

INTERPOLYMERS CONTAINING LUBRICATING OIL COMPOSITION

5

FIELD OF THE INVENTION

The present invention pertains to lubricating oil compositions comprising
10 interpolymers containing (1) ethylene; (2) one or more vinylic monomers selected from the group consisting of aromatic, hindered aliphatic and cycloaliphatic vinylic monomers, and (3) one or more polymerizable C₃ to C₂₀ olefinic monomers. These polymers serve as viscosity improving agents.

15 BACKGROUND OF THE INVENTION

The viscosity of lubricating oils, particularly the viscosity of mineral oil based lubricating oils, is generally dependent upon temperature. As the temperature of the oil is increased, the viscosity usually decreases.

The function of a viscosity improver in lubricating oil compositions is to
20 reduce the extent of the decrease in viscosity as the temperature is raised or to reduce the extent of the increase in viscosity as the temperature is lowered, or both. Thus, a viscosity improver ameliorates the change of viscosity of an oil containing it with changes in temperature. The fluidity characteristics of the oil are improved.

Viscosity improvers are usually polymeric materials and are often referred to
25 as viscosity index improvers. Many patents relating to viscosity improvers are discussed by Ranney (Ed.), "Lubricant Additives", Noyes Data Corp. (1973), pp 93-145.

A number of hydrogenated alkenylarene-conjugated diene interpolymers are known in the prior art to be effective viscosity index (VI) improvers for lubricating
30 oils. U.S. Pat. Nos. 3,554,911 (Schiff et al.); 3,630,905 (Sorgo); and 3,772,169 (Small et al.) are concerned with the use of hydrogenated random butadiene-styrene copolymers as VI improvers for lubricating oils. These copolymers are prepared by

the copolymerization, using conventional techniques, of butadiene and styrene in the presence of a randomizing agent and subsequently, the copolymers are partially hydrogenated.

U.S. Patent 2,336,195 (Sparks et al.) relates to improving viscosity
5 characteristics of hydrocarbon oils by addition of normal mono-olefin polymers.

U.S. Patent 3,772,196 (St. Clair et al.) describes lubricating oils for internal combustion engines that have wide temperature operating characteristics. The composition contains a combination of a 2-block copolymer comprising a first block of an alkenyl arene, e.g. styrene, and a second essentially completely hydrogenated
10 polyisoprene block and certain pour point depressants in a lubricant stock having viscosity index of at least 85.

Many vinyl aromatic monomer-diene copolymers of the prior art are tapered block copolymers. The interpolymers of the instant invention are random interpolymers.

15 The generic class of materials covered by alpha-olefin/hindered vinylic monomer substantially random interpolymers and including materials such as ethylene/vinyl aromatic monomer interpolymers is known in the art. For example, substantially random ethylene/styrene interpolymers, including pseudo-random interpolymers as described in EP 415815 A, offer a range of material structures and
20 properties which makes them useful for varied applications, including the compatibilization of blends of polyethylene and polystyrene as described in U.S. Patent 5,460,818. Random copolymers of aromatic vinyl monomer and an alpha-olefin having 4 to 12 carbon atoms are described in U.S. Patent 5,244,996. Interpolymers of the type now found useful in the lubricating oil compositions of this
25 invention are described in U.S. Patent 5,872,201. Other patent publications provide limited generic reference to terpolymers of ethylene/styrene/alpha-olefin materials. Examples in JP 07/278,230 are limited to 2 mole percent or less incorporation of styrene in ethylene/ alpha-olefin copolymers. None of these references teaches the use of such polymers as viscosity improving additives for lubricating oil
30 compositions.

Although of utility in their own right, efforts continue to further expand the applicability of these generic interpolymers into lubricating applications, and especially those based on alpha-olefin/vinylic aromatic monomers, such as ethylene/styrene interpolymers. Lubricating applications include use of the polymers as viscosity improvers for lubricating oils and as thickeners for lubricating greases. Desired improved or superior characteristics to current state of the art materials can include, but are not limited to performance characteristics such as extended temperature range of application and low temperature performance and improved compatibility with a variety of oils of lubricating viscosity, especially synthetic oils and high viscosity index base stocks. The interpolymers used in the lubricating oil compositions of this invention are less costly compared to hydrogenated vinylic aromatic monomer-diene copolymers. The interpolymers of this invention provide an effective technology to address such needs.

SUMMARY OF THE INVENTION

The present invention relates to lubricating oil compositions comprising a major amount of an oil of lubricating viscosity and a minor, viscosity improving amount, of a substantially random interpolymer resulting from polymerizing (1) from about 19.5 to about 98.5 mole percent of ethylene; (2) from about 0.5 to about 60 mole percent of one or more vinylic monomers selected from the group consisting of aromatic, hindered aliphatic, and cycloaliphatic vinylic monomers; and (3) from about 1 to about 80 mole percent of one or more olefinic monomers having from 3 to about 20 carbon atoms.

One aspect of the present invention pertains to lubricating oil compositions comprising interpolymers comprising (1) from about 19.5 to about 98.5 mole percent of ethylene (2) from about 0.5 to about 60 mole percent of a vinylic monomer selected from the group consisting of aromatic and hindered aliphatic, and cycloaliphatic vinylic monomers, and (3) from about 1 to about 80 mole percent of one or more C₃ to C₂₀ olefinic monomers.

In one embodiment, the interpolymers of the present invention can comprise any three such monomers enumerated herein; these interpolymers can comprise the

three enumerated polymerizable monomers, with the third monomer (3) being one C₃ to C₂₀ olefinic monomer.

The interpolymers of the present invention can be free of any component, compound or substituent not specifically enumerated herein when desired. Also, the present invention can be free of any component, compound or substituent even though such component, compound or substituent was originally believed to be a part of the invention.

The interpolymers of the present invention provide an improvement in one or more of the properties such as viscosity index in lubricating oils and improved compatibility with a wide variety of oils of lubricating viscosity, especially high viscosity index oils and particularly synthetic oils.

DETAILED DESCRIPTION OF THE INVENTION

The term "terpolymer" is used herein to indicate a polymer wherein three different monomers are polymerized to make the terpolymer. The term "interpolymer" is used herein to indicate a polymer wherein three or more different monomers are polymerized to make the interpolymer.

The term "substantially random" in the substantially random interpolymer comprising ethylene, one or more vinylic aromatic monomers or hindered aliphatic vinylic monomers, and one or more C₃ to C₂₀ olefinic monomers as used herein means that the distribution of the monomers of said interpolymer can be described by the Bernoulli statistical model or by a first or second order Markovian statistical model, as described by J. C. Randall in POLYMER SEQUENCE DETERMINATION, Carbon-13 NMR Method, Academic Press, New York (1977), pp. 71-78. Preferably, the substantially random interpolymer does not contain more than 15 percent of the total amount of vinylic aromatic monomer in blocks of vinylic aromatic monomer of more than 3 units. More preferably, the interpolymer is not characterized by a high degree of either isotacticity or syndiotacticity. This means that in the Carbon-13 NMR spectrum of the substantially random interpolymer the peak areas corresponding to the main chain methylene and methine carbons

representing either meso diad sequences or racemic diad sequences should not exceed 75 percent of the total peak area of the main chain methylene and methine carbons.

Any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that values such as 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc. are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated are to be considered to be expressly stated in this application in a similar manner.

The interpolymers used in the lubricating oil compositions of the present invention comprise at least three different monomers, (1) from about 19.5 to about 98.5, preferably from about 25 to about 95, more preferably from about 30 to about 94 mole percent of ethylene; (2) from about 0.5 to about 60, preferably from about 1 to about 55, more preferably from about 1 to about 50 mole percent of one or more aromatic vinylic monomers or hindered aliphatic vinylic monomers, and (3) from about 1 to about 80, preferably from about 4 to about 65, more preferably from about 5 to about 50 mole percent of one or more C₃ to C₂₀ olefin monomers. It is to be understood that the total amount of (1), (2) and (3) is 100 mole percent.

The weight average molecular weight ($\overline{M}_w$) of the interpolymers of the present invention is usually greater than about 10,000, preferably from about 50,000 to about 700,000, more preferably from about 80,000 to about 350,000. Molecular weights of the hydrocarbon polymer are determined using well known methods described in the literature. Examples of procedures for determining the molecular weights are gel permeation chromatography (GPC) (also known as size-exclusion chromatography) and vapor phase osmometry (VPO). These and other procedures are described in numerous publications including:

P.J. Flory, "Principles of Polymer Chemistry", Cornell University Press (1953), Chapter VII, pp. 266-316,

"Macromolecules, an Introduction to Polymer Science", F.A. Bovey and F.H. Winslow, Editors, Academic Press (1979), pp. 296-312, and

- 5 W.W. Yau, J.J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979.

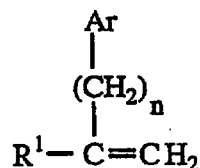
Molecular weight values referred to herein are direct molecular weights determined using GPC with multiangle light scattering and refractive index for detection. Such procedures are described in the literature, for example in Barth et al.,
10 Chemical Analysis, Vol. 113, "Modern Methods of Polymer Characterization", John Wiley & Sons, (1991). Other procedures that can be used include GPC employing polystyrene standards.

It is particularly preferred that the interpolymer of this invention is a terpolymer. Especially preferred is the terpolymer wherein component (2) is an
15 aromatic vinylic monomer, more preferably styrene, and component (3) is an alpha olefin having from 3 to about 12 carbon atoms, more preferably one or more olefinic monomers selected from the group consisting of propylene, butene-1, 4-methyl-1-pentene, pentene-1, hexene-1 and octene-1.

The present invention particularly concerns the following terpolymers:
20 ethylene/styrene/propylene; ethylene/styrene/4-methyl-1-pentene; ethylene/styrene/hexene-1; ethylene/styrene/octene-1; and ethylene/styrene/1-butene.

Suitable alpha-olefins, or combinations of alpha-olefins, which can be employed as olefinic monomer(s) (3) include for example, those containing from 3 to about 20, preferably from 3 to about 12, more preferably from 3 to about 8 carbon
25 atoms. Suitable olefinic monomers which can be employed as olefinic monomer(s) (3) include strained ring olefins such as norbornene. Particularly suitable as olefinic monomer(s) (3) include propylene, 4-methyl-1-pentene, pentene-1, hexene-1, octene-1 and butene-1. The olefinic reactant (3) does not include hindered aliphatic and cycloaliphatic olefins as defined herein for reactant (2)

30 Suitable vinylic aromatic monomers for use as component (2) include, for example, those represented by the following formula:



wherein R^1 is selected from the group of radicals consisting of hydrogen and hydrocarbyl groups, preferably alkyl or aryl groups, especially alkyl radicals
 5 containing from 1 to about 4 carbon atoms and more preferably hydrogen or methyl; and Ar is a phenyl group or a phenyl group substituted with from 1 to 3 substituents selected from the group consisting of halo, C_{1-4} -alkyl, and C_{1-4} haloalkyl; and n has a value from zero to about 6, preferably from zero to about 2, more preferably zero. Exemplary monovinyllic aromatic monomers include styrene, vinyl toluene, alpha-
 10 methylstyrene, t-butyl styrene, chlorostyrene, including all isomers of these compounds, and the like. Particularly suitable such monomers include styrene and lower alkyl- or halogen-substituted derivatives thereof. Preferred monomers include styrene, alpha-methyl styrene, the lower alkyl- or phenyl-ring substituted derivatives of styrene, such as ortho-, meta-, and para-methylstyrene, the ring halogenated
 15 styrenes, para-vinyl toluene or mixtures thereof, and the like. A more preferred monovinyllic aromatic monomer is styrene.

Suitable "hindered aliphatic or cycloaliphatic vinylic monomers" for use as components (2) include addition polymerizable vinylic monomers corresponding to the following formula:



wherein R^1 is selected from the group of radicals consisting of hydrogen and hydrocarbyl groups, preferably alkyl or aryl groups, especially alkyl radicals
 25 containing from 1 to about 4 carbon atoms and more preferably hydrogen or methyl; and R^2 is a sterically bulky, aliphatic substituent of up to 20 carbons; or alternatively R^1 and R^2 together form a ring system. By the term "sterically bulky" it is meant that the monomer bearing this substituent is normally incapable of addition polymerization by standard Ziegler-Natta polymerization catalysts at a rate comparable with ethylene

polymerizations. Preferred hindered aliphatic or cycloaliphatic vinylic monomers are those in which one of the carbon atoms bearing ethylenic unsaturation is tertiary or quaternary substituted. Examples of such substituents include cyclic aliphatic groups such as cyclohexyl, cyclohexenyl, cyclooctenyl, or ring alkyl or aryl substituted derivatives thereof, tert-butyl, norbornyl, and the like. Most preferred hindered aliphatic or cycloaliphatic vinylic compounds are vinyl cyclohexane and the various isomeric vinyl-ring substituted derivatives of cyclohexene and substituted cyclohexenes, and 5-ethylidene-2-norbornene. Especially suitable is vinyl cyclohexane.

10 The substantially random interpolymers of the present invention can be prepared as described in EP-A-0,416,815 (Stevens et al.) which is incorporated herein by reference in its entirety. Preferred operating conditions for such polymerization reactions are pressures from atmospheric up to 3000 atmospheres and temperatures from - 30° C to 200° C. Polymerizations and unreacted monomer removal at
15 temperatures above the autopolymerization temperature of the respective monomers may result in formation of some amounts of homopolymer polymerization products resulting from free radical polymerization. While preparing the substantially random interpolymers of the present invention as will be described hereinafter, an amount of atactic vinylic aromatic homopolymer may be formed due to homopolymerization of
20 the vinylic aromatic monomer. However, NMR indicates polystyrene may be present in the styrene monomer and is not always generated during the polymerization reaction. Thus, the presence of polystyrene in the polymer may be avoided by use of styrene monomer of suitable purity.

25 The presence of vinylic aromatic homopolymer is in general not desirable for the purposes of the present invention, often resulting in hazy oil blends. The vinylic aromatic homopolymer may be separated from the interpolpolymer, if desired, by extraction techniques such as selective precipitation from solution with a non-solvent for either the interpolpolymer or the vinylic aromatic homopolymer. For example, a polystyrene containing polymer is dissolved in hexane and coagulated in acetone. For
30 the purpose of the present invention it is preferred that the copolymers of this invention are substantially free of vinylic aromatic homopolymer. As used here,

"substantially free" means the copolymer contains no amount of vinylic aromatic homopolymer that would cause objectionable haze or other incompatibility in a lubricating oil composition. Preferably, the copolymer is free of vinylic aromatic homopolymer.

5 Examples of suitable catalysts and methods for preparing the substantially random interpolymers of the present invention are disclosed in EP-A-416,815; EP-A-514,828; U.S. Patent No. 5,721,185; U.S. Patent No. 5,470,993; as well as U.S. Patent Nos. 5,055,438; 5,057,475; 5,096,867; 5,064,802; 5,132,380; 5,189,192; 5,321,106; 5,347,024; 5,350,723; 5,374,696; 5,399,635; 5,556,928; 5,703,187 and
10 5,872,201, all of which patents and applications are incorporated herein by reference.

 The substantially random interpolymers of the present invention can also be prepared by the methods described by Bradfute et al. in WO 95/32095; by Pannell in WO 94/00500; and in *Plastics Technology*, p. 25 (September 1992), all of which are incorporated herein by reference in their entirety. Further preparative methods which
15 may be applicable for the interpolymers of the present invention have been described in the literature. Longo and Grassi (*Makromol. Chem.*, Volume 191, pages 2387 to 2396 [1990]) and D'Anniello et al. (*Journal of Applied Polymer Science*, Volume 58, pages 1701-1706 [1995]) reported the use of a catalytic system based on methylaluminumoxane (MAO) and cyclopentadienyltitanium trichloride (CpTiCl_3) to
20 prepare an ethylene-styrene copolymer. Xu and Lin (*Polymer Preprints, Am.Chem.Soc., Div. Polym. Chem.*) Volume 35, pages 686,687 [1994]) have reported copolymerization using a $\text{TiCl}_4/\text{NdCl}_3/\text{Al}(\text{iBu})_3$ catalyst to give random copolymers of styrene and propylene. Lu et al. (*Journal of Applied Polymer Science*, Volume 53, pages 1453 to 1460 [1994]) have described the copolymerization of ethylene and
25 styrene using a $\text{TiCl}_4/\text{NdCl}_3/\text{MgCl}_2/\text{Al}(\text{Et})_3$ catalyst. Sernetz et al. (*Macromol. Chem. Phys.*, v 197, pp 1071-1083, 1996) have described copolymerization of styrene with ethylene using $\eta^6\text{-(C}_5\text{(CH}_3\text{)}_4\text{Si(CH}_3\text{)}_2\text{N(tert-C}_4\text{H}_9\text{))TiCl}_2$ /methylaluminumoxane. Another suitable method includes the method disclosed for the manufacture of alpha - olefin/vinyl aromatic monomer interpolymers such as propylene/styrene and
30 butene/styrene described in U.S. Pat. No. 5,244,996, assigned to Mitsui Petrochemical Industries Ltd. All of the above are incorporated herein by reference.

Additives such as organic antioxidants (e.g., hindered phenols such as, for example, IRGANOXTM 1010), phosphites (e.g., IRGAFOSTM 168)), both from Ciba-Geigy, UV stabilizers, and the like can also be included in the interpolymers, additive concentrates and lubricating oil compositions of the present invention, to the extent
5 that they do not interfere with the enhanced properties discovered by Applicants.

The following examples are illustrative of the polymers used in the lubricating oil compositions of the invention, but are not to be construed as to limiting the scope of the invention in any manner. All temperatures are in degrees Celsius (°C).

Polymerization:

10 In a typical polymerization dry hexane (see Table 1) is pressurized from a stainless steel hold tank under nitrogen into a dry 1 gal (3.7 L) batch reactor equipped with a magnetically driven stirring mechanism. A heptane solution of methylaluminoxane (120 g, 165.5 mL; 7 wt% Al), which contains 30 mole% *iso*-butyl groups, is then pressurized into the reactor under nitrogen. Freshly distilled styrene
15 and α -olefin (see Tables 1-2) are added, and the homogeneous mixture is thermostated at the desired temperature (see Table 1). Once the desired temperature is reached, the reactor is pressurized with the desired amount of ethylene (see Tables 1-2). Finally, a heptane solution of methylaluminoxane (34.8 g, 47.7 mL; 7 wt% Al), which contains 30 mole% *iso*-butyl groups, is mixed with
20 η^6 -(C₅(CH₃)₄Si(CH₃)₂N(*tert*-C₄H₉))TiCl₂ (9.6 mg) to form a homogeneous solution. This solution is added to the reactor under nitrogen within 5 min of becoming homogeneous. The polymerization reaction is terminated after a given period of time (see Table 1) by venting the ethylene from the reactor and pressurizing the polymer cement from the reactor under nitrogen into *iso*-propyl alcohol (2 L), to which HCl
25 (15-25 mL; 18 M) has been added.

Polymer Purification:

The coagulated polymer is collected and rinsed with fresh *iso*-propyl alcohol (1 L). This process is repeated 2-3 times. The coagulated polymer is air dried for 24-48 h and is then dried to constant weight at 50° C in a vacuum oven. Any remaining
30 aluminum inorganic material is removed by exhaustively centrifuging a tetrahydrofuran solution (0.1-0.15 g/mL) of the polymer, in which the aluminum

inorganic material is insoluble. The polymer is decanted from the insoluble material, coagulated in fresh *iso*-propyl alcohol, air dried for 24-48 h, and then dried to constant weight at 50° C in a vacuum oven. This process is repeated from 2-3 times. Any homopolystyrene present in the polymer is removed by coagulating a tetrahydrofuran solution (0.1-0.15 g/mL) of the polymer in acetone (about 1.5-2 L). The coagulated polymer is then collected by decantation, air dried for 24-48 h, and then dried to constant weight at 50°C in a vacuum oven. This process can also be repeated if necessary. If the polymer contains polystyrene homopolymer, the polymer may, if desired, be dissolved in hexane and coagulated in acetone, effectively removing polystyrene. The interpolymer is free from impurities if a homogeneous solution is formed when a 10 wt% solution of the polymer is made with mineral oil.

Table 1

Example	Hexane (g)	Styrene (g)	α -olefin (g)	Heptane (mL) from MAO	Ethylene (psig)	Reaction	
						Temp. (°C)	Time (h)
1	489.2	454.5	oct, 163.2	212	55	60	0.583
2	339.1	318.2	oct, 228.8	212	55	60	0.5
3	496.1	374.8	hex, 201.9	212	54.5	40	2
4	496.1	374.8	hex, 201.9	212	35.6	20	3
5	496.1	374.8	hex, 201.9	212	45	30	2
6	496.1	374.8	hex, 201.9	212	54.5	40	2
7	496.1	374.8	hex, 201.9	212	58	50	2
8	496.1	374.8	hex, 201.9	212	73	60	2
9	496.1	374.8	hex, 201.9	212	86	70	0.5

- 15 (g) – grams
 (h) – hours
 (mL) – milliliters
 (psig) – pound per square inch, gauge
 (hex) – hexene
 20 (oct) – octene

Table 2

<u>Example</u>	<u>Feed (mole %)</u>			<u>Feed Ratio</u>	
	<u>Styrene</u>	<u>α-olefin</u>	<u>Ethylene</u>	<u>Styrene-ethylene</u>	<u>α-olefin-ethylene</u>
1	68.2	22.7	9.1	7.5	2.5
2	52.7	35.2	12.1	4.4	2.9
3	51.8	34.6	13.6	3.8	2.5
4	51.8	34.6	13.6	3.8	2.5
5	51.8	34.6	13.6	3.8	2.5
6	51.8	34.6	13.6	3.8	2.5
7	51.8	34.6	13.6	3.8	2.5
8	51.8	34.6	13.6	3.8	2.5
9	51.8	34.6	13.6	3.8	2.5

Results:

Results are tabulated in Tables 3-4.

5

Table 3

<u>Example</u>	<u>Conversion %</u>	<u>Yield (g)</u>	<u>Al/Ti</u>	<u>Activity *</u>
1	83	562.3	2,235	5853
2	86	510	2,235	6190
3	27	178	12,275	2967
4	9	57.1	12,275	634
5	13	84	12,275	1400
6	27	176.5	12,275	2942
7	61	350.5	12,275	5800
8	66	382.9	12,275	6300
9	69	397.3	12,275	26,200

* (Kg/mole Ti/h)

10

Compositions of the copolymers of Examples 1-9 (mole %, measured by ^1H NMR) and molecular weights, (GPC, (multiangle light scattering and refractive index for detection)) are set forth in Table 4:

Table 4

Example	Styrene	α -olefin	Ethylene	dn/dc # (mL/g)	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	27	15	58	0.137	74,340	1.63
2	23	25	53	0.137	75,230	2.59
3	27	37	36	0.137	206,800	1.48
4	27	47	26	0.137	465,200	1.4
5	27	39	34	0.137	306,300	1.69
6	31	51	18	0.137	196,400	1.65
7	23	30	47	0.137	155,000	1.73
8	25	35	40	0.137	129,000	1.9
9	28	41	31	0.137	80,000	1.81

5 # differential refractive index

Other Additives

Additive concentrates and lubricating oil compositions of this invention may contain other additives. The use of such additives is optional and the presence thereof in the compositions of this invention will depend on the particular use and level of performance required. Thus the other additive may be included or excluded. Additive concentrates of this invention typically comprise from about 0.1% to about 30% by weight of interpolymer and from about 70% to about 99.9% by weight of a substantially, inert, normally liquid, organic diluent.

Lubricating oil compositions often comprise zinc salts of a dithiophosphoric acid, often referred to as zinc dithiophosphates, zinc O,O-dihydrocarbyl dithiophosphates, and other commonly used names. They are sometimes referred to by the abbreviation ZDP. One or more zinc salts of dithiophosphoric acids may be present in a minor amount to provide additional extreme pressure, anti-wear and anti-oxidancy performance.

20 Other additives that may optionally be used in the lubricating oils of this invention include, for example, detergents, dispersants, supplemental viscosity

improvers, oxidation inhibiting agents, corrosion inhibiting agents, pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers, friction modifiers, and anti-foam agents.

5 Extreme pressure agents and corrosion and oxidation inhibiting agents which may be included in the compositions of the invention are exemplified by chlorinated aliphatic hydrocarbons, organic sulfides and polysulfides, phosphorus esters including dihydrocarbon and trihydrocarbon phosphites, molybdenum compounds, and the like.

10 Other oxidation inhibiting agents include materials such as alkylated diphenyl amines, hindered phenols, especially those having tertiary alkyl groups such as tertiary butyl groups in the position ortho to the phenolic -OH group, and others. Such materials are well known to those of skill in the art.

Auxiliary viscosity improvers (also sometimes referred to as viscosity index improvers or viscosity modifiers) may be included in the compositions of this invention. Viscosity improvers are usually polymers, including polyisobutenes, 15 polymethacrylic acid esters, hydrogenated diene polymers, polyalkyl styrenes, esterified styrene-maleic anhydride copolymers, hydrogenated alkenylarene-conjugated diene copolymers and polyolefins. Multifunctional viscosity improvers, which also have dispersant and/or antioxidancy properties are known and may optionally be used in addition to the products of this invention. Such products are 20 described in numerous publications including those mentioned in the Background of the Invention. Each of these publications is hereby expressly incorporated by reference.

Pour point depressants may be included in the additive concentrates and lubricating oils described herein. Those which may be used are described in the 25 literature and are well-known to those skilled in the art; see for example, page 8 of "Lubricant Additives" by C.V. Smalheer and R. Kennedy Smith (Lezius-Hiles Company Publisher, Cleveland, Ohio, 1967). Pour point depressants useful for the purpose of this invention, techniques for their preparation and their use are described in U. S. Patent Nos. 2,387,501; 2,015,748; 2,655,479; 1,815,022; 2,191,498; 30 2,666,748; 2,721,877; 2,721,878; 3,250,715; and 5,707,943 which are expressly incorporated herein by reference for their relevant disclosures.

Anti-foam agents used to reduce or prevent the formation of stable foam include silicones or organic polymers. Examples of these and additional anti-foam compositions are described in "Foam Control Agents", by Henry T. Kerner (Noyes Data Corporation, 1976), pages 125-162.

5 Detergents and dispersants may be of the ash-producing or ashless type. The ash-producing detergents are exemplified by oil soluble neutral and basic salts of alkali or alkaline earth metals with sulfonic acids, carboxylic acids, phenols or organic phosphorus acids characterized by a least one direct carbon-to-phosphorus linkage.

The term "basic salt" is used to designate metal salts wherein the metal is
10 present in stoichiometrically larger amounts than the organic acid radical. The relative amount of metal present in "basic salts" is frequently indicated by the expression "metal ratio" (abbreviated MR), which is defined as the number of equivalents of metal present compared to a "normal", stoichiometric amount. Thus, for example, a basic salt containing twice the amount of metal compared to the
15 stoichiometric amount, has a metal ratio (MR) of 2. Basic salts and techniques for preparing and using them are well known to those skilled in the art and need not be discussed in detail here.

Ashless detergents and dispersants are so-called despite the fact that, depending on its constitution, the detergent or dispersant may upon combustion yield
20 a nonvolatile residue such as boric oxide or phosphorus pentoxide; however, it does not ordinarily contain metal and therefore does not yield a metal-containing ash on combustion. Many types are known in the art, and any of them are suitable for use in the lubricants of this invention. The following are illustrative:

(1) Reaction products of carboxylic acids (or derivatives thereof) containing
25 at least about 34 and preferably at least about 54 carbon atoms with nitrogen containing compounds such as amine, organic hydroxy compounds such as phenols and alcohols, and/or basic inorganic materials. Examples of these "carboxylic dispersants" are described in British Patent number 1,306,529 and in many U.S. patents including the following:

30

3,163,603	3,399,141	3,574,101
3,184,474	3,415,750	3,576,743
3,215,707	3,433,744	3,630,904
3,219,666	3,444,170	3,632,510
3,271,310	3,448,048	3,632,511
3,272,746	3,448,049	3,697,428
3,281,357	3,451,933	3,725,441
3,306,908	3,454,607	4,194,886
3,311,558	3,467,668	4,234,435
3,316,177	3,501,405	4,491,527
3,340,281	3,522,179	5,696,060
3,341,542	3,541,012	5,696,067
3,346,493	3,541,678	5,779,742
3,351,552	3,542,680	RE 26,433
3,381,022	3,567,637	

- (2) Reaction products of relatively high molecular weight aliphatic or alicyclic halides with amines, preferably polyalkylene polyamines. These may be characterized as "amine dispersants" and examples thereof are described for example, in the following U.S. patents:

3,275,554	3,454,555
3,438,757	3,565,804

- (3) Reaction products of alkyl phenols in which the alkyl groups contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines), which may be characterized as "Mannich dispersants". The materials described in the following U. S. patents are illustrative:

3,413,347	3,725,480
3,697,574	3,726,882
3,725,277	

- (4) Products obtained by post-treating the carboxylic amine or Mannich dispersants with such reagents as urea, thiourea, carbon disulfide, aldehydes, ketones,

carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, phosphorus compounds or the like. Exemplary materials of this kind are described in the following U.S. patents:

3,036,003	3,282,955	3,493,520	3,639,242
3,087,936	3,312,619	3,502,677	3,649,229
3,200,107	3,366,569	3,513,093	3,649,659
3,216,936	3,367,943	3,533,945	3,658,836
3,254,025	3,373,111	3,539,633	3,697,574
3,256,185	3,403,102	3,573,010	3,702,757
3,278,550	3,442,808	3,579,450	3,703,536
3,280,234	3,455,831	3,591,598	3,704,308
3,281,428	3,455,832	3,600,372	3,708,522
			4,234,435

(5) Polymers and copolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or methacrylates, acrylamides and poly-(oxyethylene)-substituted acrylates. These may be characterized as "polymeric dispersants" and examples thereof are disclosed in the following U.S. patents:

10	3,329,658	3,666,730
	3,449,250	3,687,849
	3,519,565	3,702,300

The above-noted patents are incorporated herein by reference for their disclosures of ashless dispersants.

15 The above-illustrated other additives may each be present in lubricating compositions at a concentration of as little as 0.001% by weight, usually ranging from about 0.01% to about 20% by weight. In most instances, they each contribute from about 0.1% to about 10% by weight, more often up to about 5% by weight.

Additive Concentrates

20 The various additive compositions of this invention described herein can be added directly to the oil of lubricating viscosity. Preferably, however, they are diluted

with a substantially inert, normally liquid organic diluent such as mineral oil, a synthetic oil such as a polyalphaolefin, naphtha, benzene, toluene or xylene, to form an additive concentrate. These concentrates usually comprise about 0.1 to about 30% by weight, frequently from about 1% to about 20% by weight, more often from about 5% to about 15% by weight, of the interpolymers of this invention and may contain, in addition, one or more other additives known in the art or described hereinabove.

Additive concentrates are prepared by mixing together the desired components, often at elevated temperatures, usually less than 150° C, often no more than about 130° C, frequently no more than about 115° C.

10 Lubricating Oil Compositions

The interpolymers of this invention are useful as viscosity improving agents. They are used in viscosity improving amounts, typically minor amounts, that is less than 50% by weight of the lubricating oil composition with a major amount of an oil of lubricating viscosity, that is, the oil of lubricating viscosity comprises greater than 50% by weight of the lubricating oil composition. Preferably, they are used in amounts ranging from about 0.1 to about 5% by weight, more often from about 0.3 to about 2.5% by weight of the total weight of the lubricating oil composition.

The Oil of Lubricating Viscosity

The lubricating compositions of this invention employ an oil of lubricating viscosity, including natural or synthetic lubricating oils and mixtures thereof. Mixture of mineral oil and synthetic oils, particularly polyalphaolefin oils and polyester oils, are often used.

Natural oils include animal oils and vegetable oils (e.g. castor oil, lard oil and other vegetable acid esters) as well as mineral lubricating oils such as liquid petroleum oils and solvent-treated or acid treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Hydrotreated or hydrocracked oils are included within the scope of useful oils of lubricating viscosity.

Oils of lubricating viscosity derived from coal or shale are also useful. Synthetic lubricating oils include hydrocarbon oils and halosubstituted hydrocarbon oils such as polymerized and interpolymers of olefins, etc. and mixtures thereof, alkylbenzenes, polyphenyl, (e.g., biphenyls, terphenyls, alkylated polyphenyls, etc.), alkylated diphenyl

ethers and alkylated diphenyl sulfides and their derivatives, analogs and homologues thereof and the like.

Alkylene oxide polymers and interpolymers and derivatives thereof, and those where terminal hydroxyl groups have been modified by esterification, etherification, etc.,
5 constitute other classes of known synthetic lubricating oils that can be used.

Another suitable class of synthetic lubricating oils that can be used comprises the esters of dicarboxylic acids and those made from C₅ to C₁₂ monocarboxylic acids and polyols or polyether polyols.

Other synthetic lubricating oils include liquid esters of phosphorus-containing
10 acids, polymeric tetrahydrofurans, alkylated diphenyloxides and the like.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can used in the compositions of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. Refined oils are
15 similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils often are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

20 Specific examples of the above-described oils of lubricating viscosity are given in Chamberlin III, U.S. 4,326,972 and European Patent Publication 107,282, both of which are hereby incorporated herein by reference for relevant disclosures contained therein.

A basic, brief description of lubricant base oils appears in an article by D.V. Brock, "Lubrication Engineering", Volume 43, pages 184-5, March, 1987, which
25 article is expressly incorporated by reference for relevant disclosures contained therein.

The following examples illustrate lubricating oil compositions of this invention. All parts are parts by weight. Amounts are on an oil or diluent free basis,
30 except for products of Examples set forth herein which are as prepared, including diluent, if any.

Examples A-B

A master additive concentrate is prepared by combining 1.34 parts calcium overbased (MR 20) alkyl benzene sulfonic acid, 0.62 parts calcium overbased (MR 2.8) alkyl benzene sulfonic acid, 1.54 parts magnesium overbased (MR 14.7) alkyl benzene sulfonic acid, 16.60 parts polyisobutylene ($\overline{M}_n \sim 1750$) substituted succinic anhydride-ethylene polyamine bottoms reaction product, 7.61 parts of Zn mixed isopropyl-methyl amyl phosphorodithioate, 2.78 parts calcium overbased (MR 3.5) sulfurized alkyl phenol, 3.19 parts sulfurized butadiene-butyl acrylate Diels-Alder adduct, 0.08 parts of a kerosene solution of a commercial silicone antifoam, 1 part of sodium overbased (MR 16) polyisobutylene ($\overline{M}_n \sim 1000$) substituted succinic acid, 6.85 parts polyisobutylene ($\overline{M}_n \sim 1000$) substituted succinic anhydride-pentaerythritol-ethylene polyamine reaction product, 4.84 parts alkylated diphenyl amine and sufficient mineral oil to bring the total weight of the additive concentrate to 100 parts.

Engine oil compositions are prepared by combining 11 parts of the master concentrate, 0.02 parts by weight of a hydrogenated styrene butadiene copolymer and the indicated amount of the product of the indicated Example in sufficient mineral oil basestock (Petro-Canada SAE 5W-30) to prepare 100 parts by weight of oil composition. Details regarding each are provided in the following table:

Example	A	B	C	D	E	F
Product of Example/(pbw):	1/1.85	3/1.00	4/0.75	7/1.32	8/1.46	9/1.64
Viscosity Index (D-2270)	175	167	168	155	153	150
Shear Characteristics: 30 Pass Orbahn (D-6278) cSt @100°C	10.31	8.65	8.24	9.025	9.31	9.74
% SSI (D-6022)	17.8	49.5	67.2	38.0	30.9	20.6
Cold Cranking Vis, cP @-25°C (D-5293)	3,850	2,920	3,620	3,810	3,950	4,190
HTHS Vis, cP @150°C (D-4683)	3.44	3.11	3.29	3.21	3.20	3.24
MRV Vis cP @-35°C (D04684)	35,900	19,800	33,900	28,100	34,200	29,200

(pbw) – parts by weight

It is known that some of the materials described above may interact in the final formulation, so that the components of the final formulation may be different from those that are initially added. For instance, metal ions (of, e.g., a detergent) can migrate to other acidic sites of other molecules. The products formed thereby, including the products formed upon employing the composition of the present invention in its intended use, may not be susceptible of easy description. Nevertheless, all such modifications and reaction products are included within the scope of the present invention; the present invention encompasses the composition prepared by admixing the components described above.

Each of the documents referred to above is incorporated herein by reference. Except in the examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about". Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration.

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications that fall within the scope of the appended claims.

What is claimed is:

1 1. A lubricating oil composition comprising a major amount of an oil of
2 lubricating viscosity and a minor, viscosity improving amount, of a substantially
3 random interpolmer resulting from polymerizing (1) from about 19.5 to about 98.5
4 mole percent of ethylene; (2) from about 0.5 to about 60 mole percent of one or more
5 vinylic monomers selected from the group consisting of aromatic, hindered aliphatic,
6 and cycloaliphatic vinylic monomers; and (3) from about 1 to about 80 mole percent
7 of one or more olefinic monomers having from 3 to about 20 carbon atoms.

1 2. The lubricating oil composition of claim 1 wherein component (1) comprises
2 from about 25 to about 95 mole percent of ethylene; component (2) comprises from
3 about 1 to about 55 mole percent of one or more aromatic vinylic monomers or
4 hindered aliphatic or cycloaliphatic vinylic monomers; and component (3) comprises
5 from about 4 to about 65 mole percent of one or more olefinic monomers having from
6 3 to about 20 carbon atoms.

1 3. The lubricating oil composition of claim 2 wherein component (1) comprises
2 from about 30 to about 94 mole percent of ethylene; component (2) comprises from
3 about 1 to about 50 mole percent of one or more aromatic vinylic monomers; and
4 component (3) comprises from about 5 to about 50 mole percent of one or more
5 olefinic monomers having from 3 to about 20 carbon atoms.

1 4. The lubricating oil composition of claim 1 wherein the interpolmer has M_w
2 ranging from about 10,000 to about 700,000.

1 5. The lubricating oil composition of claim 1 wherein the interpolmer is a
2 terpolymer; component (2) is an aromatic vinylic monomer; and component (3) is an
3 alpha olefin having from 3 to about 12 carbon atoms.



1 6. The lubricating oil composition of claim 1 wherein component (2) is styrene;
2 and component (3) is one or more olefinic monomers selected from the group
3 consisting of propylene, butene-1, 4-methyl-1-pentene, pentene-1, hexene-1 and
4 octene-1.

1 7. The lubricating oil composition of claim 2 wherein the interpolymer is a
2 terpolymer; component (2) is an aromatic vinylic monomer; and component (3) is an
3 olefinic monomer having from 3 to about 12 carbon atoms.

1 8. The lubricating oil composition of claim 1 wherein the interpolymer is a
2 terpolymer; component (2) is styrene; and component (3) is selected from the group
3 consisting of propylene, butenes, hexene-1 and octene-1.

1 9. The lubricating oil composition of claim 7 wherein component (2) is styrene;
2 and component (3) is an alpha olefin having from 3 to about 8 carbon atoms.

1 10. The lubricating oil composition of claim 7 wherein component (2) is styrene;
2 and component (3) is propylene, butene-1, 4-methyl-1-pentene, pentene-1, hexene-1,
3 octene-1 or norbornene.

1 11. The lubricating oil composition of claim 10 wherein component (3) is
2 propylene.

1 12. The lubricating oil composition of claim 10 wherein component (3) is butene-1.

1 13. The lubricating oil composition of claim 10 wherein component (3) is hexene-1

1 14. The lubricating oil composition of claim 10 wherein component (3) is octene-1.

1 15. An additive concentrate comprising from about 0.1% to about 30% by weight
2 of a substantially random interpolymer resulting from polymerizing



- 3 (1) from about 19.5 to about 98.5 mole percent of ethylene;
4 (2) from about 0.5 to about 60 mole percent of one or more vinylic monomers
5 selected from the group consisting of aromatic, hindered aliphatic, and cycloaliphatic
6 vinylic monomers; and
7 (3) from about 1 to about 80 mole percent of one or more olefinic monomers
8 having from 3 to about 20 carbon atoms, and
9 from about 70% to about 99.9% by weight of a substantially inert, normally liquid,
10 organic diluent.

1 16. The additive concentrate of claim 15 further comprising at least one pour point
2 depressant.

1 17. The additive concentrate of claim 15 further comprising at least one organic
2 antioxidant.

