POLYMERIC FOUR POINT DEPRESSANTS OF VINYL AROMATIC AND ALKY FUMARATE

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U.S. Cl. 252—56 D

ABSTRACT OF THE DISCLOSURE

Four point depressants for petroleum distillates and lubricating oils comprise interpolymer, synthesized with the aid of free-radical initiators, from monomers comprising a C₉ to C₁₄ vinyl aromatic hydrocarbon with a mixture of straight chain alkyl fumarates wherein 20 to 80 mole percent of the alkyl groups are in the C₁₆–₂₀ range, and 80 to 20 mole percent are in the C₁₉ to C₁₄ range. These mixed alkyl fumarates can be obtained from: (A) an unsymmetrical fumarate in which the length of the alkyl radicals in the fumarate ester differs preferably by at least four carbon atoms; (B) at least two C₁₀ to C₂₀ symmetrical dialkyl fumarates which differ preferably in the length of the alkyl radicals in each ester by at least four carbon atoms; (C) mixtures of an unsymmetrical C₁₀ to C₂₀ dialkyl fumarate as in (A) with at least one symmetrical C₁₀ to C₂₀ dialkyl fumarate in (B); and (D) mixtures of unsymmetrical dialkyl fumarates as in (A), or at least two symmetrical fumarate esters as in (B), or mixtures of symmetrical and unsymmetrical esters as in (C), with at least one vinyl alcohol ester of a C₂ to C₆ alkyl alcohol.

The four point depressants of this invention are particularly useful in lubricants compounded with polymeric ethylene-higher alpha-olefin viscosity index improving agents.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to novel oil-soluble interpolymer, i.e., polymers comprised of at least two monomerieties, which are useful as four point depressants when compounded with petroleum distillates or lubricants containing waxy or wax-like components.

More particularly, this invention is concerned with interpolymer comprised of: (A) C₉ to C₁₄ aromatic hydrocarbons with unsymmetrical C₁₀ to C₂₀ dialkyl fumarates in which the length of the alkyl radicals in the unsymmetrical ester differs preferably by at least four carbon atoms; (B) C₂ to C₁₄ vinyl aromatic hydrocarbons with at least two C₁₀ to C₂₀ symmetrical dialkyl fumarates which differ preferably in the length of the alkyl radicals in each ester by at least four carbon atoms; (C) C₂ to C₁₄ vinyl aromatic hydrocarbons with unsymmetrical C₁₀ to C₂₀ dialkyl fumarates in which the length of the alkyl radicals in one of the monocyclic esters is equal to one of the alkyl radicals in the unsymmetrical ester or differs preferably from both by at least four carbon atoms; and (D) interpolymer of the monomers of (A), (B), (C), or mixtures thereof, with at least one vinyl alcohol ester of a C₂ to C₆ alkyl alcohol.

As used herein, the term "symmetrical," hereinafter abbreviated to sym., before a dialky fumarate indicates that both alkyl radicals in the diester are the same. The term "unsymmetrical," hereinafter abbreviated to unsym., indicates that the alkyl radicals in the dialkyl fumarate are different and differ preferably from each other by at least four carbon atoms.

Polymerization in all cases is catalyzed by free-radical initiators such as inorganic and organic peroxides and peracids, azo compounds, ultraviolet light, radiation from a cobalt-60 source of Van de Graff generator, or heat.

The polymeric four point depressants of this invention possess particular utility when added to oils which have been compounded with ethylene-higher alpha olefin copolymer for the purpose of increasing the viscosity index of the oil. Examples of these copolymers, made with the aid of Ziegler-Natta catalysts, are described in U.S. Pat. 3,522,180 and 3,551,336. In general, these ethylene copolymers comprise about 40 to 83 wt. percent ethylene, have a weight average molecular weight (M₅₅) in the range of 10,000 to 200,000; a M₆₅/M₅₅ ratio preferably less than 7.0, e.g., less than 4.0, and a degree of crystallinity of less than 25%. The higher olefin will generally be in the range of C₂ to C₆, e.g., C₂ to C₆ alpha monoolefin, and usually is propylene. Minor amounts, e.g., 0.5 to 10 wt. percent of other olefins may be included in the polymer, e.g., 1,4 hexadiene. These ethylene copolymers are generally used in oil in an amount of about 0.5 to 10 wt. percent, while additive concentrates in oil may contain 10 to 40 wt. percent of the ethylene copolymer. One problem with these ethylene copolymers has been compatibility with other polymeric additives normally used in lube oil compositions and concentrations, particularly four point depressants. Thus, these ethylene copolymers contain polyethylene segments which resemble natural petroleum waxes in structure and when compounded in an oil to which a conventional pour depressant has been added frequently interact with the pour depressant resulting in the phase separation when the compounded oil is held in storage. One aspect of this invention is the preparation of four point depressant which are compatible in storage with Ziegler-Natta ethylene-higher alpha olefin viscosity index improvers.

The prior art

Lubricant compositions comprising free-radical catalyzed copolymers of a vinyl aromatic hydrocarbon, such as styrene, and an unsaturated dicarboxylic ester such as sym-dioctyl fumarate having utility as a viscosity index improver have been disclosed in U.S. Pat. 2,366,517. Polymers useful as detergent additives in lubricating oils comprising copolymers and terpolymers of an olefin, an alkyl or alkenyl ester of an unsaturated monomer or di-basic acid, and a hydroxyalkyl or aminomethyl ester of an unsaturated acid, have been described in U.S. Pat. 2,892,790.

U.S. Pat. 2,978,395 discloses the preparation of viscosity index improvers and four point depressants for lubricating oils by the copolymerization of styrene with a sym-dialky fumarate using high energy radiation.

U.S. Pat. 3,251,906 discloses the preparation of graft copolymers and terpolymers in which a lower alkyl acrylate is graft polymerized on to a partially polymerized higher alkyl acrylate which may have been copolymerized with minor proportions of vinyl aromatics such as styrene.

SUMMARY

It has now been discovered that effective four point depressants for petroleum distillates and lubricating oils, especially mineral lubricating oils which have been compounded with the aforesaid Ziegler-Natta viscosity-index improving copolymers of ethylene and higher olefin, e.g., C₂ to C₁₂ alpha olefin, e.g., propylene, may be prepared by a free-radical catalyzed interpolymerization of: a C₉ to C₁₄ vinyl aromatic hydrocarbon such as styrene with:
(A) An unsym- \( \text{C}_n \) to \( \text{C}_s \) dialkyl fumarate such as n-dodecyl, n-hexadecyl fumarate in which the chain length in each alkyl radical in the fumarate ester differs preferably by at least four carbon atoms; (B) At least two \( \text{C}_n \) to \( \text{C}_s \) sym- dialkyl fumarates in which the chain length of the alkyl radicals in each ester differs preferably by at least four carbon atoms, such as a mixture of sym- di-tetradecyl fumarate and sym- di-octadecyl fumarate; (C) Mixtures of an unsym- \( \text{C}_n \) to \( \text{C}_s \) dialkyl fumarate as in (A), with at least one \( \text{C}_n \) to \( \text{C}_s \) sym- dialkyl fumarate, in which the length of the alkyl radicals in the sym- dialkyl fumarate may be the same as one of the alkyl radicals in the unsym- ester, such as a mixture of unsym- decyl, tetradecyl fumarate with sym- di-tetradecyl fumarate, or may be different such as a mixture of unsym- decyl, tetradecyl fumarate with sym- di-octadecyl fumarate; and (D) Mixtures of the monomers of (A), (B) and/or (C) with at least one vinyl alcohol ester of a \( \text{C}_n \) to \( \text{C}_s \) alkanoic acid such as vinyl acetate or vinyl dodecanoate.

Structurally, the interpolymers comprising this invention may be illustrated for the various combinations of monomers detailed above as random interpolymers in which the monomer moieties are linked in the polymer chain in a random sequence and varying number, as follows:

(I) \[
\begin{align*}
\text{H} & \quad \text{R} \quad \text{O} - \text{C} = \text{O} - \text{H} \\
\text{R} \quad \text{O} - \text{C} = \text{O} - \text{H} & \quad \text{H} \\
\text{ vinyl} & \quad \text{aromatic} \\
\text{unsym-dialkyl} & \quad \text{fumarate}
\end{align*}
\]

wherein \( R \) is an aromatic or alkyl aromatic hydrocarbon radical of 6 to 12 carbon atoms, \( R' \) and \( R'' \) are independently selected from the group consisting of \( \text{C}_n \) to \( \text{C}_s \) alkyl radicals and at least one of said \( R', R'' \) and \( R''' \) differs preferably in number of carbon atoms from at least one other of \( R', R'' \) and \( R''' \) by at least four, e.g. \( R' \) is \( \text{C}_4 \) and \( R'' \) is \( \text{C}_6 \), or \( R' \) and \( R'' \) are both \( \text{C}_8 \) while \( R''' \) is \( \text{C}_{10} \) or \( \text{C}_8 \) and \( R''' \) are both \( \text{C}_8 \) while \( R'' \) is \( \text{C}_{10} \), e.g. 1 to 8 alkyl radical, \( u \) and \( s \) are cardinal numbers in the range of 0 to about 20, and \( x \) and \( v \) are cardinal numbers in the range of 1 to about 20.

It will be understood that the numerical values assigned to \( m, s, v, x, y \) and \( z \) above, are not totals for any monomer moiety present in any interpolymer of a given molecular weight, but that these numerical values generally express the number of times a given monomer may be repeated in the polymer chain before another monomer is interposed in the chain.

In general, the oil soluble, pour depressing polymers of the invention will have number average molecular weights in the range of about 2000 to 50,000, preferably about 4000 to 30,000 as by vapor pressure osmometry. These polymers will be interpolymers of about 10 to 90, preferably 20 to 70, mole percent vinyl aromatic; 0 to 30 preferably 5 to 20, mole percent of vinyl alkanoate; and 90 to 10, preferably 80 to 30, mole percent of dialkyl fumarate. The alkyl groups of the monomers will be predominantly a mixture of straight chain \( \text{C}_n \) to \( \text{C}_s \) alkyl groups, wherein in 20, preferably 30 to 70, mole percent of the alkyl groups will have chain lengths in the range of \( \text{C}_n \) to \( \text{C}_s \) and 80 to 20, preferably 70 to 30, mole percent of the alkyl groups will have alkyl groups in the range of \( \text{C}_n \) to \( \text{C}_s \) preferably the mole equivalent average chain length of the \( \text{C}_{14} \) to \( \text{C}_{18} \) fraction will be about 4 carbons or more higher than the mole equivalent average chain length of the \( \text{C}_{16} \) to \( \text{C}_{18} \) fraction. To illustrate, if the \( \text{C}_{14}-\text{C}_{16} \) fraction consists of 10 mole percent \( \text{C}_{16} \), 30 mole percent \( \text{C}_{16} \) and 10 mole percent of \( \text{C}_{18} \) alkyl groups, then its mole equivalent average chain length will be:

\[
10 \times \frac{20 + 30 + 18 + 10 + 16}{100} = \frac{560 + 160}{50} = C_{18}
\]

If the \( \text{C}_{10} \) to \( \text{C}_{14} \) alkyl fraction is 20 mole percent \( \text{C}_{10} \) and 50 mole percent \( \text{C}_{12} \), then its mole equivalent average chain length will be:

\[
20 \times \frac{10 + 30 + 12}{50} = \frac{560}{50} = C_{11}
\]

Thus, in this aforesaid illustration, the mole equivalent average chain length of the \( \text{C}_{14}-\text{C}_{16} \) fraction, i.e. \( C_{18} \) is greater than 4 carbons from the mole equivalent average chain length of the \( \text{C}_{16}-\text{C}_{18} \) fraction, i.e. \( C_{14} \), or a difference of 5 carbons, and this example is for the preferred scope of the invention.

The vinyl aromatic hydrocarbons useful in the invention include: styrene, para-toluyl styrene, p-ethyl styrene, and p-ethyl styrene, all of which are made in commercial quantities and are available in a state of purity designated "polymerization grade." Examples of other vinyl aromatics included in the invention are 3,5-dimethyl styrene, p-n-hexyl styrene, 1-vinyl naphthalene or 4-methyl, 1-vinyl naphthalene which may be made by standard synthesis procedures in the literature such as reduction of the appropriate alkyl or dialkyl acetophenone or methyl alkyl naphthyl ketone to the alpha aryl ethanol followed by dehydration over a molten eutectic of sodium and potassium hydroxides.

Examples of vinyl alkanoates include vinyl alcohol esters of \( \text{C}_n \) to \( \text{C}_s \), preferably \( \text{C}_8 \) to \( \text{C}_s \) saturated fatty acids. Preferred is vinyl acetate in a state of purity suitable for polymerization, and which is readily available in commercial quantities. Vinyl esters of the higher alkanoic acids may be obtained by direct synthesis from the higher acid and acetylene in the presence of a zinc phosphate catalyst, or may be made from the higher acid and vinyl...
acetate by ester interchange using a mercuric acetate cata-
lyst.

The sym- dialkyl fumarates in which both alkyl radicals
in the ester are the same are readily prepared from
fumaric acid and the appropriate alcohol. A typical labora-
tory procedure is as follows: A mixture of fumaric acid,
contained in a reaction flask fitted with a Dean-
Stark water trap and a reflux condenser, is mixed with
from 10 to 20 mole percent excess of the alcohol, about
0.5 to 2 percent of an acid catalyst such as p-toluene
sulfonic acid monohydrate, based on weight of reactants,
and about 10 to 50 percent of an entraining agent such as
benzene, toluene or xylene based on volume of re-
antants, and the mixture heated under reflux. The lower
layer of water settling in the trap is usually withdrawn as
formed, and the upper layer of hydrocarbon and alcohol
returned to the flask. When no further formation of water
is observed, the flask contents are cooled, washed with a
dilute solution of an alkali to neutralize the acid catalyst,
water washed, dried, filtered and the entrainer and excess
alcohol removed by distillation, preferably under reduced
pressure. The ester may be further purified by contacting
with active charcoal, clay, or alumina or may be distilled
under inert vacuum.

Alternatively, the same procedure may be used with a
small molal excess of fumaric acid, and the excess acid
and half-ester removed by extraction with an alkaline
solution. Final purification is the same as in the case
where excess alcohol is used.

The unsymmetrical dialkyl fumarates can be prepared
by a number of methods. In one method, which is similar
to the aforesaid method used to prepare the sym-
esters, one molar equivalent of fumaric acid is mixed with
one molar equivalent of each alcohol forming the unsym-
ester. The acid catalyst and entraining agent are added
and the mixture heated under a Dean-Stark trap and re-
flux condenser until the theoretical quantity of water has
been obtained. The unsym-
ester product is recovered
and purified by the same procedures used for purification
of the sym-
esters.

In a second method, one molar equivalent of fumaryl
chloride, which may be prepared by the action of phos-
phorus pentoxide-chloride on either fumaric acid or maleic
anhydride, is reacted with one molar equivalent of each
of the alcohols forming the unsym-
ester in the presence
of an excess of pyridine. Isolation and recovery of the
unsym-
ester is the same as for the sym-
esters.

In a third method, a slight excess of both alcohols may
be used and the excess alcohols removed after esterifica-
tion is complete, or an excess of acid may be used and
the excess acid and any half-ester removed by extraction
with an alkaline solution.

Mixed esters, comprising a mixture of both sym-
and unsym-esters, may be prepared by any of the three
methods by the simultaneous esterification of a total of two
moles of three or more alcohols with one mole of fumaric
acid or fumaryl chloride. As in method three, an excess
of alcohols or acid may be used.

Where the unsyn-
ester is not further purified by frac-
tional distillation, it is to be understood that small quan-
tities of sym-dialkyl fumarate esters corresponding to
the individual alcohols comprising the unsyn-
ester may be
present in the final product. Estimates of the purity of
either the sym- or unsyn-
ester may be obtained from
analyses for neutralization number, saponification num-
er and from gas-chromatographic analysis.

A variety of polymerization methods, suitable for the
preparation of the interpolymers of this invention, have
been described in the scientific and patent literature. Emul-
sion and suspension systems may be used, but preferred
are solution methods using peroxide, hydroperoxide, per-
acid and azo free-radical initiators. In a typical solution
procedure, monomers, solvent and initiator contained in
a reactor, are sparged with oxygen-free nitrogen to dis-
place the air, the reactor sealed and the mixture gently
agitated at a suitable temperature until polymerization is
complete. Isolation and recovery of the polymer is by
precipitation with an excess of methanol and drying under
vacuum. All of the polymers prepared in the examples
given below were made in this manner using an azobisiso-
butyronitrile) catalyst.

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

EXAMPLES 1-5

A series of sym-dialkyl fumarates from sym-didecyl
fumarate to sym-dioctadecyl fumarate was prepared as
follows: 87.5 gms. of fumaric acid (0.75 mole) was
mixed with 200 gms. of mixed xylene, 1.35 moles of
the appropriate straight chain alcohol added, along with 2
wt. percent of p-toluene, sulfonic acid monohydrate,
based on weight of fumaric acid and alcohol, and the
mixture heated to reflux under a Dean-Stark trap. When
no further water was formed, the flask contents were
cooled, filtered and washed three times with 300 ml.
portions of 3 wt. percent aqueous sodium hydroxide,
adding diethyl ether if necessary to aid separation of
layers. The upper organic layer was then washed twice
with 300 ml. portions of distilled water, dried over 30
gms. of anhyd. sodium sulfate, filtered, the ether re-
moved on the steam bath and the xylene removed under
a pressure of about 10 mm. Hg. The product was sparged
with nitrogen under vacuum to remove the last traces
of xylene. Table 1 gives the amounts of each alcohol and
the quantity of toluene sulfonic acid used for each prepa-
ration.

<table>
<thead>
<tr>
<th>Table 1—Preparation of Sym-Dialkyl Fumarates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

1 Monohydrate.

2 Theoretical water equals 34.3 grams.

EXAMPLE 6

Unsym-n-decyl, n-hexadecyl fumarate was prepared by
essentially the same procedure used for the sym-
esters in Examples 1 to 5. A reaction flask fitted with a heating
mantine, Dean-Stark trap and reflux condenser was charged
with: 87.5 gms. of fumaric acid, 106.7 gms. n-decaneol,
163.4 gms. n-hexadecanol, 7.2 gms. p-toluene sulfonic
acid monohydrate, and 200 gms. of mixed xylene. The
mixture was heated to boiling under reflux and the water
formed in the reaction drawn off from the trap. 23.5 ml.
of water was obtained. Isolation and recovery of the ester
was the same as above for the sym-
esters.

All of the polymerization experiments were run in
thick-walled borosilicate polymerization tubes, contained
in an oil bath maintained at 70° C., for a period of 6
hours. The tube contents were stirred during the reaction
period by means of a glass enclosed magnetic stirring bar.
Monomers, solvent and free-radical initiator were
charged to the tube, air displaced by bubbling oxygen-
free nitrogen through the reaction mixture and the tube
then sealed. At the end of the reaction period the tube
was opened and the viscous contents were added to
about 20 volumes of rapidly agitated anhydrous methanol.
The polymeric product which separates as a solid was
collected and dried overnight in a vacuum oven at a
pressure of 100 torr. Samples of each product were
checked for monomer content by infra-red spectroscopy
and number average molecular weight at vapor pressure.
osmometry. The number average molecular weights of the resultant products were estimated to be in the range of about 5000 to about 20,000.

Samples of each of the polymeric products were tested for pour point at a concentration of 0.35 wt. percent in a compounded 10W40 base oil consisting of 84.7 parts of a solvent extracted, dewaxed neutral oil having a viscosity at 100°F of 150 S.U.S., 5.4 parts of a solvent extracted, dewaxed neutral oil having a viscosity at 100°F of 330 SUS and 9.9 parts of a detergent-inhibitor mixture comprising the condensation product of a poly(ethylene amine) with a polyisobutylene succinic anhydride; an alkaline earth mahogany sulfonate; zinc dithiodialkyl phosphate and an antioxidant. The compounded base oil had an A.S.T.M. pour point of 0°F and a viscosity of 6.2 centistokes.

Each of the polymeric products was tested for compatibility and pour point with a commercially available ethylene-propylene copolymer (hereinafter designated EPC) which had an ethylene content of about 75 wt. percent, a crystalline content of about 5%, a weight average molecular weight (Mw) of about 80,000, and a number average molecular weight (Mn) of about 40,000, made by a hydrogen moderated Ziegler-Natta synthesis. Approximately 10 wt. percent of the EPC was blended into the above compounded 10W40 base oil to yield an oil having a viscosity at 210°F of 14.0 centistokes. The compounded base oil containing the EPC had a pour point of 0°F.

**EXAMPLE 7**

Type (A) and (AD) polymers

The unsym-ester from Example 6, unsym-n-decyl, n-hexadecyl fumarate, was polymerized with styrene, and with styrene and vinyl acetate as follows:

**TABLE II**

<table>
<thead>
<tr>
<th>Example number</th>
<th>7 (A)</th>
<th>7 (AD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsym-ester of Example 6, gms.</td>
<td>9.6</td>
<td>9.6</td>
</tr>
<tr>
<td>Styrene, gms.</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Vinyl acetate, gms.</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Azo bis(isobutryonitrile), gms</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Cyclohexane, gms.</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Yield of polymer, gms.</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>Pour point, °F (A.S.T.M. D97)</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
<tr>
<td>0.35 wt. percent polymer in base oil</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
<tr>
<td>0.35 wt. percent polymer in base oil plus EPC</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
</tbody>
</table>

1 Quantities of monomers, catalyst and solvent sealed in air-free tube, heated and stirred for 6 hrs. at 70°C.
2 Polymeric solid isolated by precipitation in methanol, dried under vacuum at 160 torr.

8 **EXAMPLE 8**

Type (B) and (BD) polymers

The sym-ester of Example 2, sym-didodecyl fumarate, and the sym-ester of Example 4, sym-dihexadecyl fumarate were mixed and interpolymerized with styrene (Type (B) interpolymer) and with styrene and vinyl acetate (Type (BD) interpolymer) as follows:

<table>
<thead>
<tr>
<th>Example number</th>
<th>8 (B)</th>
<th>8 (BD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sysm-didodecyl fumarate, gms.</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Sysm-dihexadecyl fumarate, gms.</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Styrene, gms.</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>Vinyl acetate, gms.</td>
<td>3.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Azo bis(isobutryonitrile), gms</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Cyclohexane, gms.</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Yield of polymer, gms.</td>
<td>11.8</td>
<td>11.4</td>
</tr>
<tr>
<td>Pour point, °F (A.S.T.M. D97)</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
<tr>
<td>0.35 wt. percent polymer in base oil</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
<tr>
<td>0.35 wt. percent polymer in base oil plus EPC</td>
<td>&lt;31</td>
<td>&lt;31</td>
</tr>
</tbody>
</table>

Footnotes 1 and 2 same as for Table II.

**EXAMPLE 9**

Type (C) interpolymer

Unsym-decyl, hexadecyl fumarate from Example 6 was mixed with sym-didodecyl fumarate of Example 1 and sym-dihexadecyl fumarate of Example 4, and interpolymerized with styrene as follows:

**TABLE IV**

<table>
<thead>
<tr>
<th>Example No.</th>
<th>9a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsym-ester of Example 6, gms.</td>
<td>4.8</td>
</tr>
<tr>
<td>Sym-ester of Example 4, gms.</td>
<td>4.6</td>
</tr>
<tr>
<td>Styrene, gms.</td>
<td>4.6</td>
</tr>
<tr>
<td>Azo bis(isobutryonitrile), gms</td>
<td>0.2</td>
</tr>
<tr>
<td>Cyclohexane, gms.</td>
<td>10.0</td>
</tr>
<tr>
<td>Yield polymer, gms.</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Pour point, °F (A.S.T.M. D97) 0.35 wt. percent polymer in base oil + EPC = -24

Notes 1 and 2 same as for Table II.

Samples of the interpolymers compounded with the base oil and EPC showed no signs of incompatibility and were stable in storage. In contrast to the above results, samples of the same base oil containing EPC when mixed with several commercially available pour point depressants showed a rise in pour points and separation in storage. While only one test concentration has been shown for the pour point depressants of this invention, namely 0.35 wt. percent, the interpolymers of this invention are effective at a concentration in the range of 0.1 to 5.0, e.g. 0.1 to 2.0 wt. percent in a wide variety of distillates, solvent extracted neutrals and residual bright stocks. The interpolymers are also compatible with a wide variety of viscosity index improvers, oiliness agents, antiwear additives, metallic and ashless detergents, antioxidants and anti-foaming agents. The polymers of the invention can be used in mineral lubricating oils to thereby form automotive crankcase lubricants, aircraft engine lubricants, gear oils, transmission fluids, etc. The mineral lubricating oils can be of any usual type, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oils by suitable refining methods. Concentrations comprising a minor proportion, e.g. 5 to 45, wt. percent of the polymer in a major amount of oil, e.g. 95 to 55, wt. percent oil, preferably a mineral lubricating oil, with or without other additives present, can also be prepared for ease of handling.

What is claimed is:

1. A lubricating oil composition comprising (a) a major proportion of a mineral lubricating oil, (b) 0.5 to 10 wt. percent of a Ziegler-Natta viscosity index-improving copolymer of ethylene and C2 to C12 alpha-olefin comprising about 40 to 83 wt. percent ethylene and having a weight average molecular weight of 10,000 to 200,000, said copolymer having a tendency to interact with wax molecules in lubricating oils; and (c) 0.1 to 5.0 wt. percent of an oil-soluble pour point depressant interpolymer which minimizes said interaction wherein said interpolymer has a number average molecular weight of 2,000 to 50,000 and is derived from (i) 10 to 90 mole percent styrene or vinyl naphthenate or alkyl derivatives of said styrene or vinyl naphthenate having a total of 8 to 14 carbon atoms in the molecule with (ii) 10 to 90 mole percent of an unsymmetrical C12 to C20 dialkyl fumarate being formed by the esterification of fumaric acid or fumaryl chloride with a mixture of a C16 to C20 alcohol and a C3 to C16 alcohol; and (iii) 0 to 30 mole percent of at least one vinyl alcohol ester of a C2 to C12 alkanoic acid.
2. The composition of claim 1 wherein said interpolymer is based on styrene and unsymmetrical-n-decyl, n-hexadecyl fumarate.

3. The composition of claim 1 wherein said vinyl alcohol ester is vinyl acetate.

4. The composition of claim 1 wherein said alphaolefin is propylene.

5. The composition of claim 1 wherein said copolymer is an ethylene-propylene copolymer which contains about 75 wt. percent ethylene, has a crystalline content of about 5 wt. percent, a weight average molecular weight of about 80,000 and a number average molecular weight of about 40,000.