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POUR POINT DEPRESSANT FOR MIDDLE DISTILLATES

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ABSTRACT OF THE DISCLOSURE

Petroleum distillate fuel oil containing as a pour point depressant polymer comprising ethylene and C_3 to C_{10} alpha olefin, which has been oxidized and then reduced, and having a molecular weight of about 500 to 49,000. The polymer can contain other olefin monomers.

The present invention is broadly concerned with an improved pour depressing additive for middle distillates and with its method of manufacture. The additive of the present invention in essence is a terpolymer or copolymer of ethylene that has been oxidized to form hydroperoxy materials followed by reduction to form reduced oxygenated compounds useful as additives for petroleum products. A preferred polymer is a terpolymer of ethylene, propylene and 5-methylene-2-norbornene, particularly the terpolymer which has been oxidized and reduced. The additives of the present invention are particularly effective when used in conjunction with an ethylene-vinyl acetate copolymer.

With the increase in the use of hydrocarbon fuels of all kinds, serious problems have arisen in areas frequently subjected to low temperatures in the cold test characteristics of fuels. Particularly, serious problems have been encountered with heating oils and diesel and jet fuels that have too high a pour point, resulting either in distributional 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 is not maintained, leading to equipment failures.

Also the low temperature properties of petroleum distillate fuels boiling in the range between about 250° and about 750° F. have attracted increasing attention in recent years because of the growth of market for such fuels in subarctic areas and because of the development of turbo-jet aircraft capable of operating at altitudes where temperatures of —50° F. or lower are encountered.

It is a still further object of the present invention to provide heating oils, diesel fuel oils, kerosenes and jet fuels having low pour points. Aviation turbo-jet fuels in which the polymers may be used normally boil between about 250° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL–F–5624C, MIL–F–25554A, MIL–F–25558A, and amendments thereto. Kerosenes and 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, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the polymers may be employed are described in detail in ASTM Specification D–975–53T and later versions of the same specification.

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, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitors, anti-static 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.

As pointed out, the present invention is concerned with an oxidized ethylene/propylene copolymer. The ethylene-propylene copolymer is of the linear type having a number average molecular weight in the range from about 500 to 49,000, preferably in the range of about 1,000 to 15,000. The amount of ethylene present as compared to the amount of propylene present is in the range from about 5 to 95 mole percent, the preferred range being from 20 to 80 mole percent ethylene.

In essence, the copolymer is manufactured by Ziegler-catalyzed solution copolymerization of ethylene and propylene gas to the rubbery copolymer. The Ziegler catalyst used generally consists of a transition metal halide such as Titanium tetrachloride, Vanadium tetrachloride or Vanadium oxytri chloride, and an aluminum alkyl compound such as aluminum triethyl or aluminum diethyl chloride.

The copolymer may have an inherent viscosity of about 1.5 to 3.5 decaliters per gram in decaline at 135° C. and are known in the art as ethylene-propylene rubbers. The additives of the present invention cannot be successfully manufactured by copolymerization of oxygen-containing compounds with 2-olefins. Such oxygen-containing compounds cannot be polymerized since they poison the catalyst.

The ethylene/propylene copolymer may be oxidized to form the hydroperoxy materials by any one of several methods. The copolymer may be oxidized in solution, or as a solid with an oxygen-containing gas with or without a free radical initiator such as peroxides, azo compounds or metal salts. An effective method of oxidizing the copolymer is to dissolve from about 1 to 20 weight percent in a hydrocarbon diluent such as heptane or benzene and to pass air or oxygen through the solution at the desired temperature until oxidation of the required level is reached. The type of solvent is not critical to the invention; however, some solvents may be used to advantage. The copolymer may also be oxidized as an emulsion or as a suspension in any fluid such as water. The solvent or suspending fluid need not be inert to oxidation under the conditions employed to oxidize the copolymer. The temperature and pressure conditions will vary with the type of solvent used for oxidation. Temperatures in the range of about 45° C. to 250° C. and pressures in the range of about 0.5 to 100 atmospheres are satisfactory. The oxygen-containing gas is preferably passed through the polymer solution or suspension in excess. Free radical initiators such as peroxides, hydroperoxides, azo compounds, diazo compounds, peresters, peracids, ozone, hydrogen peroxide, disulfides, persulfides, hydrozines may be used in concentrations of about 0.001 weight percent and higher. Metal salts well known in the art may also be used to promote the oxidation. Such compounds contain transition metal ions that are easily oxidized and reduced. Examples are iron, cobalt, vanadium, cerium or manganese salts. Soluble salts such as acetylacetonates or tallates of the metals are preferred for the hydrocarbon solutions, while water-soluble salts such as chlorides are preferred for the emulsions.

The oxidized material is then reduced as follows: the oxidized material, while still in solution, or suspension or as a solid, is contacted with a reducing agent. Such a reducing agent should be capable of reaction with oxidized groups on the polymer. Applicable methods include the reaction with sodium sulphite, lithium aluminum

hydride, sodium borohydride, tertiary phosphines, triethyl phosphite, hydrazine hydrate, aluminum amalgam, alkaline sodium sulphide, hydriodic acid and zine dustacetic acid. Reaction with acids or alkali as well as thermal treatment may also remove active oxygen-containing groups from the oxidized polymer. Removal of these groups is desirable, since the polymer is less reactive after reduction and may be conveniently stored without further reaction taking place.

The product produced by the oxidation procedure is a soluble polymer of lower molecular weight than the starting copolymer. The molecular weight depends on the extent and conditions employed during the oxidation. The number average molecular weight is in the range from about 500 to 49,000, wherein the amount of active oxygen before reduction is in the range from about 2 to 500 milliequivalents per 100 g. of polymer as determined iodometrically. Examination of the polymers by infrared spectroscopy shows that oxygenated groups are introduced on the polymer during oxidation and are retained during reduction. No active oxygen in the form of peroxides, hydroperoxides, or peracids is detected after reduction by any of the preferred methods.

The polymer is recovered from solution by steam distillation of the solvent or by precipitation with an acetone-methanol mixture (3:1) and dried in a vacuum.

As pointed out heretofore, the preferred polymer is a terpolymer of ethylene/propylene containing a third unsaturated monomer, such as cyclopentadiene, methylene norbornene, hexadiene. The amount of third monomer present is in the range from about 0.5 to 20 mole percent, preferably about 1 to 7 mole percent based on the total amount of ethylene and propylene present. Other satisfactory third unsaturated monomers are bicyclic, alicyclic and aliphatic nonconjugated diolefins having from about 6 to 15 carbon atoms such as dicyclopentadiene, tetrahydroindene, 5-vinyl-2-norbornene, 2-methyl-norbornadiene, 2,4-dimethyl-2,7-octadiene, 3 methallyl cyclopentane, tetradecene, and 3 (2-methyl-1-propene) cyclopentene.

The methods of preparation of the above-named terpolymers are well known to the art and are described in U.S. 3,000,866, U.S. 3,093,621, and U.S. 2,933,480.

The terpolymer may be oxidized by substantially the same methods used for the copolymer and previously described herein. The same solvents may be employed and the same temperatures and pressures are preferred. The choice of free radical initiator is more critical with the terpolymer than with the copolymer. Ozone cannot be conveniently used at low temperatures. The product obtained from this treatment is insoluble in all solvents and is not useful as an additive of the present invention. Azo compounds, such as azobisisobutryonitrile, are very effective at initiating the oxidation and any oxygen-containing gas may be used.

The terpolymer is reduced by any of the methods described for the copolymer or methods well known in the art for reduction of active oxygen compounds.

Prior to reduction, the terpolymer will contain from about 2 to 500 milliequivalents of active oxygen per 100 gram of terpolymer. The terpolymer will also be in the molecular weight range of about 500 to 49,000 number average molecular weight. After reduction the terpolymer will contain oxygen-containing groups as determined by infrared spectroscopy of the polymer sample and have substantially the same molecular weight as before reduction. The preferred range of oxidation is from about 5 to 350 milliequivalents, i.e. millimoles, of OOH/100 g. polymer as determined by the method described by A. G. Davies in Organic Peroxides, Butterworths, London (1961).

The amount of additive used based upon the base oil is in the range from .005 to 0.25% by weight, preferably in the range from .01 to .15% by weight.

As pointed out heretofore, the additives of the present invention are particularly effective when used in conjunction with an ethylene/vinyl acetate copolymer. These ethylene/vinyl acetate copolymers are described in U.S. Patent No. 3,048,479 filed Aug. 7, 1962, entitled, "Ethylene-Vinyl Ester Pour Depressant for Middle Distillates"; inventors: Stephan Ilnyckyj and Charles B. Rupar.

In essence, these polymers contain from about 1 to 40% by weight of the vinyl acetate based upon the ethylene, preferably from about 15 to 30% of vinyl acetate based upon the ethylene. The molecular weights of the ethylene/vinyl acetate copolymer are critical and should be in the range from about 1,000 to 3,000, preferably, in the range from about 1,500 to 2,200. The molecular weights are determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)). The amount of ethylene/vinyl acetate copolymer used in conjunction with the ethylene/propylene oxidized and reduced polymer is in the range from about .01 to .1, preferably in the range from about .04 to .06.

The present invention may be more readily understood by the following examples illustrating embodiments of the same.

Example 1

An ethylene/propylene copolymer having an inherent viscosity of about 2.5 decaliters per gram in decalin at 135° C. and containing about 50 weight percent ethylene was prepared in hexane by polymerizing ethylene and propylene using a Ziegler catalyst system. 50 grams of the copolymer was dissolved in 2 liters of n-heptane and oxidized by passing 200 ml. of oxygen gas containing 10 mg. of ozone per liter of oxygen through the solution. The pressure was maintained at about 1 atmosphere and the temperature at about 70° C. After 5½ hours of oxidation the polymer solution was contacted with an aqueous solution of sodium sulphite for 1 hour. The polymer solution was recovered and washed with distilled water 3 times. The polymer was recovered by steam distillation of the n-heptane followed by vacuum drying at 40° C. for 20 hours. Prior to reduction with the sodium sulphite, the polymer was found to contain about 42 milliequivalents i.e. millimoles, of active oxygen per 100 grams and an inherent viscosity of 0.58 decaliters per gram. 50 grams of the polymer were recovered after reaction.

The copolymer and the reduced oxidized copolymer were added to a base oil of approximately 50/50 volume percent straight-run and catalytically-cracked stocks from a mixture of Venezuela and Gulf Coast Crudes.

Base Oil Inspections

Cloud Pt.	°F.	+4
Pour Pt.	°F.	−5
Aniline Pt.	°F.	132
Viscosity	°F.	34.2505/100
API Gravity		33.0
Density	per ml. at 60° F.	0.8604

The results were as follows:

Additive	Millimoles OOH/100 g.	Degrees of Depression by 0.1% Additive
Ethylene-Propylene Copolymer (unoxidized)	0	0
Oxidized Ethylene-Propylene Copolymer	42	65

Example 2

In another test, a terpolymer as described[1] was prepared and then oxidized with the following results:

Additive:	Degrees of depression of base oil by 0.1 weight percent
5-methylene-2-norborene	40
As above but oxidized to 26 millimoles OOH/100 g.	55

[1] Ethylene-propylene-methylenenorbornene terpolymer composition.
Ethylene: 54 weight percent; MNB: 3.5 weight percent; Mooney Visc. @ 260° F.
Large rotor=60; Inherent Visc. 2.9 (Decalin 135° C.).

1,500 ml. of a solution of terpolymer (5 grams per 100 cc. solvent) in n-heptane cement was hydroperoxidized using 2.10 g. of azobisisobutryonitrile and excess oxygen at 80° C. for 2.5 hours. A sample of the cement was worked up and analyzed for hydroperoxide content: found 26.64 millimoles/100 g. polymer. To the remaining polymer cement in the reactor (1,000 ml.) 40 ml. of 1 molar triethyl phosphite were added and the solution was stirred for 3 hours at 75° C. The cement was clear when cool. The polymer was precipitated from solution with acetone and then vacuum dried. The kinematic viscosity of the polymer in decalin at 135° was 0.825. Solvent visc. 0.699; polymer conc. 0.905 g./ml. Decalin.

Example 3

In another test, the polymers of the present invention were used in conjunction with the ethylene/vinyl acetate copolymer as described with the following results.

A number of copolymers [1] and terpolymers [1] show appreciable activity as middle distillate pour depressants. Several of these polymers also function as flow improvers in middle distillate of a 660° FBP. This fuel, when treated with .03 weight percent of an ethylene/vinyl acetate copolymer, has a cloud point of +18° and a pour point of −20°, but plugs at +15° in the Flow and Plugging Test. This fuel also plugs somewhere between +15° and −10° when treated with .06 weight percent of the ethylene/vinyl acetate copolymer. However, this same fuel, when treated with .02 weight percent of the ethylene/vinyl acetate copolymer and with .01 weight percent of any of the polymers listed below does not plug at any temperature from +15° to −10°.

In other tests the ethylene/propylene copolymer of the present invention was reacted with a third monomer (preferably of diene) with the results as follows:

Example 4

Third Monomer	Degrees of depression of base oil* by 0.1% additive
3% methylene norbornene	40
11% cyclopentadiene	45
3.6% 1,4-hexadiene	35
4% methylene norbornene	45
4.5% methylene norbornene	60
2.0% tetradecene–1	50

*Approximately 50/50 volume percent straight-run and catalytically-cracked stocks from a mixture of Venezuela and Gulf Coast Crudes.

Cloud Pt.	°F.	+4
Pour Pt.	°F.	−5
Aniline Pt.	°F.	132
Viscosity	SUS/100° F.	34.2
API gravity		33.0
Density	g./ml. at 60° F.	0.860

Thus the terpolymers are comprised of ethylene, a C_3 to C_{10} alpha olefin, and a third monomer, preferably a nonconjugated diolefin. Representative examples of the useful C_3 to C_{10} alpha olefins are: propylene; 1-butene, 4-methyl-1-pentene; 1-pentene, 1-benzene, 1-heptene, 5-methyl - 1 - nonene; 5,5 - dimethyl - 1 - octene; 4-methyl-1 - hexene; 4,4 - dimethyl - 1 - pentene; 5 - methyl-1-hexene; 4 - methyl - 1 - heptene, 4,4 - dimethyl - 1 - hexene; and 5,6,6 - trimethyl - 1 - heptene, with propylene being the preferred alpha olefin. Straight-chain and cyclic nonconjugated hydrocarbon diolefins or monoolefins having from 6 to 15 carbon atoms such as dicyclopentadiene; tetrahydroindene; 5 - methylene - 2 - norbornene; 5-vinyl-2 - norbornene; 5(3′ - butene) - 2 - norbornene; tetradecene - 1; 2 - methyl - norbornadiene; 1,4 - hexadiene; 3 - methallylcyclopentene and 3(2′ - methyl - 1 - propene) - cyclopentene are suitable as the third component of the terpolymer.

What is claimed is:

1. A petroleum distillate fuel composition comprising a major amount of a petroleum distillate fuel boiling between about 250° and 750° F. and about .005 to .25 weight percent of an oil-soluble pour depressant having a number average molecular weight of about 1000 to 15,000 prepared by oxidizing an ethylene-propylene rubbery copolymer containing about 5 to 95 mole percent ethylene, to about 2 to 500 milliequivalents of oxygen per 100 grams of said rubbery copolymer, and then reducing said oxidized rubbery copolymer to eliminate active oxygen, wherein said rubbery copolymer is linear and is prepared by solution copolymerization using a catalyst system of a transition metal halide and an aluminum alkyl compound, wherein said rubbery copolymer has an inherent viscosity of about 1.5 to 3.5 decaliters per gram in Decaline.

2. A composition as defined by claim 1, wherein the amount of ethylene present in said copolymer is about 20 to 80 mole percent, and the balance of said copolymer is propylene.

3. A composition as defined by claim 1, wherein said copolymer also contains about 0.5 to 20 mole percent, based on the total amount of ethylene and propylene present, of a third monomer which is a nonconjugated diolefin having about 10 to 15 carbon atoms, and the balance of said copolymer is propylene.

4. A composition as defined by claim 3, wherein said third monomer is 5 - methylene - 2 - norbornene present in a concentration of about 1 to 7 mole percent based upon the total amount of ethylene and propylene present.

5. A composition as defined by claim 3, wherein a pour-depressing copolymer of ethylene and vinyl acetate is present in a concentration in the range from about .01 to .1% by weight, said copolymer comprising a major amount of ethylene and 1 to 40 weight percent of vinyl acetate and being characterized by having a molecular weight in the range from about 1000 to 3000.

6. A petroleum distillate fuel oil having a boiling range between about 250° and 750° F. containing about .005 to 0.25 weight percent of a pour depressant having a number average molecular weight of 1000 to 15,000 prepared by oxidizing a rubbery terpolymer of about 20 to 80 mole percent ethylene, about .5 to 20 mole percent of nonconjugated hydrocarbon olefin selected from the group consisting of straight chain and cyclic nonconjugated hydrocarbon diolefins of 6 to 15 carbon atoms, and the balance of a C_3 to C_{10} alpha olefin, which terpolymer has been oxidized to about 2 to 500 milliequivalents of active oxygen per 100 grams of said polymer and then reduced to eliminate free oxygen, wherein said terpolymer is prepared by solution copolymerization using a catalyst system of a transition metal halide and an aluminum alkyl compound, wherein said terpolymer has an inherent viscosity of about 1.5 to 3.5 decaliters per gram in Decaline.

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[1] Ethylene/propylene copolymer oxidized to 80 mm. OOH/100 g. and then reduced as described.
Ethylene/propylene/3% methylene norbornene oxidized to 25 mm. OOH/100 g. and reduced as described.
Ethylene/propylene/4% methylene norbornene oxidized to 300 mm. OOH/100 g. as described.