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WAX CRYSTAL MODIFIERS FOR
HYDROCARBON OILS

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16 Claims

ABSTRACT OF THE DISCLOSURE

The present invention is concerned with wax crystal modifiers, e.g. pour depressant additives, for hydrocarbon oil and with methods for their manufacture. The additives of the present invention in essence are copolymers or polyketones derived from the free radical catalysis of the polymerization of an olefin and carbon monoxide, and the invention includes the use of such products as wax crystal modifiers, such as pour depressants, fluidity of flow improvers, dewaxing aids, etc. for lubricating oil, residual oil, crude oil, middle distillate oil, etc.

This application is a continuation-in-part of Ser. No. 659,817, filed Aug. 10, 1967 which, in turn, was a streamlined continuation of Ser. No. 423,860 filed Jan. 6, 1965, both now abandoned.

The copolymers of the invention are particularly useful in fuels. Thus, with the increase in the use of hydrocarbon fuels of all kinds, serious problems have arisen in areas frequently subjected to low temperatures with respect to those properties of the fuels which may be designated as the cold test characteristics. 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 markets 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.

One main aspect of the present invention is to utilize an additive which is produced by the copolymerization of an olefin, preferably ethylene because of its low cost, and carbon monoxide. Also, while as heretofore indicated, these additives are particularly effective for middle distillates and lighter oils, they may also find utility as wax crystal modifiers in residual fuels, lubricants, crudes, and as dewaxing aids in lube stocks, etc.

Another aspect of the present invention is 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° F. and about 550° F. and are used in both military and civilian aircraft. Such fuels are more 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° F. 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. In general, these middle distillate oils boil in the range from about 250° to 750° F.

Another aspect of the invention is to provide flow improvers for residual oils boiling above 650° and having a flow point above 75°, such as the residuum of a North African crude, e.g. Brega or Zelten residuum which contains about 20 weight percent wax. This wax includes waxes of relatively high molecular weight, i.e. from about C₃₀-C₅₀ paraffins which gives rise to a number of the problems in the transporting, storing, etc. of this kind of heavy oil.

The above and other aspects of the invention will become clear from the following description and examples.

The wax crystal modifiers of the invention are in effect copolymer polyketones derived from the free radical catalyzed polymerization of olefin and carbon monoxide, under pressure and at elevated temperature.

While a single olefin can be used, mixtures of olefin with CO may also be used, and mixtures of monoolefin with diolefin and CO may be used to yield products suitable as pour depressants. It is preferable that olefins of C₄ or higher be alpha olefins thus possessing terminal unsaturation. The olefins most suitable are those containing from 2 to 30, e.g. 2 to 25, and preferably 2 to 10 carbon atoms. Examples of such olefins include ethylene, propylene, 1-butene, 1-pentene, 1-dodecene, 1-octadecene, eicosene, etc.

Various other monomers, particularly unsaturated esters, in minor weight amounts can also be copolymerized with the olefin and carbon monoxide. These unsaturated esters are believed to enter the polymer by polymerizing with the olefin rather than with the carbon monoxide. The carbon monoxide, on the other hand, is believed to polymerize primarily with the olefin, and tends to polymerize therewith in a 1:1 molar ratio. However, by having larger molar amounts of the olefin present relative to the carbon monoxide, then blocks of polyolefins will form in the polymer chain to form a product having more than a 1:1 ratio of olefin to carbon monoxide.

The unsaturated esters mentioned above include unsaturated mono and diesters of the general formula:



wherein R₁ is hydrogen or methyl; R₂ is a —OOCR₄ or —COOR₄ group wherein R₄ is hydrogen or a C₁ to C₁₆, preferably a C₁ or C₄, straight or branched chain alkyl group; and R₃ is hydrogen or —COOR₄. The monomer, when R₁ and R₃ are hydrogen and R₂ is —OOCR₄ includes vinyl alcohol esters of C₂ to C₁₇ monocarboxylic acids, preferably C₂ to C₅ monocarboxylic acids. Examples of such esters include vinyl acetate, vinyl isobutyrate, vinyl laurate, vinyl myristate, vinyl palmitate, etc. When R₂ is —COOR₄, such esters include methyl acrylate, methyl methacrylate, lauryl acrylate, palmityl alcohol ester of alpha-methyl-acrylic acid, C₁₃ Oxo alcohol esters of methacrylic acid, etc. Examples of monomers where R₁ is hydrogen and R₂ and R₃ are —COOR₄ groups, include mono and di-esters of unsaturated dicarboxylic acids such as: mono C₁₃ Oxo fumarate, di-C₁₃ Oxo fumarate, di-isopropyl maleate; di-lauryl fumarate; ethyl methyl fumarate; etc.

Generally, the molecular weights of the polymers vary in the range from about 500 to 50,000; usually 500 to 5,000, and preferably in the range from about 1,000 to 3,000. The molecular weights are number average molec-

ular weights, for example, molecular weights determined by K. Rast's method (Ber. 55, 1051, 3727 (1922)) or by Vapor Phase Osmometry, for example by using a Mechrolab Vapor Phase Osmometer Model 310A.

In general, the polymerization can be carried out as follows: Solvent, olefin, carbon monoxide and a portion of the unsaturated ester, if any, e.g., 0-50, preferably 10-30 wt. percent, of the total amount of unsaturated ester used in the batch, are charged to a stainless steel pressure vessel which is equipped with a stirrer. The temperature of the pressure vessel is then brought to the desired reaction temperature and pressure. Then free radical initiator, preferably dissolved in solvent so that it can be pumped, and additional amounts of any unsaturated ester are added to the vessel continuously, or at least periodically, during the reaction time, which continuous addition gives a more homogeneous copolymer product as compared to adding all the unsaturated ester at the beginning of the reaction. Also during this reaction time, as carbon monoxide and olefin is consumed in the polymerization reaction, additional carbon monoxide and olefin may be supplied through a pressure controlling regulator so as to maintain the desired reaction pressure fairly constant at all times. Following the completion of the reaction, the liquid phase of the pressure vessel is distilled to remove the solvent and other volatile constituents of the reacted mixture, leaving the polymer as residue.

While the above illustrates one method, other methods can be used, depending partly upon whether the olefin is normally gaseous or liquid. For example, using ethylene as the olefin, a number of polymerizations were carried out by premixing the ethylene and CO in the desired ratios and feeding this mixture to the reactor in order to maintain the desired pressure. On the other hand, using a liquid olefin such as tetradecene, all of the tetradecene can be initially charged into the reactor and no solvent at all need be used, and then CO and free radical initiator can be continuously added to the reactor until the reaction is completed. Or, all the free radical initiator can be added initially. Still other variations are possible. Generally, those methods which tend to maintain the concentrations of monomers and initiator as constant as possible in the reactor are favored since these methods give a more homogenous product.

Usually, based upon 100 parts by weight of polymer to be produced, then normally about 50 to 1200 parts by weight of solvent, and about 1 to 20 parts by weight of a free radical initiator will be used. However, in some cases the olefin, if liquid, such as tetradecene, can be used to furnish the liquid medium and no other solvent need be added.

Usually, however, a solvent will be used. The solvent can be any non-reactive organic solvent for furnishing a liquid phase reaction which will not poison the catalyst or otherwise interfere with the reaction, and preferably is a hydrocarbon solvent such as benzene, cyclohexane, and hexane.

The temperature used during the reaction will be in the range of 120 to 400° F., e.g. 120 to 350° F., preferably 120 to 275° F.

Free radical initiators or promoters will include the acyl peroxides of C₂ to C₁₈, branched or unbranched, carboxylic acids such as di-acetyl peroxide; dipropionyl peroxide; di-pelargonyl peroxide; di-lauroyl peroxide, etc. The lower peroxides such as di-acetyl and di-propionyl peroxide are less preferred because they are shock sensitive, and as a result the higher peroxides such as di-lauroyl peroxide are more preferred. Other initiators include various azo free radical initiators such as azodiisobutyronitrile; azobis - 2-methylheptonitrile and azobis-2-methylvaleronitrile. Still other examples of initiators are di-t-butyl peroxide, t-butyl perbenzoate and di-benzyl peroxide.

The pressure employed can range between 200 to 30,000 p.s.i.g. However, relatively moderate pressures of 200 to

about 15,000, and preferably 1,000 to 6,000 p.s.i.g. will generally suffice. In general, the pressure should be at least sufficient to maintain a liquid phase medium under the reaction conditions, and to maintain the desired concentration of carbon monoxide in solution.

The time of reaction will depend upon, and is inter-related to, the temperature of the reaction, the choice of catalyst, and the pressure employed. In general, however ½ to 10, usually 2 to 5 hours will complete the desired reaction.

The amount of additive used may vary appreciably depending upon the base stock but will generally be in the range of .001 to 2.0 wt. percent, based on the weight of oil to be treated. Usually, in a middle distillate the amount of additive added is in the range of about .005 to .75 percent by weight, preferably in the range from about .05 to .10 percent by weight. Usually, when the additive is used in a residual fuel, or crude, or lubricating oil, or as a dewaxing aid, the amount of additive is in the range from about .005 to 1.5 percent by weight, preferably in the range from about .05 to 1.0, e.g. .2 to .9 percent by weight.

The polymers of the invention may be used alone as the sole oil additive, or in combination with other oil additives such as other pour depressants or dewaxing aids; corrosion inhibitors; antioxidants; sludge inhibitors; etc.

The invention will be further understood by reference to the following examples which include preferred embodiments of the invention.

EXAMPLE I

A copolymer was produced from a mixture of 94 percent ethylene and 6 percent carbon monoxide by weight using 4 grams di-tertiary-butyl peroxide in 150 ml. cyclohexane in a 1 liter bomb maintained at 145° C. for 5 hours and a pressure of 3,000 to 4,000 p.s.i.g. After evaporation of the cyclohexane diluent, there was obtained 173 grams of a white, waxy solid copolymer having an average molecular weight of about 1,867. The polymer contained about 6.7 percent by weight of carbon monoxide.

The polymer was fractionated into products with varying carbon monoxide content by continuous extraction with solvents of varying polarity in a Soxhlet extraction which had been fitted with a rubber finger cot in place of the usual extraction cup. The following Table I shows the level of carbon monoxide in each of these fractions. Potencies of these polymers as pour depressants in a typical heating oil are tabulated in Table I when using 0.1 percent by weight of the additive in the base oil.

TABLE I

Fraction	ASTM Pour Point of Blends, °F	Percent CO
Reference Base Oil 1	-5	
Total Polymer (crude)	-30	6.7
Isocetane solubles	-20	
Benzene solubles	-30	17.5
Acetone solubles	-25	13.2
Isocetane-Isopropyl alcohol solubles	-10	13.4
Isopropyl alcohol solubles	-10	8.8

¹ Typical middle distillate heating oil consisting of approximately 50 volume percent straight run and 50 volume percent catalytically cracked stocks from a mixture of Venezuela and Gulf Coast crudes, and boiling in the range of 340° to 636° F. Typical inspections on this base oil are as follows:

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

EXAMPLE II

A 2-liter stirred reactor was charged with about 1200 ml. benzene as solvent, heated to 110° C., and pressured to 2000 p.s.i.g. with a mixture consisting of 98.85

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wt. percent ethylene and 1.15 wt. percent carbon monoxide. This mixture was made by charging the aforesaid percentages of ethylene and carbon monoxide to a storage tank, from which tank the mixture was fed to the reactor through a regulating system set to maintain 2000 p.s.i.g. $\pm$ 50 p.s.i.g. pressure. Then a solution consisting of about 23 wt. percent di-lauroyl peroxide (DLP) in 73 wt. percent benzene as solvent, was pumped into the reactor continuously over four hours, until a total of 16 grams of di-lauroyl peroxide had been added. The reaction conditions of 110° C. and 2000 p.s.i.g. were maintained for another 0.25 hour after the peroxide addition ceased in order to soak the reaction mixture to ensure a more complete reaction. The reactor was depressurized and the contents blown with nitrogen while heating on a steam bath to give a polymer product as the residue which contained 4.7 wt. percent CO and 95.3 wt. percent ethylene, and had a number average molecular weight of 2,650 as measured by osmometry.

EXAMPLES III TO X

These examples were carried out in a manner similar to that of Example II with minor variations in temperature, pressure, initiator, amount of initiator, time ratio of monomers, etc.

The reaction conditions of Examples II to X, and characteristics of the polymers produced thereby are summarized in Table II, which follows.

TABLE II.—PREPARATION OF ETHYLENE/CARBON MONOXIDE COPOLYMERS

	Temp., °C.	Press., p.s.i.g.	Gm. Initiator ¹	Reaction Time, Hrs.		Mole percent CO in—		Copolymer, Mol. Wt.	Yield, Gm.
				Add Initiator	Total	Reactants	Product		
Example:									
II.....	110	2,000	16 gm. DLP.....	4.0	4.25	1.15	4.7	2,650	158
III.....	110	1,000	16 gm. DLP.....	4.0	4.25	2.77	5.7	1,460	92
IV.....	110	1,100	16 gm. DLP.....	4.0	4.00	2.63	8.1	1,010	108
V.....	150	2,000	26 gm. DTBP.....	4.0	4.50	9.7	10.0	1,750	432
VI.....	110	6,000	10 gm. DLP.....	2.5	2.50	1.53	11.8	11,200	147
VII.....	110	1,000	8 gm. DLP.....	2.0	2.25	3.23	12.0	1,650	75
VIII.....	150	2,000	12 gm. DTBP.....	2.0	5.00	24.2	13.6	2,840	421
IX.....	150	4,000	12 gm. DTBP.....	2.0	5.00	24.2	15.5	3,435	687
X.....	150	1,150	20 gm. DTBP.....	3.0	3.50	9.7	19.5	2,520	432

¹ DLP=di-lauroyl peroxide; DTBP=di-tert-butyl peroxide.

All the reactions of Table II were carried out in 1200 ml. of benzene as solvent. The higher yields of polymer occurred at the 150° C. temperature, while use of 110° C. resulted in much smaller yields.

EXAMPLE XI

500 grams of n-tetradecene-1 was added to a one liter reactor along with 15 gm. of di-tert-butyl peroxide as the initiator. No solvent was added. The reactor was heated to 135° C. and CO was pressured in to give a pressure of 3000 p.s.i.g. After 24 hours at said temperature and pressure the reactor was depressurized and the reactor contents were distilled under a pressure of 1 mm. Hg to give a residue of 135 gm. of polymer consisting of .5 wt. percent CO and 99½ wt. percent tetradecene, or a mole ratio of 28.6 moles of tetradecene per mole of CO. The polymer had an average molecular weight of 1360.

EXAMPLE XII

A copolymer of ethylene, n-tetradecene-1, and carbon monoxide was prepared by charging a 2-liter stirred reactor with 1200 ml. benzene as solvent and 90 gm. of n-

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tetradecene-1. The reactor was heated to 150° C. and a premixed mixture of CO and ethylene, containing 14.1 wt. percent CO and 85.9 wt. percent ethylene was pressured into the reactor to give a pressure of 2000 p.s.i.g. 20 gm. of di-tert. butyl peroxide in a benzene solution was added over 2¼ hours, after which the reaction temperature and pressure were maintained for an additional ¼ hour. The reactor was depressurized and the reaction was distilled under 1 mm. Hg pressure to give 419 gm. of polymer having a molecular weight by osmometry of 910 and containing 6.9 wt. percent CO.

EXAMPLE XIII

This example was carried out exactly as that of Example XII except that the pressure was 3000 p.s.i.g., 13 gr. of di-tert-butyl peroxide was added over 2¼ hours, and 175 gm. of n-tetradecene-1 was added along with the peroxide over 2¼ hours. No tetradecene was added initially. 519 gm. of polymer was obtained having a mol wt. of 1230 and containing 9.6 wt. percent CO.

The various polymers of the preceding examples were tested for pour depression in the following base oils.

	Middle Distillate Oil	
	A	B
Cloud Point, ° F.....	+4	+25
Pour Point, ° F.....	0	+20
Density, g./ml. at 25° C.....	0.853	0.8622
Viscosity, cs. at 100° F.....	2.438	3.11
Aniline Point, ° F.....	132.0	135
Distillation, ° F.:		
Initial Boiling Point.....	340	370
5% Boiling Point.....	403	415
50% Boiling Point.....	497	531
95% Boiling Point.....	618	632
Final Boiling Point (97%).....	636	
Final Boiling Point (99%).....		644
Heavy Lubricant, Oil C:		
Pour Point, ° F.....		+30
Viscosity, SUS at 100° F.....		554
Viscosity, SUS at 210° F.....		67.5
Viscosity Index.....		101
Crude Oil, Oil D (Raccoon Bend):		
Pour Point, ° F.....		+70
Viscosity, cs. at 122° F.....		5.732
Wt. Percent Carbon.....		86.47
Wt. Percent Hydrogen.....		13.10
Residual Fuel Oil (Brega), Oil E:		
Pour Point, ° F.....		+110
Viscosity, cs. at 122° F.....		325.52
Wt. Percent Carbon.....		86.57
Wt. Percent Hydrogen.....		12.73

The following tables show the reduction in ASTM pour point of oils A to E when mixed with various polymers previously described.

TABLE III.—POUR DEPRESSANT ACTION OF CARBON MONOXIDE COPOLYMERS

Polymers of Example	Oil	Wt. Percent Copolymer	ASTM Pour Point, ° F.
	A	0.00	0
	B	0.00	+20
II-----	B	0.10	+5
III-----	B	0.10	0
IV-----	B	0.10	+5
V-----	A	0.02	-10
VI-----	B	0.10	+10
VII-----	B	0.10	-20
VIII-----	A	0.02	-5
IX-----	A	0.02	-10
X-----	A	0.02	-5
XI-----	A	0.02	-10
XII-----	A	0.02	-10
XIII-----	A	0.02	-15
	C	0.00	+30
VI-----	C	0.05	+20
VI-----	C	0.10	+10
VI-----	C	0.30	0
VII-----	C	0.10	+20
VII-----	C	0.30	+15
VII-----	C	0.00	+70
IV-----	D	0.05	+50
	E	0.00	+110
VI-----	E	0.05	+95

As seen by Table III, copolymers of carbon monoxide and olefins form useful polymers which can be used as hydrocarbon oil additives. In terms of weight percent, polymers are included wherein the amount of olefin plus any minor amounts, e.g. 0 to 30 wt. percent of unsaturated esters used, as compared to the carbon monoxide may vary in the range from about 70 percent to 99.5 percent by weight, the remainder being carbon monoxide. A preferred polymer contains an amount of olefin in the range from about 80 percent to 95 percent by weight as compared to 20 percent to 5 percent by weight of the carbon monoxide. All of said weight percent are based on the weight of total polymer. As an example of a terpolymer containing an unsaturated ester, a polymer can be prepared by the general method of Example V, but adding 10 grams of vinyl acetate to the reactor along with the solvent so as to form polymers of ethylene, CO, and vinyl acetate. Or instead of using vinyl acetate, 10 grams of isobutyl methacrylate can be added to the reactor either initially, or by slow addition over the course of the reaction.

In terms of molar ratio: about 0.5 to 40, e.g. .5 to 20, molar proportion of alpha olefin will be used per molar proportion of carbon monoxide.

What is claimed is:

1. A hydrocarbon oil composition comprising a major amount of hydrocarbon oil and about 0.001 to 2.0 wt. percent of a copolymer comprising a major weight proportion of C₂ to C₃₀ alpha olefin and carbon monoxide in a relative molar ratio of about 0.5 to 40 molar proportion of said alpha olefin per molar proportion of carbon monoxide; said copolymer having a molecular weight in the range of 500 to 50,000.

2. A composition according to claim 1, wherein said polymer includes 0 to 30 wt. percent of an unsaturated ester of the formula:



wherein: R₁ is hydrogen or methyl; R₂ is —OOCR₄ or —COOR₄, wherein R₄ is hydrogen or a C₁ to C₁₆ alkyl group; and R₃ is hydrogen or —COOR₄.

3. A composition according to claim 2, wherein said ester is a vinyl alcohol ester of C₂ to C₁₇ monocarboxylic acid.

4. A composition according to claim 3, wherein said ester is vinyl acetate.

5. A composition according to claim 2, wherein said ester is isobutyl methacrylate.

6. A composition according to claim 1, wherein said oil is a residual oil.

7. A composition according to claim 1, wherein said oil is a distillate oil.

8. A composition according to claim 1, wherein said oil is a crude oil.

9. A composition according to claim 1, wherein said oil is a lubricating oil.

10. A hydrocarbon oil of improved pour which comprises a major amount of petroleum distillate fuel having a boiling range between about 250° F. and about 750° F. which has been improved with respect to pour point by the incorporation therein of a pour depressing effective amount in the range from about .005 to .75 percent by weight of a polyketone copolymer of 0.05 to 40 molar proportion of C₂ to C₂₅ alpha monoolefin per molar proportion of carbon monoxide; said copolymer having a molecular weight in the range from about 500 to 5,000.

11. An oil as defined by claim 10, wherein said olefin is ethylene.

12. An oil according to claim 10, wherein said olefin is n-tetradecene-1.

13. An oil composition according to claim 10, wherein said olefin is a mixture of ethylene and n-tetradecene-1.

14. An oil as defined by claim 10, wherein said copolymer has a molecular weight in the range from about 1,000 to 3,000 and wherein said copolymer contains from about 5 to 20 percent by weight of carbon monoxide.

15. A hydrocarbon oil composition comprising a major amount of hydrocarbon oil and about .005 to 1.5 wt. percent of a polyketone consisting essentially of 70 to 99.5 wt. percent ethylene and 3 to 30 wt. percent carbon monoxide, said polymer having a number average molecular weight in the range of 500 to 50,000 and depressing the pour point of said oil.

16. Composition as defined by claim 15, wherein said polymer has a molecular weight in the range from about 1,000 to 3,000 and contains from about 5 to 20 wt. percent carbon monoxide.

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