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POUR DEPRESSANTS FOR MIDDLE DISTILLATES

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ABSTRACT OF THE DISCLOSURE

Petroleum middle distillate fuel oil containing as a pour point depressant a polymer of ethylene and C_{10} to C_{22} alpha monoolefin, said polymer having a molecular weight of about 1,000 to 50,000.

PRIOR APPLICATIONS

This application is a continuation-in-part of Ser. No. 500,267 filed Oct. 21, 1965, now abandoned.

SUMMARY OF THE INVENTION

This invention relates to certain polymeric products which are particularly useful as pour depressants for petroleum middle distillates. More particularly, the present invention relates to certain polymers of straight chain C_{10}–C_{22} alpha-olefins with ethylene which are particularly useful as pour point depressants for middle distillates having a high wax content.

The hydrocarbon oils with which this invention is particularly concerned broadly comprise petroleum distillates which are commonly employed in various burner systems, as fuels for diesel engines, as jet fuels and as domestic or industrial heating oils. Such fuel oils may be generally characterized as those that consist of a major proportion of hydrocarbons boiling in the range of from about 350° F. to about 900° F.

In order for a hydrocarbon fuel oil to be utilized effectively, it must be capable of flowing freely through oil lines between the oil reservoir and its ultimate place of combustion at relatively low temperatures. The temperature at which a hydrocarbon fuel oil ceases to pour is called its "pour point." If a hydrocarbon fuel oil does not have a suitably low pour point, the fact that it is a very effective fuel is irrelevant since it will be unable to flow to the place for its combustion.

It is often found that common hydrocarbon fuel oils which are employed for the purposes mentioned above have undesirably high pour points and are incapable of free flow during low temperature operation such as is encountered seasonally in many areas. In such case, it is necessary to modify the flow properties of the base oil so as to lower its pour point. This is commonly done by the addition of agents which are termed "pour depressants" since they act in such manner as to modify the crystal structure of the wax in the oil so as to depress the pour point of the oil.

From the above description, it can be readily seen that proper pour depression of hydrocarbon fuel oils could possibly present many problems. It is, therefore, an object of the present invention to provide a hydrocarbon fuel oil having improved flow and pour characteristics. It is another object of this invention to improve the pour point of petroleum middle distillates. It is a still further object of this invention to provide improved pour-point depressants, and improved methods of preparation of the same, for accomplishing the objects stated above. These and other objects of the invention will become apparent from the following detailed description thereof.

In accordance with the present invention, it has been found that copolymers of straight chain C_{10}–C_{22} alpha-olefins with ethylene, prepared by heating a monomer feed in the absence of air under autogenous pressure to a temperature in the range of 150°–350° C. for a sufficient time to effect polymerization and which have subsequently been distilled to remove fractions boiling in the lubricating oil range to leave a residue having a molecular weight in excess of 1,000, are potent pour depressants for hydrocarbon oils, especially, paraffinic middle distillates. It has been found that the potency of these pour point depressants may be further enhanced by dialysis of the thus treated product whereby products are obtained having molecular weights in excess of 2,000. These higher molecular weight products have been found to depress the pour point of paraffinic distillates by as much as 75° F. when added in a concentration of from 0.05 to 0.1 wt. percent to the oil.

In accordance with the present invention, it has been found that a group of copolymers that can be made by thermal- or catalytically initiated free-radical polymerization reactions are found suitable for the preparation of products having desirable pour depressing properties. These polymeric materials may be made by polymerizing a mixture of monomeric C_{10}–C_{22} alpha-olefins with ethylene. Accordingly, suitable alpha-olefins comprise, by way of example, 1-decene, 1-hendecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene.

The alpha-olefins which are suitably employed in the present invention may be obtained by any conventionally known means, e.g. by the catalytic dehydration of primary alcohols, pyrolysis of esters of primary alcohols, steam cracking of paraffins and de-oiled petrolatum and by growth of ethylene on aluminum trialkyls. These methods are conventionally known and, therefore, do not constitute any of the essence of the present invention.

The copolymers utilized herein may conveniently be prepared by the thermally initiated polymerization of the monomeric starting materials. It has been found that the yield and potency of these and other resulting polymeric materials are dependent on the selection of optimum temperature-time relationships in the polymerization reaction. Thus, the optimum conditions are found to be in a temperature range of 250°–350° C. for a reaction period of from 5 to 30 hours. At temperatures below 250° C. excessively long reaction times are required to effect satisfactory conversions. Under extreme conditions, i.e. higher than the above-defined range, the product quality falls rapidly. In the case of copolymers where ethylene is the comonomer, pressures in excess of 10,000 p.s.i.g. may be employed, in order to maintain most of the charge in the liquid phase. While superatmospheric pressures in excess of the autogenous pressure may be used, it is found that such pressures have little effect on the product performance.

In addition to the foregoing, it is found that the number of carbons of the alpha-olefin charged to the polymerization unit affects the characteristics of the resulting product. For example, it is found that an increase of the chain length from 1-decene to 1-hexadecene results in not only higher potency, but also somewhat higher product yield.

Polymerization can also be effected by any of the well-known free radical initiators. The polymerization is initiated and propagated by virtue of free-radicals which can be derived from the monomers themselves on simple heating of the monomeric mixture to a suitable temperature, or can be derived from added free-radical-supplying catalysts, especially the "per" compounds and the "azo" compounds, or can be derived by ultraviolet or other

irradiation of the reaction mixture with or without the presence of photosensitizers, e.g., organic disulfides. The examples set forth hereinafter describe "thermal" polymerizations in which the polymerization reaction was initiated merely by heating the monomeric mixture in the absence of any added catalyst. In many instances, however, it will be desired to add a suitable polymerization catalyst, in which case sufficient catalyst is employed to give a desired reaction rate. Suitable catalysts are of the free-radical-promoting type, principal among which are peroxide-type polymerization catalysts, and azo-type polymerization catalysts. Those skilled in the art are now fully familiar with a large number of peroxide-type polymerization catalysts and a suitable one can readily be chosen by simple trial. Such catalysts can be inorganic or organic, the latter having the general formula: R'ORR'', wherein R' is an organic radical and R'' is an organic radical or hydrogen. These compounds are broadly termed peroxides, and in a more specific sense are hydroperoxides when R'' is hydrogen. R' and R'' can be hydrocarbon radicals or organic radicals substituted with a great variety of substituents. By way of example, suitable peroxide-type catalysts include benzoyl peroxide, ditertiary butyl peroxide, tertiary butyl hydroperoxide, diacetyl peroxide, diethyl peroxycarbonate, 2-phenyl propane-2-hydroperoxide (known also as cumene hydroperoxide) among the organic peroxides; hydrogen peroxide, potassium persulfate, perborates and other "per" compounds among the inorganic peroxides. The azo-type polymerization catalysts are also well-known to those skilled in the art. These are characterized by the presence in the molecule of the group —N=N— bonded to one or two organic radicals, preferably at least one of the bonds being to a tertiary carbon atom. By way of example of suitable azo-type catalysts can be mentioned α,α'-azodiisobutyronitrile, p-bromobenzenediazonium fluoroborate, N - nitroso-p-bromoacetanilide, azomethane, phenyldiazonium halides, diazoaminobenzene, p-bromobenzenediazonium hydroxide, p-tolyldiazoaminobenzene. Also contemplated are the bis (perhalogenoalkyl) sulfones, bis(perhalogenoalkyl) sulfoxides, molecular oxygen and the like. The polymerization catalyst is used in small amounts, which are generally not in excess of one percent by weight based upon the monomeric material. A suitable quantity is often in the range of 0.05 to 0.5 percent by weight. An example of a peroxide initiated copolymerization of dodecene-1 and ethylene is given below.

Choice of a suitable temperature for the catalytically initiated polymerization will readily be made by those skilled in the art having been given the benefit of the present disclosure. In general, suitable temperatures will be found within the range of 125° C. to 200° C., although temperatures outside this range are not beyond the scope of the invention in its broadest aspects. As above, the time required for complete polymerization will depend not only upon the temperature but also upon the catalyst if any is employed, and the particular monomers employed.

In accordance with the present invention, the pour-depressants to which the present invention is directed are prepared by separating from the total polymerization product fractions boiling in the lubricating oil range thereby leaving a residual pour depressant having a molecular weight in excess of 1,000. Separation can be effected by conventional means such as vacuum distillation. In this operation, fractions boiling up to about 200° C. at .01 torr are removed overhead as distillate products.

The copolymers comprising the pour depressants of this invention consist essentially of random or block copolymers of the following units:

$$(CH_2-CH_2)_x\cdots\left(CH_2-\underset{R}{CH}\right)_y$$

where R is a straight chain alkyl group of from C_8 to C_{20}. The copolymer will comprise a major molar proportion of

ethylene and preferably will comprise about 1.1 to 30, more preferably 3 to 20, molar proportions of ethylene per mole proportion of the higher olefin, for example x is preferably 1.1 to 30, more preferably x is 3 to 20, while y is 1. The molecular weight of the polymer product utilized, in terms of number average, e.g. as determined by vapor-pressure osmometry or ebullioscope, is in excess of 1,000. Generally the number average molecular weight will range from 1,000 to 50,000, preferably 1,000 to 4,000, and most preferably from 2,000 to 3,000.

In a preferred embodiment of the present invention, the residue is subsequently subjected to dialysis. As employed herein, the term dialysis relates to the preferential diffusion of one or more lower molecular weight components, of a solution of hydrocarbons in a specific solvent through a semi-permeable membrane in the direction of a liquid phase consisting predominantly of solvent. In general, higher molecular weight components are found to diffuse very slowly or not at all while, lower molecular weight components in true solution diffuse rapidly. Accordingly, it has been found from dialysis experiments that the active pour depressant components of suitable molecular weight will not diffuse through a thin rubber membrane while the impotent, e.g. diluent oil, diffuses quite rapidly through said membrane. It is found, advantageously, that such dialysis can be effected at temperatures ranging from about 20 to 150° C. and preferably 30° to 125° C.

The copolymers of the instant invention are effective in the hydrocarbon oil composition in concentrations ranging from about .001 to 5.0 wt. percent, for example 0.02 to 2.0 wt. percent and preferably from 0.05 to 0.5 wt. percent based on the weight of oil.

In addition to the above-described copolymers, the hydrocarbon fuel oil compositions may be modified with other additives such as other pour point depressants, viscosity index improvers, corrosion inhibitors, extreme pressure additives, anti-oxidants and the like. Among such materials V.I. and pour point agents, e.g. high molecular weight polymers, e.g., "Acryloids"; chlorinated wax-naphthalene condensation products, isobutylene polymers, alkyl-styrene polymers; corrosion inhibitors, e.g. inorganic and organic nitrities, such as $NaNO_2$ or $LINO_2$ and diisopropyl ammonium nitrite or dicyclohexyl ammonium nitrite, metal organic phosphates, e.g., calcium or zinc dicyclohexylthiophosphate or methylcyclohexylthiophosphate; extreme pressure agents such as organic phosphites, phosphates and phosphonates, organic sulfides; anti-oxidants such as phenols and amines, e.g., octadecylamine, 2,6-ditertbutyl-4-methylphenol and the like.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and that the invention is not to be regarded as limited to any of the specific materials recited therein.

In the examples, the pour point tests were performed in accordance with ASTM method D–97. In this test the sample is maintained at a temperature of 115° F. or lower for at least 24 hours prior to the test. The sample is then cooled systematically under quiescent conditions and observed at intervals of 5° F. The pour point is the lowest temperature at which the oil flows when the container is tilted.

Example 1.—Thermal copolymer of ethylene and α-dodecene

A three liter reaction bomb was charged with:

One liter (752 gms., i.e., 4.5 moles) of freshly distilled dodecene-1, air was purged from the bomb with nitrogen, then pressured at room temperature to 2000 p.s.i.g. with ethylene. The bomb and contents were heated with rocking to 200° C.±10° C. over the course of 1½ hours during which time the pressure was held at a maximum of 10,000 p.s.i.g.±300 p.s.i.g. by bleeding off gas. The bomb was then heated at 300° C. for an additional 12 hours and

cooled to room temperature. Prior to cooling it was noted that the pressure had dropped from 10,000 ps.i.g. at 300° C. to 1500 p.s.i.g. at 300° C.

Excess gas was bled from the system and the raw product which weighed 1300 grams was distilled at reduced pressure. Subtracting the 752 grams of starting dodecene-1 from the 1300 grams of product shows that 548 grams, or 19.6 moles, of ethylene had combined with the 4.5 moles of dodecene-1, giving a molar ratio of 4.35 moles of ethylene per mole of dodecene-1 in the polymer. There was recovered overhead a light lubricating oil fraction boiling up to 145° C. at 0.05 torr (pot temp.=215° C.) which weighed 372 grams; a heavy lube distillate boiling up to 190° C. at 0.01 torr (pot temp. 300° C.) which weighed 342 grams and a bottoms of 575 grams.

The heavy lube distillate had a kin. vis. at 100° F. of 74.52, a kin. vis. at 210° F. of 10.48 and a pour point of −30° F.

The bottoms, which had a ebullioscopic molecular weight of 1027, was blended into a No. 2 heating oil at a concentration of 0.1 wt. percent and the pour points determined on the original and on the blended oil. Results were:

A.S.T.M. pour:	° F.
Original No. 2 heating oil	+5
No. 2 oil+0.1% bottoms	−20

Example 2

A quantity of the bottoms of Example 1 was dissolved in pentane and dialyzed at reflux temperature for 24 hours through a thin rubber membrane against pure pentane. Recovery of product which had not dialyzed, after removal of the pentane under reduced pressure, yielded a viscous material which had a molecular weight of 2100 when determined by vapor pressure osmometry and reduced the pour point of the above No. 2 heating oil to −55° F. when blended in the oil to a concentration of 0.1 wt. percent.

Example 3.—Peroxide initiated copolymer of dodecene-1 and ethylene

Using the same equipment as in Example 1, 752 grams of dodecene-1 was mixed with 5 grams of ditertbutyl peroxide, air purged from the system with nitrogen and the bomb pressured with ethylene to 2000 p.s.i.g. at room temperature. The bomb was heated to 160±10° C. and maintained at temperature for 5 hours, cooled and the light and heavy lube fractions taken overhead as in Example 1 by distillation under reduced pressure. The residue when dialyzed as in Example 1, showed for the undialyzed portion a molecular weight of 2000 by vapor pressure osmometry and reduced the pour point of the No. 2 heating oil to −75° F.

While the foregoing examples have illustrated this invention in detail, it should be realized that the present invention in its broadest aspects is not necessarily limited to the specific materials, reaction conditions, etc. as set forth therein.

What is claimed is:

1. A composition comprising a major amount of a hydrocarbon middle distillate fuel oil and a pour depressing amount of a pour depressant copolymer consisting essentially of about 1.1 to 30 molar proportions of ethylene per molar proportion of straight chain C_{10} to C_{22} alpha-olefin, said copolymer having a molecular weight of about 1,000 to 50,000.

2. A composition according to claim 1, wherein said pour depressing amount is about 0.001 to 5 wt. percent, said copolymer consisting essentially of 3 to 20 molar proportions of ethylene per molar proportion of said C_{10} to C_{22} alpha-olefin, and said molecular weight is about 1,000 to 4,000.

3. A composition according to claim 2, wherein said C_{10} to C_{22} alpha-olefin is dodecene-1.

4. A composition according to claim 3, wherein said mole ratio is about 4.35 of ethylene per mole of said dodecene-1.

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