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3,697,429

**LUBRICANT CONTAINING LOW ETHYLENE CONTENT AND HIGH ETHYLENE CONTENT ETHYLENE-ALPHA-OLEFIN COPOLYMERS**

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11 Claims

**ABSTRACT OF THE DISCLOSURE**

A lubricating oil composition comprising a lubricating oil and a viscosity index improving amount of an oil-soluble polymer composition comprising a first copolymer of ethylene and a C<sub>3</sub> to C<sub>18</sub> higher alpha-olefin having an ethylene content of 50–95 mole percent (40–83 wt. percent), and a second copolymer of ethylene and a C<sub>3</sub> to C<sub>18</sub> higher alpha-olefin having an ethylene content of 5–80 mole percent (3–70 wt. percent), the ethylene content of the first copolymer being at least 5 mole percent (4 wt. percent) more than the ethylene content of the second polymer.

**BACKGROUND OF THE INVENTION**

**Field of the invention**

This invention relates to novel lubricant additives and the preparation thereof. More particularly, it relates to improvement in the viscosity index of lubricating oils by addition thereto of certain polymers.

**Description of the prior art**

As is well known to those skilled in the art, lubricating oils may be evaluated by many criteria each of which relates to the proposed use of the oil. One of the more important of these criteria is the viscosity index which may be determined in standard manner by ASTM Test D567–53. In accordance with this test, the viscosity index (VI) may be calculated; and, as is well known, a low VI signifies a large change in viscosity with change in temperature, while a high VI signifies a small change in viscosity with change in temperature.

It has been found that it is possible to increase the VI of lubricating oils to a satisfactory degree in many cases. Typical of prior art VI improvers are polyisobutylenes, polymethacrylates, copolymers of polymethacrylate esters, copolymers of vinyl esters and fumaric acid esters, polyacrylates, polystyrenes, and terpolymers of polystyrene, methacrylate esters, and nitrogen-containing esters. Other prior art VI improvers may include polymers of ethylene and propylene. Frequently it is found that the presence of these additives in conventionally-formulated lubricating oils undesirably raises the pour point of the lubricating oil to a point which renders the oil less than fully satisfactory at low temperature. This appears to occur, at least in part, because the VI improvers employed interfere with the operation of conventional lubricating oil pour point depressants.

Among the prior art VI improvers is that of Jacobson et al. in U.S. Pat. No. 3,551,336, issued Dec. 29, 1970, and having an assignee common to that of the instant application. That application teaches the attainment of a haze-free lubricating oil of improved VI by the use of certain ethylene-high alpha olefin polymers containing 60 mole percent–80 mole percent (50–70 wt. percent) ethylene, less than 1.3 wt. percent decane-insoluble polymer, a crystallinity of less than 25%,  $\bar{M}_w/\bar{M}_n \leq 4.0$ , and  $M_v$  of 10,000–200,000.

It is an object of this invention to provide a system

which permits attainment of improvement in viscosity index.

Other objects will be apparent to those skilled in the art.

**SUMMARY OF THE INVENTION**

In accordance with certain of its aspects, the novel lubricating oil composition of this invention may comprise a lubricating oil and contained therein, in amount sufficient to modify the viscosity index of said lubricating oil, a viscosity index improving amount of an oil-soluble polymer composition comprising a first copolymer of ethylene and a C<sub>3</sub> to C<sub>18</sub> alpha-olefin having an ethylene content of 50–95 mole percent (40–83 wt. percent) and a second copolymer of ethylene and a C<sub>3</sub> to C<sub>18</sub> alpha-olefin having an ethylene content of 5–80 mole percent (3–70 wt. percent), the ethylene content of the first copolymer being at least 5 mole percent (4 wt. percent) more than the ethylene content of the second copolymer. This permits attainment of lubricating oils of increased viscosity index.

**DESCRIPTION OF THE INVENTION**

The first copolymer and the second copolymer may be prepared by the copolymerization of ethylene, a C<sub>3</sub> to C<sub>18</sub> higher alpha olefin, and optionally a copolymerizable third monomer.

The higher alpha-olefins which may be used in the preparation of the copolymers used in practice of this invention may include those monomers typically containing from 3 to about 18 carbon atoms. The alpha-olefins may be linear, or branched where the branching occurs three or more carbon atoms from the double bond. While a single olefin is preferable, mixtures of C<sub>3</sub> to C<sub>18</sub> olefins may be employed. Suitable examples of C<sub>3</sub> to C<sub>18</sub> 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. It is most preferred, however, that the ethylene monomer be copolymerized with propylene.

Ethylene-propylene copolymers are preferred for the purposes of this invention. It is also possible to use a third monomer which may be one or more of the aforesaid C<sub>4</sub> to C<sub>18</sub> alpha-olefins and/or C<sub>6</sub> to C<sub>28</sub> diolefins. These unsaturated monomers are also 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 olefinic monomers may also be employed. The amount of the third monomer contained in the polymer may range from 0 to about 10 mole percent, e.g., 0.1 to 5.0 mole percent (0–37.0 wt. percent, say 0.3–18.5 wt. percent).

The diolefins which are useful as third monomer for copolymerization with ethylene and propylene include the bicyclic, alicyclic, or aliphatic nonconjugated diolefins containing about 6–28 carbon atoms, preferably about 6–12 carbon atoms. Suitable monomers include 1,5-cyclooctadiene, 1,4-hexadiene, dicyclopentadiene, 5-methylene-2-norbornene, 5-vinyl-2-norbornene, 1,5-cyclodecadiene, 2,4-dimethyl-2,7-octadiene, 3(2-methyl-1-propenyl) cyclopentene, 1,5-octadecadiene, 5-ethylidene-2-norbornene, etc.

The copolymer may be a two-component copolymer or a terpolymer.

The copolymers of ethylene and higher alpha olefin which may be employed as the first (high) copolymer and in the second (low) copolymer may be prepared by forming a mixture of the monomer components contain-

ing the following components by weight, these being per 100 parts of solvent employed.

TABLE I

Component	Broad range	Preferred range	High C <sub>2</sub> -typical	Low C <sub>2</sub> -typical
Ethylene.....	0.1-10.0	1.0-6.0	4.7	3.0
Higher alpha olefin.....	0.1-20.0	1.0-15.0	2.8	4.9
Di olefin.....	0.0-2.0	0.0-1.0	0	0
Hydrogen.....	1×10 <sup>-7</sup> -1×10 <sup>-2</sup>	1×10 <sup>-6</sup> -6×10 <sup>-3</sup>	2.35×10 <sup>-4</sup>	6×10 <sup>-5</sup>

In Table I, as elsewhere in this specification, all parts are parts by weight unless otherwise specifically stated.

Mixtures of these monomers may be used, i.e., more than one alpha-olefin and/or more than one diolefin may be employed. Other compatible components, including those which are copolymerizable to form tetrapolymers, may be present, etc.

The monomer mixture may be polymerized (either batchwise or continuously) to form the desired polymer in the presence of a catalytic amount of a catalyst composition containing, a catalyst, a compound of a transition metal and, as cocatalyst, an organometal compound. Thus, the catalyst composition may typically include:

(a) A compound, preferably a halide, of a transition metal, i.e., a metal of Groups IB through VIIB and VIII of the Periodic Table and having an atomic number falling within the range of 21-30, 39-48, 57-80, and 80-130. The first category including metals starting with scandium (21) and ending with zinc (30) may be preferred; and titanium (22) and vanadium (23) may be most preferred. The halide may be a chloride, bromide, or iodide, preferably chloride. The preferred compound may be titanium tetrachloride, vanadium oxychloride, or vanadium tetrachloride.

(b) An organometal compound (of a metal of Groups I-A, II-A, II-B, and III-A), preferably an organoaluminum compound R<sup>'''</sup><sub>n</sub>AlX<sub>3-n</sub> wherein R<sup>'''</sup> may be hydrocarbon moiety, typically alkyl, aryl, aralkyl, or alkaryl, X is a halogen, and n is an integer 1-3. An organometal compound is one characterized by the presence of at least one carbon-to-metal bond. The preferred metal is aluminum. Typical compounds may be R<sup>'''</sup><sub>2</sub>Zn R<sup>'''</sup><sub>3</sub>Al, R<sup>'''</sup><sub>2</sub>AlX<sub>2</sub>, and most preferably R<sup>'''</sup><sub>2</sub>AlX<sub>2</sub>; and the preferred compound may be diethyl aluminum chloride or triisobutyl aluminum or ethyl aluminum sesquichloride.

The preferred catalyst composition may include 0.0001 to 0.0001 mole, say 0.00005 mole of transition metal halide catalyst and 0.00007-0.0007 mole, say 0.0035 mole of organoaluminum cocatalyst per 100 parts of solvent employed.

Polymerization may be effected to produce first copolymers having a greater ethylene content of 50-95 mole percent (40-83 wt. percent) by passing 0.1-10, say 4.7 parts of ethylene, 0.1-20, say 2.8 parts of alpha olefin, typically propylene, and 0-1.0, say 0.22 part of diolefin third monomer, typically 5-ethylidene-2-norbornene, when employed, and 4×10<sup>-6</sup> to 4×10<sup>-3</sup>, say 2.35×10<sup>-4</sup> parts of hydrogen into 100 parts of liquid inert-diluent-solvent reaction medium containing vanadium oxytrichloride catalyst and ethyl aluminum sesquichloride cocatalyst in catalytic amounts, i.e., 0.0017 to 0.017, say 0.00865 parts of catalyst and 0.0084-0.084, say 0.042 parts of cocatalyst per 100 parts of diluent solvent. The nonreactive reaction medium may be an aromatic hydrocarbon such as toluene, a saturated aliphatic hydrocarbon such as heptane, pentane, and hexane, or a chlorohydrocarbon such as tetrachloroethylene. All steps in this reaction should preferably be carried out in the absence of oxygen, moisture, carbon dioxide or other harmful materials. Preferably, all reactants and catalysts may be pure and dry and blanketed with inert gas such as nitrogen or methane.

During polymerization, the reaction mixture may be agitated and maintained at temperatures of -40° C. to

100° C., say -10° C. to 70° C., preferably about 30° C. and pressures of 0-1000 p.s.i.g., preferably 0-300 p.s.i.g.,

say 60 p.s.i.g., during a period of 1-300 minutes, preferably 3-60 minutes, say 15 minutes.

At the end of this period, the reaction mixture may be worked up to separate product copolymer.

In the preferred embodiment the ethylene content of the copolymer may be controlled by varying the mole ratio of ethylene to propylene.

Preparation of the first copolymer (from e.g. 4.7 parts of ethylene, 2.8 parts of higher alpha olefin and 2.35×10<sup>-4</sup> parts of hydrogen) may be carried out by maintaining this ratio during the reaction at 0.1-10, preferably 0.5 to 4, say 2.5 which will permit attainment of first copolymer having ethylene content of 50-95 mole percent (40-83 wt. percent), preferably 60-85 mole percent (50-79 wt. percent), say 75 mole percent (65 wt. percent).

Preparation of the second copolymer (from e.g. 3.0 parts of ethylene, 4.9 parts of higher alpha olefin, and 6×10<sup>-5</sup> parts of hydrogen) may be carried out by maintaining this ratio during the reaction at 0.01-10, preferably 0.1-4, say 0.9, which will permit attainment of the second copolymer having ethylene content of 5-80 mole percent (3-70 wt. percent), preferably 30-70 mole percent (22-60 wt. percent), say 54 mole percent (44 wt. percent).

The first copolymer used in practice of this invention may be characterized by the following properties:

TABLE II

Property	Broad range	Preferred range	Typical
Ethylene content:			
Mole percent.....	50-95	60-85	75
(Wt. percent).....	(40-83)	(50-79)	(65)
Third monomer content:			
Mole percent.....	0-10	0-5	0
(Wt. percent).....	(0-37)	(0-17.5)	(0)
Degree of crystallinity, wt. percent.....	0-25	5-15	8
M <sub>v</sub> ×10 <sup>-3</sup> .....	10-200	20-140	48
M <sub>n</sub> ×10 <sup>-3</sup> .....	5-100	10-70	10
M <sub>w</sub> ×10 <sup>-3</sup> .....	10-800	10-400	400
M <sub>w</sub> /M <sub>n</sub> .....	≤8	≤6	>0

A preferred first high-ethylene copolymer may be the copolymer of United States Patent 3,551,336 supra which is an oil-soluble polymer of ethylene and a C<sub>3</sub>-C<sub>18</sub> alpha-olefin characterized by the following parameters:

(a) an ethylene content of about 60-80 mole percent (53-73 wt. percent);

(b) a content of less than about 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45° C.;

(c) a degree of crystallinity less than about 25%;

(d) an M<sub>w</sub>/M<sub>n</sub> ratio less than about 4.0; and

(e) a viscosity average molecular weight of about 10,000-200,000.

A specific preferred first copolymer may be that disclosed in Example 1 of United States patent No. 3,551,336. This copolymer of ethylene and propylene contains 77 mole percent (69 wt. percent) ethylene.

Other illustrative first copolymers may include the following:

(a) a copolymer of ethylene and propylene containing 75 mole percent (67 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing VOCl<sub>3</sub> as catalyst and (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub> as cocatalyst, with an ethylene to propylene mole ratio of 2.5;

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(b) a copolymer of ethylene and propylene containing 72 mole percent (63 wt. percent) ethylene and prepared at 35° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 2.5;

(c) a copolymer of ethylene and propylene containing 76 mole percent (68 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$  as cocatalyst, with an ethylene to propylene mole ratio of 2.5;

(d) a copolymer of ethylene and propylene containing 75 mole percent (67 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing vanadium tris(acetylacetonate) as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 3.2;

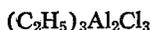
(e) a copolymer of ethylene, propylene, and 5-methylene-2-norbornene containing 74 mole percent (64 wt. percent) ethylene, 24 mole percent (35.7 wt. percent) propylene, and 2 mole percent (0.3 wt. percent) 5-methylene-2-norbornene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$  as cocatalyst, with an ethylene to propylene mole ratio of 2.5.

The second copolymer used in practice of this invention may be characterized by the following properties:

TABLE III

Property	Broad range	Preferred range	Typical
Ethylene content:			
Mole percent (Wt. percent)	5-80 (3-70)	30-70 (22-60)	54 (44)
Third monomer content:			
Mole percent (Wt. percent)	0-10 (0-37.0)	0-5 (0-18.5)	0 0
Degree of crystallinity, wt. percent	0-25	0-15	0
$\overline{M}_v \times 10^{-3}$	10-400	10-200	150
$\overline{M}_n \times 10^{-3}$	5-200	5-100	75
$\overline{M}_w \times 10^{-3}$	5-1,600	5-600	200
$\overline{M}_w/\overline{M}_n$	$\leq 8$	$\leq 6$	$\leq 4$

A preferred second copolymer may be that prepared by the copolymerization of ethylene and propylene at 35° C. and 65 p.s.i.g., using  $\text{VOCl}_3$  as catalyst and



as cocatalyst and with an ethylene to propylene mole ratio of 0.9 and containing 54 mole percent (44 wt. percent) ethylene.

Other illustrative second copolymers may be the following:

(a) a copolymer of ethylene and propylene containing 57 mole percent (41 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 0.5;

(b) a copolymer of ethylene and propylene containing 53 mole percent (43 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing vanadium tris(acetylacetonate) as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 0.8;

(c) a copolymer of ethylene and propylene containing 63 mole percent (53 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing vanadium tris(acetylacetonate) as catalyst and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$  as cocatalyst, with an ethylene to propylene mole ratio of 1:1;

(d) a copolymer of ethylene and propylene containing 46 mole percent (36 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 0.2;

(e) a copolymer of ethylene, propylene, and 5-methyl-

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ene-2-norbornene containing 50 mole percent (40 wt. percent) ethylene, 48 mole percent (59.7 wt. percent) propylene, and 2 mole percent (0.3 wt. percent) 5-methylene-2-norbornene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst with an ethylene to propylene mole ratio of 0.9.

In practice of the process of this invention the first copolymer and the second copolymer may be added to lubricating oil in the relative parts by weight as set forth in the following table:

TABLE IV

Component	Broad	Preferred	Typical
15 First copolymer	1-99	30-70	5
Second copolymer	1-99	30-70	5
Total	2-198	60-140	10

It will be apparent to those skilled in the art that the amount of each copolymer added to the lubricating oil may be dependent upon the properties of the oil (including viscosity, viscosity index, pour point, etc.) and of the copolymers (including ethylene content, etc.).

In the case of each base stock, e.g., lubricating oil, which may be improved by the technique of this invention, it will be found that there is a characteristic modal weight percent ethylene content at which the pour point is a maximum. This may be determined by adding to the base stock a standard quantity (e.g. 0.7 wt. percent) of each of a series of ethylene-propylene copolymers prepared in manner to yield different ethylene contents but otherwise possessing similar properties. If one plots the pour point of the oil as a function of the ethylene content, it will be observed that there is a mode point for each oil at which the pour point is at a maximum. The ethylene content of the polymer at this maximum is the "modal weight percent ethylene." Typically, the modal weight percent ethylene may be 36% to 70%, commonly 40% to 65%, say 54%. This may correspond to 46-78 mole percent, say 50-74 mole percent, say 63 mole percent.

Similarly, it will be observed that on each side of the modal weight percent ethylene, there will be a point at which the pour point of the treated base stock is at a minimum. The lower minimum may commonly be at 25-60 wt. percent (33-69 mole percent), typically 35-55 wt. percent (45-64 mole percent), say 45 wt. percent (55 mole percent) ethylene; and the upper minimum may commonly be at 58-80 wt. percent (64-86 mole percent), typically 60-75 wt. percent (60-82 mole percent), say 67 wt. percent (75 mole percent) ethylene.

In practice of this invention, the first copolymer will preferably be chosen to have an ethylene content above the modal weight percent ethylene; although this ethylene content may be 40-83 wt. percent (50-95 mole percent), it will more commonly be 50-79 wt. percent (60-85 mole percent) and typically about 62 wt. percent to 70 wt. percent (71-78 mole percent).

Similarly, the second copolymer will preferably be chosen to have an ethylene content below the modal weight percent ethylene; although this ethylene content may be 5 wt. percent to 80 wt. percent (3-70 mole percent), it will more commonly be 22 wt. percent to 60 wt. percent (30-70 mole percent) and typically about 40 wt. percent to 55 wt. percent (50-64 mole percent).

The relative amount of first copolymer and second copolymer may preferably be such that the weight average of the ethylene content of the amounts of first copolymer and of second copolymer may be within 5-10 wt. percent (i.e., 4-8 mole percent) of the modal weight percent ethylene—and preferably at about the modal weight percent ethylene. Preferably, the ethylene content of the first and second copolymers may differ by at least about 5-20 wt. percent, say 10 wt. percent (i.e., 4-16 mole percent), i.e., the ethylene content of the first polymer may preferably be at least 5-20 wt. percent, say 10 wt. percent higher than (and typically, 5-50 wt. percent or 4-40 mole per-

cent higher than) the ethylene content of the second copolymer.

It is unexpectedly found, when a mixture of said first and second copolymers are added to lubricating oils (preferably containing a pour point depressant) as so indicated in amount sufficient to modify the VI of the oil (i.e., in viscosity index-improving amount) of only 0.01-5.0 wt. percent say 0.7 wt. percent that the viscosity index of the oil may be increased by 5% to 50%, say 25%, and that pour point may actually remain essentially constant in most instances.

It is a feature of this invention that it may be possible to prepare polymer compositions containing 1 to 99 parts of a first copolymer and 1 to 99 parts of second copolymer and add these directly to the base stock to be treated. In accordance with certain of its preferred aspects, it is a feature of this invention that the first copolymer and the second copolymer may be pre-blended in a diluent-solvent. Typical diluent-solvents may include toluene, hexane, heptane, isooctane, lubricating oils, etc.

Such pre-blends may contain the following:

TABLE IV

Component	Broad range	Preferred	Typical
First copolymer	1-99	30-70	50
Second copolymer	1-99	30-70	50
Diluent-solvent	0-20,000	700-3,500	1,500

The polymers of the invention can be employed alone in lubricant compositions or they can be employed in combination with other viscosity index improvers. If desired, the polymers may be employed in combination with other additives, for example, pour point depressants; ashless dispersants such as the reaction product of polyisobutenyl succinic anhydride with tetraethylene pentamine; detergent type additives, such as barium nonyl phenol sulfide, calcium tertiaryamylphenol sulfide, nickel oleate, barium octadecylate, calcium phenol stearate, zinc di-isopropyl salicylate, aluminum naphthenate, calcium cetyl phosphates, barium di-tertiaryamylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate and calcium dichlorostearate; etc. It is contemplated that the invention polymers can be blended with other polymers so as to impart various desired properties thereto.

It is a feature of this invention that significant improvement in VI may be achieved without undesirable effect on pour point when the additive system is present in base stock. It is a particular feature, however, that lubricating oils containing pour point depressants may be unexpectedly treated in manner to yield significant increase in VI with little or no adverse effect on pour point.

The lubricating oils which may be particularly improved by the technique of this invention may include the following:

- Midcontinent having a +15° F. pour point;
- Midcontinent having a 0° F. pour point;
- Pennsylvania having a 0° F. pour point;
- West Coast having a +15° F. pour point.

The benefits of the novel technique of this invention may be particularly noted when the lubricating oil contains pour point depressant compositions, typically in amount of 0 wt. percent to 1.0 wt. percent, say 0.7 wt. percent. Illustrative pour point depressants which may be present in the compositions of this invention may include:

(a) Alkylated naphthalenes—i.e., naphthalenes which have been alkylated with e.g. chlorinated paraffinic waxes by use of Friedel Crafts-type catalysts typified by those set forth in U.S. Pats. 1,815,022; 2,062,354; 2,087,682; and 2,174,246;

(b) Polymers (including copolymers) of n-alkyl methacrylates typified by those set forth in U.S. Pat. 2,710,842;

(c) Polymers (including copolymers) of n-alkyl acrylates;

(d) Copolymers of di-n-alkyl fumarate and vinyl acetate typified by those set forth in U.S. Pat. 3,048,479;

(e) Copolymers of alpha-olefins;

(f) Copolymers of terpolymers of alpha-olefins and styrene and/or alkyl styrenes; etc.

Although it is possible to achieve by practice of this invention improved VI (with little or no undesirable effect on pour point and commonly with decrease in pour point) of oils which contain no pour point depressant, it is unexpected that when pour point depressant is present that it is possible to achieve desired increase in VI without any diminution (and frequently with augmentation) of the advantages obtained by the pour point depressant.

In practice of the process of this invention, there may be employed as a base stock, lubricating oil Solvent, 150 N having the following properties (all viscosity measurements are in Saybolt Universal Seconds—SUS—unless otherwise indicated):

TABLE VI

Viscosity at 0° F.	6000
Viscosity at 210° F.	44
VI <sup>1</sup>	105
Pour point <sup>2</sup>	0° F.

<sup>1</sup> VI as determined by ASTM Test D-567-53.

<sup>2</sup> Pour Point as determined by ASTM Test D-97.

A typical lubricating oil composition containing an additive package, including a pour point depressant, which may be treated by this invention may be as follows:

TABLE VII

(i) 92.5 wt. percent of LP Solvent 150 N—a low pour solvent-refined Midcontinent hydrocarbon lube base stock characterized by viscosity of 150-160 SUS at 100° F., a VI of 105, and a pour point of about 0° F.

(ii) 4.5 wt. percent ashless dispersant containing the condensation product of 1 mole of tetraethylenepentamine and 2.8 moles of polyisobutenyl succinimide in a 50 wt. percent solution in LP Solvent 150 N;

(iii) 1.0 wt. percent of a 75% concentrate in lube oil diluent of antioxidant-antiwear agent containing zinc salts of the reaction product of P<sub>2</sub>S<sub>5</sub> and C<sub>4</sub>-C<sub>5</sub> aliphatic alcohols;

(iv) 1.5 wt. percent of detergent anti-rust agent containing overbased calcium sulfonate concentrate (in lubricating oil) of about 300 base number containing about 11.4 wt. percent total calcium and derived from alkyl aromatic sulfonic acids of about 420 molecular weight (as the sodium salt);

(v) 0.5 wt. percent of pour depressant containing a 50-50 wt. percent mixture of

(a) The condensation product having a molecular weight of about 2000 of (1) naphthalene and (2) a 123° F. softening point wax chlorinated to about 23%, the condensation effected in the presence of AlCl<sub>3</sub> and

(b) The condensation product of equimolar amounts of a di(C<sub>8</sub>-C<sub>18</sub> even-numbered carbon alkyl) fumarate and vinyl acetate having a molecular weight of about 15,000.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Practice of this invention may be illustrated by the following examples which show how the invention may be carried out. In these examples, as elsewhere in this specification, all parts are by weight unless specifically otherwise indicated.

#### EXAMPLE 1

In this example, which represents practice of one embodiment of the process of this invention, the copolymers may be both ethylene-propylene copolymers prepared from ethylene and propylene which may be purified by

contact at 150° C. with copper oxide and molecular sieves. Solvent n-heptane may be purified by passage through a bed of alumina and silica gel; and charge hydrogen may be dried by passage through a bed of silica gel. All reactants may be maintained pure, dry, and anaerobic.

Polymerization may be carried out in a reactor equipped with monomer inlet conduit, catalyst inlet conduit, cocatalyst inlet conduit, solvent inlet conduit, hydrogen inlet conduit, reflux condenser, stirring means, temperature control jacket, and product recovery outlet. The reactor may preferably be also equipped with means to continuously control the rates of addition of monomers, hydrogen, solvent, catalyst, and cocatalyst—and to provide a blanket of dry nitrogen.

To prepare the first copolymer of this embodiment, 4.7 parts of ethylene, 2.8 parts of propylene and  $2.35 \times 10^{-7}$  parts of hydrogen may be admitted to the reaction vessel together with 100 parts of diluent-solvent n-heptane, 0.0094 parts of vanadium oxychloride  $\text{VOCl}_3$  catalyst and 0.034 parts of ethyl aluminum sesquichloride. The catalyst composition was characterized by a molar ratio of Al/V of 5.0.

After the effective residence time of 20 minutes, product stream may be recovered and steam distilled to yield a solvent-free crude product which may then be dried to yield a product having the properties set forth in Table VIII.

The second copolymer of this embodiment may be prepared in manner similar to that in which the first copolymer may be prepared except that the amount of ethylene may be 3.0 parts and the propylene 4.9 parts and the hydrogen may be maintained at  $6 \times 10^{-5}$  parts.

Product second copolymer may be recovered having the properties as set forth in Table VI.

TABLE VIII

	First	Second
Mole percent ethylene.....	77	54
(Wt. percent ethylene).....	(69)	(44)
Inherent viscosity at 135° C. decalin, dl/g.....	2.01	2.0
V.I. ....	135	135
Thickening efficiency %.....	2.7	2.7
Fraction of polymer insoluble in normal decane at 45° C.....	0	0
Crystallinity, percent.....	11.5	0
Molecular weight distribution, $\overline{M}_w/\overline{M}_n$ .....	2.2	2.2

<sup>1</sup> Viscosity Index as determined by ASTM D-567 in Reference Oil of Table V.

<sup>2</sup> Thickening Efficiency is the ratio of wt. percent polyisobutylene (20,000 Staudinger mol. wt.) required to thicken the Reference Oil of Table VII to a viscosity of 12.4 centistokes (cs.) at 210° F./wt. percent ethylene-propylene copolymer required to thicken the Reference Oil of Table VII to the same viscosity.

## EXAMPLE 2

In this experimental example, 0.7 parts total of a 50–50 wt. percent mixture of the first copolymer and of the second copolymer of Table VIII may be employed. This mixture, containing 54 wt. percent ethylene (equivalent to a modal wt. percent of 56.5%) may be added to 100 parts of the Reference Oil of Table VII. The VI of the product mix may be found to be 135 and the pour point may be found to be –25° F.

## EXAMPLE 3

In this control example, the procedure of Example 2 was followed except that the additive was 0.7 part of a single copolymer. The copolymer was prepared by the process used to prepare the first polymer of Table IX except that the ethylene:propylene mole ratio was modified to yield a product containing 54 wt. percent ethylene. The VI of the product mix may be found to be 135 and the pour point may be found to be 0° F.

TABLE IX

	VI	Pour point
Reference oil.....	115	–25° F.
Example 2 (invention).....	135	–25° F.
Example 3 (control).....	135	0° F.

From the above examples, it will be apparent that use of the novel product of this invention (Example 2) permitted an increase in VI (of 20) to a value of 135 and desirably no change in pour point.

From Example 2, it will be apparent that addition of a comparable single polymer increased the viscosity index to 135 but undesirably increased the pour point (by 25° F.) to a value of 0° F.

It is unexpected that one should be able to increase the viscosity index by such a significant amount, by practice of this invention, without change in pour point.

## EXAMPLE 4

In this experimental example, 0.7 part total of a 66–34 wt. percent mixture of the first copolymer and of the second copolymer of Table VIII may be employed. This mixture, containing 57.3 wt. percent ethylene, may be added to 100 parts of the base stock of Table VII. The VI of the product mix may be found to be 135 and the pour point may be found to be –25° F.

## EXAMPLE 5

In this control example, the procedure of Example 2 was followed except that the additive was 0.7 part of a single copolymer containing 57.3 wt. percent ethylene. The copolymer was prepared by the process used to prepare the polymer of Table VIII except that the ethylene:propylene mole ratio was modified to yield a product containing 57.3 wt. percent ethylene. The VI of the product mix may be found to be 135 and the pour point may be found to be –10° F.

From the above examples, it will be apparent that addition of the novel product of this invention (Example 4) permitted an increase in VI of 20 to a value of 135 with no change in the pour point.

From Example 5, it will be apparent that addition of a comparable single polymer increased the viscosity index to 135 but undesirably increased the pour point (by 15° F.) to –10° F.

It is unexpected that one should be able to increase the viscosity index by such a significant amount and simultaneously, by practice of this invention, maintain the desired pour point with no change.

## EXAMPLE 6

Results comparable to the above may be attained when one uses as the first copolymer (in place of the first copolymer of Example 2) the following:

(a) The ethylene-propylene copolymer A of U.S. patent No. 3,551,336 prepared by copolymerization of ethylene and propylene in the presence of hydrogen using vanadium oxychloride catalyst and ethyl aluminum sesquichloride cocatalyst and containing 76 mole percent (68 wt. percent) ethylene.

(b) The ethylene-propylene copolymer B of U.S. patent No. 3,551,336 prepared by copolymerization of ethylene and propylene in the presence of hydrogen using vanadium tetrachloride catalyst and ethyl aluminum sesquichloride cocatalyst and containing 77 mole percent (69 wt. percent) ethylene.

(c) The ethylene-propylene copolymer C of U.S. patent No. 3,551,336 prepared by copolymerization of ethylene and propylene in the presence of hydrogen using vanadium tetrachloride catalyst and diethyl aluminum chloride as cocatalyst and containing 77 mole percent (69 wt. percent) ethylene.

(d) The ethylene-propylene copolymer prepared by copolymerization of ethylene and propylene in the presence of hydrogen using  $\text{VOCl}_3$  catalyst and  $(\text{C}_2\text{H}_5)_2\text{Al}_2\text{Cl}_3$  cocatalyst and containing 90 mole percent (86 wt. percent) ethylene.

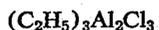
The copolymer containing 74 mole percent (64 wt. percent) ethylene, 24 mole percent (35.7 wt. percent) propylene, and 2 mole percent (0.3 wt. percent) 5-methylene-2-norbornene prepared from the noted monomers in

the presence of hydrogen at 55° C. and 65 p.s.i.g. using  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$  as cocatalyst.

### EXAMPLE 7

Results comparable to the above may be attained when one uses as the second copolymer (in place of the second copolymer of Example 1) the following:

(a) A copolymer of ethylene and propylene containing 57 mole percent (41 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and



as cocatalyst, with an ethylene: propylene mole ratio of 0.5.

(b) A copolymer of ethylene and propylene containing 53 mole percent (43 wt. percent) ethylene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing vanadium tris(acetylacetonate) as catalyst and  $(\text{C}_2\text{H}_5)_3\text{Al}_2\text{Cl}_3$  as cocatalyst, with an ethylene to propylene mole ratio of 0.8.

(c) A copolymer of ethylene, propylene, and 5-methylene-2-norbornene containing 50 mole percent (40 wt. percent) ethylene, 48 mole percent (59.7 wt. percent) propylene, and 2 mole percent (0.3 wt. percent) 5-methylene-2-norbornene and prepared at 55° C. and 65 p.s.i.g. by the use of a catalyst composition containing  $\text{VOCl}_3$  as catalyst and  $(\text{C}_2\text{H}_5)_2\text{AlCl}$  as cocatalyst with an ethylene to propylene mole ratio of 0.9.

Generally speaking, the invention is particularly useful when the oil contains 0.05 to 2.0 wt. percent of a lube oil pour depressant. These pour depressants commonly have a molecular weight (Staudinger) of 1,000 to 50,000 and usually are characterized by straight chain alkyl groups having 6-18 carbon atoms attached as side chains to a hydrocarbon nucleus. In one common type, the nucleus may be a polymethylene backbone or an aromatic or naphthalene group with the alkyl side chains directly attached to carbon atoms of said nucleus (e.g., copolymers of the alpha olefins or alkylated naphthalenes). In another type the alkyl groups will be linked to the nucleus through ether or ester linkages (e.g., copolymers of dialkyl fumarates and vinyl acetate).

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

What is claimed is:

1. A lubricating oil composition comprising a major amount of mineral lubricating oil containing a pour point depressant, and a viscosity index improving amount of an oil soluble polymer mixture comprising:

(1) about 1-99 parts by weight of a first copolymer consisting essentially of 60-80 mole percent of ethylene, a  $\text{C}_3$ - $\text{C}_{18}$  alpha olefin, and 0 to 10 mole percent of a third monomer, said third monomer being a  $\text{C}_4$ - $\text{C}_{28}$  aliphatic or alicyclic nonconjugated diolefin, said first copolymer having a content of less than about 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45° C., a degree of crystallinity of less than about 25 weight percent, a viscosity average molecular weight of about 10,000-200,000, and an  $\bar{M}_w/\bar{M}_n$  ratio less than about 4; and

(2) about 1-99 parts by weight of a second copolymer consisting essentially of 30-70 mole percent of ethylene, a  $\text{C}_3$ - $\text{C}_{18}$  alpha olefin, and 0-10 mole percent of a third monomer, said third monomer being a  $\text{C}_4$ - $\text{C}_{18}$  alpha olefin or a  $\text{C}_6$ - $\text{C}_{28}$  aliphatic or alicyclic nonconjugated diolefin, said second copolymer having a degree of crystallinity of 0-25 weight percent, a viscosity average molecular weight of 10,000-400,000, and an  $\bar{M}_w/\bar{M}_n$  ratio not greater than 8;

(3) said first copolymer having an ethylene content

greater than the ethylene content which gives a maximum pour point of said composition, and said second copolymer having an ethylene content less than the ethylene content which gives a maximum pour point of said composition;

(4) said first copolymer having an ethylene content at least 5 mole percent greater than said second copolymer, and said first and second copolymers being produced by separate polymerizations.

2. A lubricating oil composition as claimed in claim 1 wherein said  $\text{C}_3$ - $\text{C}_{18}$  alpha-olefin is propylene.

3. A lubricating oil composition as claimed in claim 1 wherein at least one of said copolymers is a terpolymer.

4. A lubricating oil composition as claimed in claim 1 wherein said oil-soluble polymer composition is present in amount of 0.01-5.0 wt. percent in said lubricating oil.

5. A lubricating oil composition according to claim 1 in which said second copolymer has an ethylene content of 30-70 mole percent, a degree of crystallinity of 0-15%, and an  $\bar{M}_w/\bar{M}_n$  ratio not greater than 6.

6. A lubricating oil composition according to claim 1 in which the  $\text{C}_3$ - $\text{C}_{18}$  alpha olefin in said first and second copolymers is propylene and the third monomer content in said first and second copolymers is zero.

7. A lubricating oil composition according to claim 1 containing 30-70 parts by weight of said first copolymer and 30-70 parts by weight of said second copolymer.

8. A concentrate according to claim 7 in which said mineral diluent-solvent is present in an amount of 700-3500 parts by weight, said first copolymer is present in an amount of 30-70 parts by weight, and said second copolymer is present in an amount of 30-70 parts by weight.

9. An oil soluble concentrate adapted to be added to a mineral lubricating oil containing a pour point depressant in order to improve the viscosity index thereof, said concentrate comprising a mineral diluent solvent and an oil soluble copolymer mixture comprising:

(1) about 1-99 parts by weight of a first copolymer consisting essentially of 60-80 mole percent of ethylene, a  $\text{C}_3$ - $\text{C}_{18}$  alpha olefin, and 0 to 10 mole percent of a third monomer, said third monomer being a  $\text{C}_4$ - $\text{C}_{18}$  alpha olefin or a  $\text{C}_6$ - $\text{C}_{28}$  aliphatic or alicyclic nonconjugated diolefin, said first copolymer having a content of less than about 1.3% by weight of a polymer fraction which is insoluble in normal decane at 45° C., a degree of crystallinity of less than about 25 weight percent, a viscosity average molecular weight of about 10,000-200,000, and an  $\bar{M}_w/\bar{M}_n$  ratio less than about 4; and

(2) about 1-99 parts by weight of a second copolymer consisting essentially of 30-70 mole percent of ethylene, a  $\text{C}_3$ - $\text{C}_{18}$  alpha olefin, and 0-10 mole percent of a third monomer, said third monomer being a  $\text{C}_6$ - $\text{C}_{28}$  aliphatic or alicyclic nonconjugated diolefin, said second copolymer having a degree of crystallinity of 0-25 weight percent, a viscosity average molecular weight of 10,000-400,000, and an  $\bar{M}_w/\bar{M}_n$  ratio not greater than 8;

(3) said first copolymer having an ethylene content greater than the ethylene content which gives a maximum pour point of said composition, and said second copolymer having an ethylene content less than the ethylene content which gives a maximum pour point of said composition;

(4) said first copolymer having an ethylene content at least 5 mole percent greater than said second copolymer, and said first and second copolymers being produced by separate polymerizations.

10. An oil-soluble concentrate adapted to be used as a viscosity index modifier for a lubricating oil as claimed in claim 9 wherein said diluent-solvent is a liquid miscible with said lubricating oil.

11. A concentrate according to claim 9 in which said second copolymer has an ethylene content of 30-70 mole

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percent, a degree of crystallinity of 0-15%, and an  $\bar{M}_w/\bar{M}_n$  ratio not greater than 6.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,697,429

Dated October 10, 1972

Inventor(s) Lawrence J. Engel and Marvin F. Smith, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, lines 12-17, in Table IV, the values in the column headed "Typical" should be as follows:

	<u>Typical</u>
First Copolymer	50
Second Copolymer	50
Total	100

Column 9, line 34, "VI" should read --VIII--.

Column 12, line 15, "composition" should be --mixture--.

Column 12, line 23, "complymers" should be --copolymers--.

Column 12, line 28, claim 8 should be renumbered --9--;  
same line, claim reference numeral "7" should read --8--.

Column 12, line 33, claim 9 should be renumbered --8--.

Column 12, lines 72 and 74, claim reference numeral "9"  
should read --8--.

Column 12, line 75, "copolymer" should be --copolymer--.

Signed and sealed this 20th day of November 1973.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

RENE D. TEGTMEYER  
Acting Commissioner of Patents