about 250° and about 550° F. Such fuels are more fully defined by U.S. Military Specifications MIL-F-5624C, MIL-F-25554A, MIL-F-25558A, and amendments thereto. 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. Virgin gas oils will normally boil in the range of from about 350° to 700° F. and the cracked gas oil will normally boil in the range of from about 350° to 650° F. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D-975-35T and later versions of the same specification.

The copolymers or terpolymers of this invention are employed as additives in concentrations of about 0.005 to about 2.5 weight percent, preferably between about 0.01 and about 0.15 weight percent based on the particular middle distillate being treated, so as to accomplish the desired objects. It is to be understood that such ranges are flexible and will be determined by the particular character of the composition to which the additive is added. Typically such polymeric additives are sold as concentrates in which the additive is combined with a hydrocarbon solvent in amounts ranging from 15 to 90, preferably 30 to 55, weight percent additive based on the total amount of the solvent and additive present. Typical hydrocarbon solvents include, among others, mineral oils, hexane, heptane and the like.

The polymeric pour depressants may, 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 rust inhibitors, antiemulsifying agents, corrosion inhibitors, antioxidants, 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.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

Ethylene and propylene were copolymerized in a continuous process using as the reactor a stainless steel pressure vessel having a volume of about 1 gallon and equipped with a multiblade agitator operating at 400 r.p.m. The reactor was jacketed to provide temperature control.

The following liquid streams were separately and concurrently fed into the reactor which was maintained at a pressure of about 40 p.s.i.g. and 80° F.:

1. A solution of ethylene and propylene in n-hexane main-

tained at a temperature of -20° F. and a pressure of 80 p.s.i., said solution having a concentration of 1.5 grams ethylene per liter solution and 4.0 grams of propylene per 100 grams solvent;

2. A solution of ethyl aluminum sesquichloride ($\text{Al}_2\text{Et}_3\text{Cl}_3$) in n-hexane maintained at a temperature of about 75° F. and a pressure of about 80 p.s.i., corresponding to a concentration of 0.5 moles of catalyst per liter of solution; and

3. A solution of vanadium oxychloride (VOCl_3) in n-hexane containing 0.1 moles VOCl_3 per liter of solution.

The reactor was operated under essentially steady state conditions by feeding the monomer solution at a feed rate of 25 pound/hour, the VOCl_3 at a feed rate of 0.010 pound/100 lb. of n-hexane in the monomer feed, the $\text{Al}_2\text{Et}_3\text{Cl}_3$ at a feed rate such that the catalyst Al/V ratio was 5/1 and withdrawing a product stream at the same rate at which the feedstreams were fed into the reactor. The product recovered had an ethylene content of about 61.5 mol. % and a viscosity average molecular weight of 85,000.

Example 2

The polymerization of Example 1 was repeated except that the polymer feed of Example 1 was replaced by an n-hexane solution containing 1.5 grams of ethylene per 100 g. of solvent, 4.2 grams of propylene per 100 g. of solvent and 0.090 grams per liter methylene norbornene. The terpolymer recovered contained about 55 mol. % ethylene, 44 mol. % propylene and 1 mol. % methylene norbornene and had a viscosity average molecular weight of about 125,000.

Example 3

A chlorinated ethylene-propylene copolymer was prepared as follows: 100 grams of the ethylene-propylene copolymer prepared in Example 1 and 3,000 grams of carbon tetrachloride were placed in a 5 liter flask equipped with a mechanical stirrer, heating mantle, thermometer, condenser and gas sparger situated near the bottom of the flask. Chlorination was effected by passing chlorine (at about 25° C. and 800 mm. Hg absolute pressure) through said mixture at the rate of about 20 ml./min. over a period of about 3 hours. The temperatures were maintained within the range between about 70° to 75° C. The chlorinated ethylene-propylene polymer recovered had a chlorine content of about 2.15 weight percent.

Example 4

In the manner of Example 3, 100 grams of the terpolymer of Example 2 and 3,000 grams of carbon tetrachloride were placed in a stirred flask which was cooled by a wet ice/salt bath. The solution was brominated at about -10° C. by the addition of bromine at the rate of about 20 ml./min. over a period of about 1.0 hour. The resultant polymer product contained about 1.6 weight percent bromine.

Example 5

The halogenated and nonhalogenated polymers prepared in Examples 1 through 4 were individually blended with a typical middle distillate fuel in order to demonstrate the improvement obtained by the utilization of the halogenated polymers of this invention. The results are tabulated below in Table I.

TABLE I

Pour Depressant Activity in Middle Distillate Fuel*

0.1 Wt. % Additive in Base Oil*	ASTM Pour Point ° F.
No Additive	0
Ethylene-Propylene Copolymer of Example 1	-35
Chlorinated Ethylene-Propylene Copolymer of Example 3	-60
Ethylene-Propylene-Methylene Norbornene Terpolymer of Example 2	-40
Brominated Ethylene-Propylene Methylene Norbornene of Example 4	-70

* 50/50 straight run/cracked fuel having a cloud point of 4° F., an aniline point of 132.0° F. an API gravity of 33.0, a viscosity of 34.2 SUS at 100° F. and boiling within the range between about 340° and 636° F.

Although the invention has been described with some degree of particularity, it will be understood that variations and modifications can be made therein without departing from the spirit of the invention as hereinafter claimed. The scope of the invention is limited only by the appended claims.

We claim:

1. A petroleum distillate fuel composition having improved flow and pour characteristics, which comprises a major proportion of a petroleum distillate fuel having an atmospheric boiling range between about 250° F. and about 800° F., and from about 0.005 to about 2.5 weight percent of a halogenated, amorphous, random, oil-soluble, polymer comprised of 20–80 weight percent ethylene and 20–80 weight percent C_3 – C_{18} alpha-olefin, said polymer having a degree of crystallinity less than about 8 percent, having a viscosity average molecular weight in the range from about 50,000 to about 150,000 and halogenated to contain from about 0.25 to 20 percent by weight of halogen.

2. A composition as defined by claim 1 wherein said halogen is chlorine or bromine present in an amount ranging from 0.5 to 10 percent by weight.

3. A composition as defined by claim 2 wherein said halogenated polymer is comprised of 40–70 weight percent ethylene and 30–60 weight percent C_3 – C_{18} alpha-olefin.

4. A composition as defined by claim 3 wherein said alpha-olefin is propylene, said viscosity average molecular weight is about 85,000, said halogen is chlorine, the amount of said halogen is about 2.15 weight percent, and said polymer is prepared by copolymerizing ethylene and propylene in the presence of a catalyst mixture of ethyl aluminum sesquichloride and vanadium oxychloride.

5. A composition according to claim 2 wherein said halogenated polymer is comprised of 20–80 weight percent ethylene, 20–80 weight percent propylene and 0–15 weight percent of a third monomer selected from the group consisting

of C_4 – C_{28} alpha-olefin, C_4 – C_{28} diolefin and mixtures thereof.

6. A composition as defined by claim 5 wherein said third monomer is a nonconjugated diolefin containing from about six to about 28 carbon atoms, the third monomer being present in an amount ranging from 0.5 to 10 percent by weight.

7. A composition as defined by claim 6 wherein said nonconjugated diolefin contains from about six to 12 carbon atoms.

8. A composition as defined by claim 7 wherein said third monomer is methylene norbornene, said halogen is bromine, the amount of said halogen is about 1.6 weight percent, and said polymer is prepared in the presence of a catalyst mixture of ethyl aluminum sesquichloride and vanadium oxychloride.

9. An oil concentrate comprising from about 10 to about 85 weight percent of a hydrocarbon solvent and from about 15 to about 90 weight percent of the oil-soluble halogenated polymer of claim 1.

10. An oil concentrate comprising from about 10 to about 85 weight percent of a hydrocarbon solvent and from about 15 to about 90 weight percent of the halogenated product of claim 5.

11. A petroleum distillate fuel composition having improved flow and pour characteristics, which comprises a major proportion of a petroleum distillate fuel having an atmospheric boiling range between about 250° F. and about 800° F., and from about 0.005 to about 2.5 weight percent of a halogenated, amorphous, random, oil-soluble, polymer comprised of 20–80 weight percent ethylene and 20–80 weight percent C_3 – C_{18} alpha-olefin, said polymer having a degree of crystallinity less than about 8 percent, having a viscosity average molecular weight in the range from about 50,000 to about 500,000 and halogenated to contain from about 0.25 to 20 percent by weight of halogen.

12. An oil concentrate comprising about 10 to 85 weight percent hydrocarbon and about 15 to 90 weight percent of the oil-soluble halogenated polymer of claim 11.

* * * * *

40

45

50

55

60

65

70

75