(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 925 657 A2

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
28.05.2008 Bulletin 2008/22

(51) Int Cl.:
C10M 143/00 *(2006.01)*

(21) Application number: **07116715.9**

(22) Date of filing: **19.09.2007**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(30) Priority: **10.10.2006 US 545703**

(71) Applicant: **Infineum International Limited
Abingdon
Oxfordshire OX13 6BB (GB)**

(72) Inventors:
- **Tse, Kwok-Leung,c/o Infineum USA L.P.
Linden, NJ 07036 (US)**
- **Emert, Jacob, c/o Infineum USA L.P.
Linden, NJ 07036 (US)**
- **Bansai, Jai, c/o Infineum USA L.P.
Linden, NJ 07036 (US)**

(74) Representative: **Goddard, Frances Anna et al
Infineum UK Limited,
PO Box 1,
Milton Hill
Abingdon,
Oxfordshire OX13 6BB (GB)**

(54) Lubricating oil compositions

(57) Lubricating oil compositions and viscosity index (VI) improver concentrates containing combinations of first polymers that arc amorphous ethylene α-olefin copolymers; and second polymers that are star polymers, the arms of which are derived from diene, and optionally vinyl aromatic hydrocarbon monomer, wherein the star polymers have a Shear Stability Index (SSI) of from about 1% to about 35% (30 cycle).

Printed by Jouve, 75001 PARIS (FR)

Description

FIELD OF THE INVENTION

[0001] The invention is directed to lubricating oil compositions formulated with blended viscosity index improver compositions. More specifically, the present invention is directed to lubricating oil compositions comprising a major amount of oil of lubricating viscosity and a viscosity index improver composition containing at least two polymeric viscosity index improvers, which lubricating oil compositions provide simultaneously improved viscometric properties, particularly at low temperatures, and shear stability performance.

BACKGROUND OF THE INVENTION

[0002] Lubricating oil compositions for use in crankcase engine oils comprise a major amount of base oil and minor amounts of additives that improve the performance and increase the useful life of the lubricant. Crankcase lubricating oil compositions conventionally contain polymeric components that are used to improve the viscometric performance of the engine oil, i.e., to provide multigrade oils such as SAE 5W-30, 10W-30, 10W-40 and 15W-40. These viscosity performance enhancing material, commonly referred to as viscosity index (VI) improvers, can increase the viscosity of a lubricating oil formulation at higher temperatures (typically above 100°C) without increasing excessively the high shear rate viscosity at lower temperatures (typically -10 to -35°C). These oil-soluble polymers are generally of higher molecular weight (>100,000 M_n) compared to the base oil and other components. Well known classes of polymers suitable for use as viscosity index improvers for lubricating oil compositions include ethylene α-olefin copolymers, polymethacrylates, diblock copolymers having a vinyl aromatic segment and a hydrogenated polydiene segment, and star copolymers and hydrogenated isoprene linear and star polymers.

[0003] Viscosity index improvers for lubricating oil compositions advantageously increase the viscosity of the lubricating oil composition at higher temperatures when used in relatively small amounts (have a high thickening efficiency (TE)), provide reduced lubricating oil resistance to cold engine starting (as measured by "CCS" performance) and be resistant to mechanical degradation and reduction in molecular weight in use (have a low shear stability index (SSI)). Further, as viscosity index improving polymers are often provided to lubricant blenders as a concentrate in which the viscosity index improving polymer is diluted in oil, which concentrate is then blended into a greater volume of oil to provide the desired lubricant product, it is further preferred that viscosity index improving polymers can be blended into concentrates in relatively large amounts, without causing the concentrate to have an excessively high kinematic viscosity. Some polymers are excellent in some of the above properties, but are deficient in one or more of the others.

[0004] Amorphous olefin copolymers (OCP) are one class of VI improver. Conventionally, OCP are copolymers of ethylene and propylene monomers (EPM) and optionally a diene monomer (EPDM). Amorphous OCP has very low, or no crystallinity and are relatively insensitive to base stock and pour point depressant selection. However, amorphous OCP provide relatively poor thickening efficiency (TE) in oil for a given shear stability index (30-cycle SSI).

[0005] Semi-crystalline OCP show improved TE in oil for a given SSI, however, the crystalline nature of such copolymers causes both intermolecular and intramolecular interactions, which leads to network formations. Formation of such networks causes difficulties in handling of copolymer concentrates, even at room temperature, and interactions between such copolymers and base stocks can lead to poor low temperature viscometric properties, such as high MRV viscosities and scanning Brookfield gelation index values.

[0006] Star polymers are a third class of VI improver. The arms of the star polymers are derived from diene, and optionally, vinyl aromatic hydrocarbon monomer. Star polymers provide improved TE and SSI (30-cycle) relative to semi-crystalline OCP. However, when the number of cycles of the test used to measure SSI are extended (a 90 cycle shear stability test (ASTM D7109) was approved in 2004), the kinematic viscosity (kv_{100}) of star polymer-containing solutions continue to decrease, while the kv_{100} of an OCP-containing solution approaches an asymptotic value (see Shear Stability Index of Viscosity Modifiers - Effect of Polymer Architecture, presented by Huang et al. at the 8th Annual Fuels and Lubes Asian Conference and Exhibition, Singapore, 2002).

[0007] It would be advantageous to be able provide lubricating oil compositions that provide simultaneously the high overall thickening efficiency and concentrate-handling properties of a star polymer, and the low temperature viscometric performance and extended shear stability performance of an amorphous or semi-crystalline OCP.

[0008] PCT Publication WO 96/17041, June 6, 1996, discloses certain blends of star-branched styrene-isoprene polymers and ethylene α-olefin copolymers. The publication describes the addition of an amount of the ethylene α-olefin copolymer to the star-branched styrene-isoprene polymer as being effective to improve the dimensional stability of the star branched polymer so that the star branched polymer can be formed as a stable, solid bale.

[0009] U.S. Patent No. 4,194,057, March 18, 1980, discloses viscosity index improving compositions containing a combination of a certain class of relatively low molecular weight vinyl aromatic/conjugated diene diblock copolymers and ethylene α-olefin copolymer. The patent describes the specified class of vinyl aromatic/conjugated diene diblock copolymer as being relatively insoluble in oil and that blending with ethylene α-olefin copolymer improves solubility and allows for the formation of polymer concentrates.

[0010] PCT Publication WO 2004/087849, October 14, 2004, discloses a viscosity index improver composition containing a blend of a select class of high ethylene content ethylene α-olefin copolymer, and vinyl aromatic/diene diblock copolymer, in certain proportions, which are describes as providing good low temperature performance and durability.

SUMMARY OF THE INVENTION

[0011] In accordance with a first aspect of the invention, there is provided a lubricating oil composition comprising a major amount of oil of lubricating viscosity, and a viscosity index (VI) improver composition comprising a first polymer that is an amorphous or semi-crystalline ethylene α-olefin copolymer comprising no greater than 66 mass % of units derived from ethylene; and a second polymer comprising a star polymer, the arms of which are derived from diene, and optionally vinyl aromatic hydrocarbon monomer, wherein the star polymer has a Shear Stability Index (SSI) of from about 1% to about 35% (30 cycle).

[0012] In accordance with a second aspect of the invention, there is provided a lubricating oil composition of the first aspect in which the first polymer and the second polymer are present in a mass % ratio of from about 80:20 to about 20:80.

[0013] In accordance with a third aspect of the invention, there is provided a lubricating oil composition as in the first or second aspect, further comprising a nitrogenous dispersant derived from a polyalkene having a number average molecular weight (M_n) of greater than about 1500

[0014] In accordance with a fourth aspect of the invention, there is provided a lubricating oil composition, as in the first, second or thirds aspects, wherein the base oil of the lubricating oil composition has a saturates content of at least about 80%, and said lubricating oil composition contains less than about 0.4 mass % of sulfur, less than about 0.12 mass % phosphorus and less than about 1.2 mass % of sulfated ash.

[0015] In accordance with a fifth aspect of the invention, there is provided a VI improver concentrate comprising diluent oil, a first polymer that is an amorphous ethylene α-olefin copolymer having a crystallinity of less than 1.0 %; and a second polymer comprising a star polymer, the arms of which are derived from diene, and optionally vinyl aromatic hydrocarbon monomer, wherein the star polymer has a Shear Stability Index (SSI) of from about 1% to about 35% (30 cycle), wherein the total amount of polymer in the concentrate (including at least the first polymer and the second polymer) is at least 5 mass%, based on the total mass of the concentrate.

[0016] Other and further objects, advantages and features of the present invention will be understood by reference to the following specification.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Ethylene-α-olefin copolymers (OCP) useful in the practice of the invention include amorphous OCP synthesized from ethylene monomer and at least one other α-olefin comonomer. The average mass % of the OCP derived from ethylene (hereinafter "ethylene content") of OCP useful in the present invention can be as low as about 20 mass %, preferably no lower than about 25 mass %; more preferably no lower than about 30 mass %. The maximum ethylene content can be about 66 mass %. Preferably the ethylene content of the OCP is from about 25 to 55 mass %, more preferably from about 35 to 55 mass %.

[0018] Ethylene content can be measured by ASTM-D3900 for ethylene-propylene copolymers containing between 35 mass % and 85 mass % ethylene. Above 85 mass %, ASTM-D2238 can be used to obtain methyl group concentration, which is related to percent ethylene in an unambiguous manner for ethylene-propylene copolymers. When comonomers other than propylene are employed, no ASTM tests covering a wide range of ethylene contents are available; however, proton and carbon-13 nuclear magnetic resonance spectroscopy can be employed to determine the composition of such polymers. These are absolute techniques requiring no calibration when operated such that all nuclei of a given element contribute equally to the spectra. For ethylene content ranges not covered by the ASTM tests for ethylene-propylene copolymers, as well as for any ethylene-propylene copolymers, the aforementioned nuclear magnetic resonance methods can also be used.

[0019] "Crystallinity" is defined as:

$$\text{Crystallinity (\%)} = (\text{Heat of Fusion of (co)polymer in J/g}) / 292\ \text{J/g} \times 100;$$

wherein heat of fusion is determined by DSC and 292 J/g is the heat of fusion for polyethylene (see SAE Paper No. 971696; "Evaluation of Polyolefin Elastomers Produced by Constrained Geometry Chemistry as Viscosity Modifiers for Engine Oil", McGirk et al. (1997)).

[0020] As noted, the ethylene-α-olefin copolymers are comprised of ethylene and at least one other α-olefin. The "other" α-olefins typically include those containing 3 to 18 carbon atoms, e.g., propylene, butene-1, pentene-1, etc. Preferred are α-olefins having 3 to 6 carbon atoms, particularly for economic reasons. The most preferred OCP are those comprised of ethylene and propylene.

[0021] As is well known to those skilled in the art, copolymers of ethylene and higher alpha-olefins such as propylene can optionally include other polymerizable monomers. Typical of these other monomers are non-conjugated dienes such as the following non-limiting examples:

a. straight chain acyclic dienes such as: 1,4-hexadiene; 1,6-octadiene;
b. branched chain acyclic dienes such as: 5-methyl-1, 4-hexadiene; 3, 7-dimethyl-1,6-octadiene; 3, 7-dimethyl-1,7-octadiene and the mixed isomers of dihydro-mycene and dihydroocinene;
c. single ring alicyclic dienes such as: 1, 4-cyclohexadiene; 1,5-cyclooctadiene; and 1,5-cyclododecadiene; and
d. multi-ring alicyclic fused and bridged ring dienes such as: tetrahydroindene; methyltetrahydroindene; dicyclopentadiene; bicyclo-(2,2,1)-hepta-2, 5-diene; alkenyl, alkylidene, cycloalkenyl and cycloalkylidene norbornenes such as 5-methylene-2-norbornene (MNB), 5-ethylidene-2-norbornene (ENB), 5-propylene-2-norbornene, 5-isopropylidene-2-norbornene, 5-(4-cyclopentenyl)-2-norbornene; 5-cyclohexylidene-2-norbornene.

[0022] Of the non-conjugated dienes typically used to prepare these copolymers, dienes containing at least one of the double bonds in a strained ring are preferred. The most preferred diene is 5-ethylidene-2-norbornene (ENB). When present, the amount of diene (on a weight basis) in the copolymer can be from greater than 0% to about 20%; preferably from greater than 0% to about 15%; most preferably greater than 0% to about 10%. OCP VI improver useful in the practice of the present invention is preferably ethylene-propylene copolymer containing less than 2 % of diene units

[0023] The molecular weight of OCP useful in accordance with the present invention can vary over a wide range since ethylene copolymers having number-average molecular weights (M_n) as low as about 2,000 can affect the viscosity properties of an oleaginous composition. The preferred minimum M_n is about 10,000; the most preferred minimum is about 20,000. The maximum M_n can be as high as about 12,000,000; the preferred maximum is about 1,000,000; the most preferred maximum is about 750,000. An especially preferred range of number-average molecular weight for OCP useful in the present invention is from about 15,000 to about 500,000; preferably from about 20,000 to about 250,000; more preferably from about 25,000 to about 150,000. The term "number average molecular weight", as used herein, refers to the number average weight as measured by Gel Permeation Chromatography ("GPC") with a polystyrene standard.

[0024] Useful OCP include those prepared in bulk, suspension, solution or emulsion. As is well known, polymerization of monomers to produce hydrocarbon polymers may be accomplished using free-radical, cationic and anionic initiators or polymerization catalysts, such as transition metal catalysts used for Ziegler-Natta and metallocene type (also referred to as "single-site") catalysts.

[0025] "Thickening Efficiency" ("TE") is representative of a polymers ability to thicken oil per unit mass and is defined as:

$$TE = \frac{2}{c \ln 2} \ln\left(\frac{kv_{oil+polymer}}{kv_{oil}}\right);$$

wherein c is polymer concentration (grams of polymer/100 grams solution), $kv_{oil + polymer}$ is kinematic viscosity of the polymer in the reference oil, and kv_{oil} is kinematic viscosity of the reference oil.

[0026] "Shear Stability Index" ("SSI") measures the ability of polymers used as V.I. improvers in crankcase lubricants to maintain thickening power during use and is indicative of the resistance of a polymer to degradation under service conditions. The higher the SSI, the less stable the polymer, i.e., the more susceptible it is to degradation. SSI is defined as the percentage of polymer-derived viscosity loss and is calculated as follows:

$$SSI = 100 \times \frac{kv_{fresh} - kv_{after}}{kv_{fresh} - kv_{oil}};$$

wherein kv_{fresh} is the kinematic viscosity of the polymer-containing solution before degradation and kv_{after} is the kinematic viscosity of the polymer-containing solution after degradation. SSI is conventionally determined using ASTM D6278-98 (known as the Kurt-Orban (KO) or DIN bench test). The polymer under test is dissolved in suitable base oil (for example, solvent extracted 150 neutral) to a relative viscosity of 9 to 15 centistokes at 100°C and the resulting fluid is pumped through the testing apparatus specified in the ASTM D6278-98 protocol for 30 cycles. As noted above, a 90 cycle shear stability test (ASTM D7109) was approved in 2004.

[0027] "Viscosity Loss" measures the ability of the V.I polymer in a formulated lubricant to maintain thickening power in use and is defined as:

$$\text{Viscosity Loss (\%)} = kv_{fresh} - kv_{used}/kv_{fresh} \text{ x } 100.$$

[0028] "Cold Cranking Simulator" ("CCS") is a measure of the cold-cranking characteristics of crankcase lubricants and is conventionally determined using a technique described in ASTM D5293-92.

[0029] The OCP of the present invention preferably has an SSI (30 cycles) of from about 15 to about 60 %, preferably from about 20 % to about 55%, more preferably from about 25% to about 50 %. The OCP of the present invention preferably has a TE of from about 1.5 to about 4.0, preferably from about 1.6 to about 3.3, more preferably from about 1.7 to about 3.0.

[0030] In one preferred embodiment, the OCP VI improver of the present invention is an amorphous ethylene-propylene copolymer or copolymer blend having an SSI (30 cycle) of about 20 to about 55 %. More preferably, such OCP VI improver is either produced via Ziegler-Natta catalysis and contains from about 40 mass % to about 55 mass % of ethylene, or is produced via single site (metallocene) catalysis and contains from about 35 mass % to about 55 mass % of ethylene.

[0031] The star (or radial) polymers or copolymers useful in the practice of the present invention have multiple arms derived from diene, and optionally vinyl aromatic hydrocarbon monomer, and have a Shear Stability Index (SSI) of from about 1% to about 35% (30 cycle). Dienes, or diolefins, contain two double bonds, commonly located in conjugation in a 1,3 relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered within the definition of "diene" as used herein. Useful dienes include those containing from 4 to about 12 carbon atoms, such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, 4,5-diethyl-1,3-octadiene, with 1,3-butadiene and isoprene and mixtures thereof being preferred. Preferred isoprene monomers that may be used as the precursors of the copolymers of the present invention can be incorporated into the polymer as either 1,4- or 3,4-configuration units, and mixtures thereof. Preferably, the majority of the isoprene is incorporated into the polymer as 1,4-units, such as greater than about 60 wt.%, more preferably greater than about 80 wt.%, such as about 80 to 100 wt.%, most preferably greater than about 90 wt.%., such as about 93 wt.% to 100 wt.%. Preferred butadiene monomers that may be used as the precursors of the copolymers of the present invention can be incorporated into the polymer as either as either 1,2- or 1,4-configuration units. Preferably, at least about 70 wt. %, such as at least about 75 wt. %, more preferably at least about 80 wt. %, such as at least about 85 wt. %, most preferably at least about 90, such as 95 to 100 wt. %, of the butadiene is incorporated into the polymer as 1,4- units.

[0032] Useful vinyl aromatic hydrocarbon monomers include those containing from 8 to about 16 carbon atoms such as aryl-substituted styrenes, alkoxy-substituted styrenes, vinyl naphthalene, alkyl-substituted vinyl naphthalenes and the like. Dienes, or diolefins, contain two double bonds, commonly located in conjugation in a 1,3-relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered within the definition of "diene" as used herein. Useful dienes include those containing from 4 to about 12 carbon atoms, such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene, 4,5-diethyl-1,3-octadiene, with 1,3-butadiene and isoprene being preferred.

[0033] The arms of the star polymer may be a homopolymer of a diene, e.g., polyisoprene, a copolymer of two or more dienes; e.g., an isoprene-butadiene copolymer; or a copolymer of a diene and another monomer, e.g., an isoprene-styrene copolymer.

[0034] The arms of the star polymer may also be a block copolymer such as one represented by the following general formula:

$$A_z\text{-}(B\text{-}A)_y\text{-}B_x$$

wherein:

A is a polymeric block derived predominantly vinyl aromatic hydrocarbon monomer;
B is a polymeric block derived predominantly conjugated diene monomer;
x and z are, independently, a number equal to 0 or 1; and
y is a whole number ranging from 1 to about 15.

[0035] The arms of the star polymer may also be a tapered linear block copolymer such as one represented by the following general formula:

A-A/B-B

wherein:

A is a polymeric block derived predominantly from vinyl aromatic hydrocarbon monomer;
B is a polymeric block derived predominantly conjugated diolefin monomer; and
A/B is a tapered segment derived from both vinyl aromatic hydrocarbon monomer and conjugated diolefin monomer.

[0036] As used herein in connection with polymer block composition, "predominantly" means that the specified monomer or monomer type that is the principle component in that polymer block is present in an amount of at least 85% by weight of the block.

[0037] Preferably, the arms of the star polymer are formed via anionic polymerization to form a living polymer. Anionic polymerization has been found to provide copolymers having a narrow molecular weight distribution (Mw/Mn), such as a molecular weight distribution of less than about 1.2

[0038] As is well known, and disclosed, for example, in U.S. Patent No. 4,116,917, living polymers may be prepared by anionic solution polymerization of a mixture of the conjugated diene monomers in the presence of an alkali metal or an alkali metal hydrocarbon, e.g., sodium naphthalene, as anionic initiator. The preferred initiator is lithium or a monolithium hydrocarbon. Suitable lithium hydrocarbons include unsaturated compounds such as allyl lithium, methallyl lithium; aromatic compounds such as phenyllithium, the tolyllithiums, the xylyllithiums and the naphthyllithiums, and in particular, the alkyl lithiums such as methyllithium, ethyllithium, propyllithium, butyllithium, amyllithium, hexyllithium, 2-ethylhexyllithium and n-hexadecyllithium. Secondary-butyllithium is the preferred initiator. The initiator(s) may be added to the polymerization mixture in two or more stages, optionally together with additional monomer. The living polymers are olefinically unsaturated.

[0039] The solvents in which the living polymers are formed are inert liquid solvents, such as hydrocarbons e.g., aliphatic hydrocarbons such as pentane, hexane, heptane, octane, 2-ethylhexane, nonane, decane, cyclohexane, methylcyclohexane, or aromatic hydrocarbons e.g., benzene, toluene, ethylbenzene, the xylenes, diethylbenzenes, propylbenzenes. Cyclohexane is preferred. Mixtures of hydrocarbons e.g., lubricating oils, may also be used.

[0040] The temperature at which the polymerization is conducted may be varied within a wide range, such as from about -50°C to about 150°C, preferably from about 20°C to about 80°C. The reaction is suitably carried out in an inert atmosphere, such as nitrogen, and may optionally be carried out under pressure e.g., a pressure of from about 0.5 to about 10 bars.

[0041] The concentration of the initiator used to prepare the living polymer may also vary within a wide range and is determined by the desired molecular weight of the living polymer.

[0042] To form the star polymer, the living polymers formed via the foregoing process are reacted in an additional reaction step, with a polyalkenyl coupling agent. Polyalkenyl coupling agents capable of forming star polymers have been known for a number of years and are described, for example, in U.S. Patent No. 3,985,830. Polyalkenyl coupling agents are conventionally compounds having at least two non-conjugated alkenyl groups. Such groups are usually attached to the same or different electron-withdrawing moiety e.g. an aromatic nucleus. Such compounds have the property that at least of the alkenyl groups are capable of independent reaction with different living polymers and in this respect are different from conventional conjugated diene polymerizable monomers such as butadiene, isoprene, etc. Pure or technical grade polyalkenyl coupling agents may be used. Such compounds may be aliphatic, aromatic or heterocyclic. Examples of aliphatic compounds include the polyvinyl and polyallyl acetylene, diacetylenes, phosphates and phosphates as well as dimethacrylates, e.g. ethylene dimethylacrylate. Examples of suitable heterocyclic compounds include divinyl pyridine and divinyl thiophene.

[0043] The preferred coupling agents are polyalkenyl aromatic compounds and most preferred are the polyvinyl aromatic compounds. Examples of such compounds include those aromatic compounds, e.g. benzene, toluene, xylene, anthracene, naphthalene and durene, which are substituted with at least two alkenyl groups, preferably attached directly thereto. Specific examples include the polyvinyl benzenes e.g. divinyl, trivinyl and tetravinyl benzenes; divinyl, trivinyl and tetravinyl ortho-, meta- and para-xylenes, divinyl naphthalene, divinyl ethyl benzene, divinyl biphenyl, diisobutenyl benzene, diisopropenyl benzene, and diisopropenyl biphenyl. The preferred aromatic compounds are those represented by the formula $A\text{-}(CH{=}CH_2)_x$ wherein A is an optionally substituted aromatic nucleus and x is an integer of at least 2. Divinyl benzene, in particular meta-divinyl benzene, is the most preferred aromatic compound. Pure or technical grade divinyl benzene (containing other monomers e.g. styrene and ethyl styrene) may be used. The coupling agents may be used in admixture with small amounts of added monomers which increase the size of the nucleus, e.g. styrene or alkyl styrene. In such a case, the nucleus can be described as a poly(dialkenyl coupling agent/monoalkenyl aromatic compound) nucleus, e.g. a poly(divinylbenzene/monoalkenyl aromatic compound) nucleus.

[0044] The polyalkenyl coupling agent should be added to the living polymer after the polymerization of the monomers is substantially complete, i.e. the agent should be added only after substantially all the monomer has been converted to the living polymers.

[0045] The amount of polyalkenyl coupling agent added may vary within a wide range, but preferably, at least 0.5 mole of the coupling agent is used per mole of unsaturated living polymer. Amounts of from about 1 to about 15 moles, preferably from about 1.5 to about 5 moles per mole of living polymer are preferred. The amount, which can be added in two or more stages, is usually an amount sufficient to convert at least about 80 mass % to 85 mass % of the living polymer into star-shaped polymer.

[0046] The coupling reaction can be carried out in the same solvent as the living polymerization reaction. The coupling reaction can be carried out at temperatures within a broad range, such as from 0°C to 150°C, preferably from about 20°C to about 120°C. The reaction may be conducted in an inert atmosphere, e.g. nitrogen, and under pressure of from about 0.5 bar to about 10 bars.

[0047] The star polymers thus formed are characterized by a dense center or nucleus of crosslinked poly(polyalkenyl coupling agent) and a number of arms of substantially linear unsaturated polymers extending outward from the nucleus. The number of arms may vary considerably, but is typically between about 4 and 25.

[0048] The resulting star polymers can then be hydrogenated using any suitable means. A hydrogenation catalyst may be used e.g. a copper or molybdenum compound. Catalysts containing noble metals, or noble metal-containing compounds, can also be used. Preferred hydrogenation catalysts contain a non-noble metal or a non-noble metal-containing compound of Group VIII of the periodic Table i.e., iron, cobalt, and particularly, nickel. Specific examples of preferred hydrogenation catalysts include Raney nickel and nickel on kieselguhr. Particularly suitable hydrogenation catalysts are those obtained by causing metal hydrocarbyl compounds to react with organic compounds of any one of the group VIII metals iron, cobalt or nickel, the latter compounds containing at least one organic compound that is attached to the metal atom via an oxygen atom as described, for example, in U.K. Patent No. 1,030,306. Preference is given to hydrogenation catalysts obtained by causing an aluminum trialkyl (e.g. aluminum triethyl ($Al(Et_3)$) or aluminum triisobutyl) to react with a nickel salt of an organic acid (e.g. nickel diisopropyl salicylate, nickel naphthenate, nickel 2-ethyl hexanoate, nickel di-tert-butyl benzoate, nickel salts of saturated monocarboxylic acids obtained by reaction of olefins having from 4 to 20 carbon atoms in the molecule with carbon monoxide and water in the presence of acid catalysts) or with nickel enolates or phenolates (e.g., nickel acetonylacetonate, the nickel salt of butylacetophenone). Suitable hydrogenation catalysts will be well known to those skilled in the art and the foregoing list is by no means intended to be exhaustive.

[0049] The hydrogenation of the star polymer is suitably conducted in solution, in a solvent which is inert during the hydrogenation reaction. Saturated hydrocarbons and mixtures of saturated hydrocarbons are suitable. Advantageously, the hydrogenation solvent is the same as the solvent in which polymerization is conducted. Suitably, at least 50%, preferably at least 70%, more preferably at least 90%, most preferably at least 95% of the original olefinic unsaturation is hydrogenated.

[0050] The hydrogenated star polymer may then be recovered in solid form from the solvent in which it is hydrogenated by any convenient means, such as by evaporating the solvent. Alternatively, oil e.g. lubricating oil, may be added to the solution, and the solvent stripped off from the mixture so formed to provide a concentrate. Suitable concentrates contain from about 3 mass % to about 25 mass %, preferably from about 5 mass % to about 15 mass % of the hydrogenated star polymer VI improver.

[0051] The star polymers useful in the practice of the present invention can have a number average molecular weight of from about 10,000 to 700,000, preferably from about 30,000 to 500,000. The term "number average molecular weight", as used herein, refers to the number average weight as measured by Gel Permeation Chromatography ("GPC") with a polystyrene standard, subsequent to hydrogenation. It is important to note that, when determining the number average molecular weight of a star polymer using this method, the calculated number average molecular weight will be less than the actual molecular weight due to the three dimensional structure of the star polymer.

[0052] In one preferred embodiment, the star polymer of the present invention is derived from about 75 % to about 90 % isoprene and about 10 % to about butadiene, and greater than 80 % of the butadiene units are incorporated 1,4-addition product. In another preferred embodiment, the star polymer of the present invention comprises amorphous butadiene units derived from about 30 to about 80 % 1,2-, and from about 20 to about 70 % 1,4-incorporation of butadiene. In another preferred embodiment, the star polymer is derived from isoprene, butadiene, or a mixture thereof, and further contains from about 5 to about 35 % styrene units.

[0053] Optionally, one or both types of VI improvers used in the practice of the invention can be provided with nitrogen-containing functional groups that impart dispersant capabilities to the VI improver. One trend in the industry has been to use such "multifunctional" VI improvers in lubricants to replace some or all of the dispersant. Nitrogen-containing functional groups can be added to a polymeric VI improver by grafting a nitrogen- or hydroxyl- containing moiety, preferably a nitrogen-containing moiety, onto the polymeric backbone of the VI improver (functionalizing). Processes for the grafting of a nitrogen-containing moiety onto a polymer are known in the art and include, for example, contacting the polymer and nitrogen-containing moiety in the presence of a free radical initiator, either neat, or in the presence of a solvent. The free radical initiator may be generated by shearing (as in an extruder) or heating a free radical initiator precursor, such as hydrogen peroxide.

[0054] The amount of nitrogen-containing grafting monomer will depend, to some extent, on the nature of the substrate polymer and the level of dispersancy required of the grafted polymer. To impart dispersancy characteristics to both star and linear copolymers, the amount of grafted nitrogen-containing monomer is suitably between about 0.4 and about 2.2 wt. %, preferably from about 0.5 to about 1.8 wt. %, most preferably from about 0.6 to about 1.2 wt. %, based on the total weight of grafted polymer.

[0055] Methods for grafting nitrogen-containing monomer onto polymer backbones, and suitable nitrogen-containing grafting monomers are known and described, for example, in U.S. Patent No. 5,141,996, WO 98/13443, WO 99/21902, U.S. Patent No. 4,146,489, U.S. Patent No. 4,292,414, and U.S. Patent No. 4,506,056. (See also J Polymer Science, Part A: Polymer Chemistry, Vol. 26, 1189-1198 (1988); J. Polymer Science, Polymer Letters, Vol. 20, 481-486 (1982) and J. Polymer Science, Polymer Letters, Vol. 21, 23-30 (1983), all to Gaylord and Mehta and Degradation and Crosslinking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides; J. Applied Polymer Science, Vol. 33, 2549-2558 (1987) to Gaylord, Mehta and Mehta.

[0056] Both the amorphous OCP and star polymer components of the present invention are available individually as commercial products. Infineum V534™ and Infineum V501™ available from Infineum USA L.P. and Infineum UK Ltd. are examples of commercially available amorphous OCP. Other examples of commercially available amorphous OCP VI improvers include Lubrizol 7065™ and Lubrizol 7075™, available from The Lubrizol Corporation; Jilin 0010™, available from PetroChina Jilin Petrochemical Company; and NDR0135™, available from Dow Elastomers L.L.C. An example of a commercially available star polymer VI improver having an SSI equal to or less than 35 is Infineum SV200™, available from Infineum USA L.P. and Infineum UK Ltd. Other examples of commercially available star polymer VI improver having an SSI equal to or less than 35 include Infineum SV250™, and Infineum SV270™, also available from Infineum USA L.P. and Infineum UK Ltd.

[0057] Compositions of the present invention contain the specified OCP and star polymers in a mass % ratio of from about 80:20 to about 20:80, preferably from about 35:65 to about 65:35; more preferably from about 45:55 to about 55:45. The polymer compositions of the invention can be provided in the form of a dimensionally stable, compounded solid polymer blend, or as a concentrate, containing from about 3 to about 20 mass %, preferably from about 6 to about 16 mass %, more preferably from about 9 to about 12 mass % of polymer, in oil. Alternatively, concentrates in accordance with present invention may comprise from about 0.6 to about 16.0 mass %, preferably from about 2.1 to about 10.4 mass %, more preferably from about 4.0 to about 6.6 mass % of amorphous OCP and from about 2.1 to about 10.4 mass %, preferably from about 4.0 to about 6.6 mass % of the star polymer.

[0058] Such concentrates may contain the polymer blend as the only additive, or may further comprise additional additives, particularly other polymeric additives, such as lubricating oil flow improver ("LOFI"), also commonly referred to as pour point depressant ("PPD"). The LOFI or PPD is used to lower the minimum temperature at which the fluid will flow or can be poured and such additives are well known. Typical of such additives are C_8 to C_{18} dialkyl fumarate/vinyl acetate copolymers, polymethacrylates and styrene/maleic anhydride ester copolymers. Concentrates of the present invention may contain from about 0 to about 5 mass % of LOFI. Preferably, at least about 98 mass %, more preferably at least about 99.5 mass %, of the concentrates of the present invention are VI improver, LOFI and diluent oil.

[0059] Such VI improver concentrates can be prepared by dissolving the VI improver polymer(s), and optional LOFI, in diluent oil using well known techniques. When dissolving a solid VI improver polymer to form a concentrate, the high viscosity of the polymer can cause poor diffusivity in the diluent oil. To facilitate dissolution, it is common to increase the surface are of the polymer by, for example, pelletizing, chopping, grinding or pulverizing the polymer. The temperature of the diluent oil can also be increased by heating using, for example, steam or hot oil. When the diluent temperature is greatly increased (such as to above 100°C), heating should be conducted under a blanket of inert gas (e.g., N_2 or CO_2). The temperature of the polymer may also be raised using, for example, mechanical energy imparted to the polymer in an extruder or masticator. The polymer temperature can be raised above 150°C; the polymer temperature is preferably raised under a blanket of inert gas. Dissolving of the polymer may also be aided by agitating the concentrate, such as by stirring or agitating (in either the reactor or in a tank), or by using a recirculation pump. Any two or more of the foregoing techniques can also be used in combination. Concentrates can also be formed by exchanging the polymerization solvent (usually a volatile hydrocarbon such as, for example, propane, hexane or cyclohexane) with oil. This exchange can be accomplished by, for example, using a distillation column to assure that substantially none of the polymerization solvent remains.

[0060] To provide a fully formulated lubricant, the solid copolymer or VI improver concentrate can be dissolved in a major amount of an oil of lubricating viscosity together with an additive package containing other necessary or desired lubricant additives. Fully formulated lubricants in accordance with the present invention may comprise from about 0.4 to about 2.5 mass %, preferably from about 0.6 to about 1.7 mass %, more preferably from about 0.8 to about 1.2 mass % of the polymer composition of the present invention, in oil. Alternatively, fully formulated lubricants in accordance with the present invention may comprise from about 0.1 to about 2.0 mass %, preferably from about 0.2 to about 1.1 mass %, more preferably from about 0.4 to about 0.7 mass % of OCP and from about 0.1 to about 2.0 mass %, preferably from about 0.2 to about 1.1 mass % of the star polymer.

[0061] Oils of lubricating viscosity that are useful in the practice of the present invention may be selected from natural oils, synthetic oils and mixtures thereof.

[0062] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0063] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivative, analogs and homologs thereof.

[0064] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_3-C_8 fatty acid esters and C_{13} Oxo acid diester of tetraethylene glycol.

[0065] Another suitable class of synthetic oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Examples of such esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0066] Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0067] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl) disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorous-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0068] The oil of lubricating viscosity useful in the practice of the present invention may comprise one or more of a Group I Group II, Group III, Group IV or Group V oil or blends of the aforementioned oils. Definitions for the oils as used herein are the same as those found in the American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998. Said publication categorizes oils as follows:

a) Group I oils contain less than 90 percent saturates and/or greater than 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1.

b) Group II oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table 1. Although not a separate Group recognized by the API, Group II oils having a viscosity index greater than about 110 are often referred to as "Group II+" oils.

c) Group III oils contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table 1.

d) Group IV oils are polyalphaolefins (PAO).

e) Group V oils are all other base stocks not included in Group I, II, III, or IV.

Property	Test Method
Saturates	ASTM D2007
Viscosity Index	ASTM D2270
Sulfur	ASTM D4294

[0069] Preferably the volatility of the oil of lubricating viscosity, as measured by the Noack test (ASTM D5880), is less than or equal to about 40%, such as less than or equal to about 35%, preferably less than or equal to about 32%, such as less than or equal to about 28%, more preferably less than or equal to about 16%. Preferably, the viscosity index (VI) of the oil of lubricating viscosity is at least 100, preferably at least 110, more preferably greater than 120.

[0070] In addition to the VI improver and LOFI, a fully formulated lubricant can generally contain a number of other performance improving additives selected from ashless dispersants, metal-containing, or ash-forming detergents, anti-wear agents, oxidation inhibitors or antioxidants, friction modifiers and fuel economy agents, and stabilizers or emulsifiers. Conventionally, when formulating a lubricant, the VI improver and/or VI improver and LOFI, will be provided to the formulator in one concentrated package, and combinations of the remaining additives will provided in one or more additional concentrated packages, oftentimes referred to as DI (dispersant-inhibitor) packages.

[0071] Dispersants useful in the context of the present invention include the range of nitrogen-containing, ashless (metal-free) dispersants known to be effective to reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. The ashless, dispersants of the present invention comprise an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants have amine, amine-alcohol or amide polar moieties attached to the polymer backbone, often via a bridging group. The ashless dispersant may be, for example, selected from oil soluble salts, esters, amino-esters, amides, imides and oxazolines of long chain hydrocarbon-substituted mono- and polycarboxylic acids or anhydrides thereof; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

[0072] Preferred dispersant compositions for use with the VI improving copolymers of the present invention are nitrogen-containing dispersants derived from polyalkenyl-substituted mono- or dicarboxylic acid, anhydride or ester, which dispersant has a polyalkenyl moiety with a number average molecular weight of from about 1500 to 3000, preferably from about 1800 to 2500. Further preferable, are succinimide dispersants derived from polyalkenyl moieties with a number average molecular weight of from about 1800 to 2500 and from about 1.2 to about 1.7, preferably from greater than about 1.3 to about 1.6, most preferably from greater than about 1.3 to about 1.5 functional groups (mono- or dicarboxylic acid producing moieties) per polyalkenyl moiety (a medium functionality dispersant). Functionality (F) can be determined according to the following formula:

$$F = (SAP \text{ x } M_n)/((112,200 \text{ x A.I.}) - (SAP \text{ x } 98))$$

wherein SAP is the saponification number (i.e., the number of milligrams of KOH consumed in the complete neutralization of the acid groups in one gram of the succinic-containing reaction product, as determined according to ASTM D94); M_n is the number average molecular weight of the starting olefin polymer; and A.I. is the percent active ingredient of the succinic-containing reaction product (the remainder being unreacted olefin polymer, succinic anhydride and diluent).

[0073] Generally, each mono- or dicarboxylic acid-producing moiety will react with a nucleophilic group (amine, alcohol, amide or ester polar moieties) and the number of functional groups in the polyalkenyl-substituted carboxylic acylating agent will determine the number of nucleophilic groups in the finished dispersant.

[0074] A preferred dispersant composition is one comprising at least one polyalkenyl succinimide, which is the reaction product of a polyalkenyl substituted succinic anhydride (e.g., PIBSA) and a polyamine (PAM) that has a coupling ratio of from about 0.65 to about 1.25, preferably from about 0.8 to about 1.1, most preferably from about 0.9 to about 1. In the context of this disclosure, "coupling ratio" may be defined as a ratio of succinyl groups in the PIBSA to primary amine groups in the polyamine reactant.

[0075] The dispersant(s) are preferably non-polymeric (e.g., are mono- or bis-succinimides). The dispersant(s) of the present invention can be borated by conventional means, as generally taught in U.S. Patent Nos. 3,087,936, 3,254,025 and 5,430,105. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound such as boron oxide, boron halide boron acids, and esters of boron acids.

[0076] The dispersant or dispersants can be present in an amount sufficient to contribute at least 0.08 wt. % of nitrogen, preferably from about 0.10 to about 0.18 wt. %, more preferably from about 0.115 to about 0.16 wt. %, and most preferably from about 0.12 to about 0.14 wt. % of nitrogen to the lubricating oil composition.

[0077] Additional additives that may be incorporated into the compositions of the invention to enable particular performance requirements to be met are detergents, metal rust inhibitors, corrosion inhibitors, oxidation inhibitors, friction modifiers, anti-foaming agents, anti-wear agents and pour point depressants. Some are discussed in further detail below.

[0078] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts may contain a substantially stoichiometric amount of the metal in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base may be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents may have a TBN of 150 or greater, and typically will have a TBN of from 250 to 450 or more.

[0079] Dihydrocarbyl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal may be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil and may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohol or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one are entirely secondary in character and the hydrocarbyl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0080] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioesters having preferably C_5 to C_{12} alkyl side chains, calcium nonylphenol sulfide, oil soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Patent No. 4,867,890, and molybdenum-containing compounds and aromatic amines.

[0081] Known friction modifiers include oil-soluble organo-molybdenum compounds. Such organo-molybdenum friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-molybdenum compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sulfides, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates and alkylthioxanthates.

[0082] Other known friction modifying materials include glyceryl monoesters of higher fatty acids, for example, glyceryl mono-oleate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimerized unsaturated fatty acid; oxazoline compounds; and alkoxylated alkyl-substituted monoamines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ether amine.

[0083] Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethyl siloxane.

[0084] Some of the above-mentioned additives can provide a multiplicity of effects; thus for example, a single additive may act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

[0085] It may also be necessary to include an additive which maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed.

[0086] Representative effective amounts of such additional additives, when used in crankcase lubricants, are listed below:

ADDITIVE	Mass % (Broad)	Mass % (Preferred)
Ashless Dispersant	0.1 - 20	1 - 8
Metal Detergents	0.1 - 15	0.2 - 9
Corrosion Inhibitor	0 - 5	0 - 1.5
Metal Dihydrocarbyl Dithiophosphate	0.1 - 6	0.1 - 4
Antioxidant	0 - 5	0.01 - 2
Pour Point Depressant	0.01 - 5	0.01 - 1.5
Antifoaming Agent	0 - 5	0.001 - 0.15
Supplemental Antiwear Agents	0 - 1.0	0 - 0.5
Friction Modifier	0 - 5	0 - 1.5

(continued)

ADDITIVE	Mass % (Broad)	Mass % (Preferred)
Basestock	Balance	Balance

[0087] Fully formulated passenger car diesel engine lubricating oil (PCDO) compositions of the present invention preferably have a sulfur content of less than about 0.4 mass %, such as less than about 0.35 mass %, more preferably less than about 0.03 mass %, such as less than about 0.15 mass %. Preferably, the Noack volatility of the fully formulated PCDO (oil of lubricating viscosity plus all additives) will be no greater than 13, such as no greater than 12, preferably no greater than 10. Fully formulated PCDOs of the present invention preferably have no greater than 1200 ppm of phosphorus, such as no greater than 1000 ppm of phosphorus, or no greater than 800 ppm of phosphorus. Fully formulated PCDOs of the present invention preferably have a sulfated ash (SASH) content of about 1.0 mass % or less.

[0088] Fully formulated heavy duty diesel engine (HDD) lubricating oil compositions of the present invention preferably have a sulfur content of less than about 1.0 mass %, such as less than about 0.6 mass % more preferably less than about 0.4 mass %, such as less than about 0.15 mass %. Preferably, the Noack volatility of the fully formulated HDD lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 20, such as no greater than 15, preferably no greater than 12. Fully formulated HDD lubricating oil compositions of the present invention preferably have no greater than 1600 ppm of phosphorus, such as no greater than 1400 ppm of phosphorus, or no greater than 1200 ppm of phosphorus. Fully formulated HDD lubricating oil compositions of the present invention preferably have a sulfated ash (SASH) content of about 1.0 mass % or less.

[0089] This invention will be further understood by reference to the following examples. All weight percents expressed herein (unless otherwise indicated) are based on active ingredient (AI) content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the AI weight of each additive plus the weight of total oil and/or diluent.

EXAMPLES

Example 1

[0090] Various polymeric VI improvers and VI improver blends were tested, in the form of a 1 wt. % polymer solution in diluent oil, to determine shear stability index, or SSI (30 cycle; ASTM D6278-98); and thickening efficiency, or TE.

> VII-1 is a commercially available star polymer having a number average molecular weight (Mn) of 360,000 and comprising at least 5 arms; each of which is hydrogenated isoprene.
> VII-2 is a commercially available star polymer having a number average molecular weight (Mn) of 460,000 and comprising at least 5 arms; each of which is a styrene - hydrogenated isoprene copolymer having a styrene content of about 4 mass %.
> VII-3 is a commercially available, Ziegler-Natta catalyzed amorphous OCP having an ethylene-derived content of 46.2 mass % and a number average molecular weight (Mn) of 67,700.
> VII-4 is a commercially available, metallocene catalyzed amorphous OCP having an ethylene-derived content of 43.8 mass % and a number average molecular weight (Mn) of 44,800.
> VII-5 is a commercially available semicrystalline OCP having an ethylene-derived content of 65.9 mass % and a number average molecular weight (Mn) of 39,200.
> VII-6 is a commercially available amorphous OCP having an ethylene-derived content of 48.1 mass % and a number average molecular weight (Mn) of 44,000.

Table 1

Component	VII-type	Ethylene Content (mass %)	kv_{100} before 30-cycle KO	kv_{100} after 30-cycle KO	SSI (%)	TE
VII-1	Star	N/A*	9.15	9.11	0.9	1.91
VII-2	Star	N/A*	11.25	10.47	11.9	2.51
VII-3	Amorphous OCP Zeigler-Natta	46.2	10.37	8.45	34.0	2.27

(continued)

Component	VII-type	Ethylene Content (mass %)	kv_{100} before 30-cycle KO	kv_{100} after 30-cycle KO	SSI (%)	TE
VII-4	Amorphous OCP Metallocene	43.8	10.66	8.62	34.3	2.35
VII-5	Semi-crystalline OCP	65.9	9.61	8.64	19.8	2.05
VII-6	Amorphous OCP Zeigler-Natta	48.1	11.53**	10.10	21.0	1.72
* not applicable **solution containing 1.5 mass % polymer; all others solution containing 1.0 mass % polymer						

[0091] The above VI improvers were used, together with a commercial detergent-inhibitor (DI) package and lubricating oil flow improver (LOFI) to blend a series of 15W40 grade lubricating oil compositions as follows (all amounts reported as mass %):

Table 2

Component	Example 1 (Comparative)	Example 2 (Comparative)	Example 3 (Invention)	Example 4 (Invention)
DI Package	16.20	16.20	16.20	16.20
LOFI	0.20	0.20	0.20	0.20
Base Oil	83.01	83.13	83.01	83.01
VII-5	0.59	----	----	----
VII-2	----	0.47	----	----
VII-1 & VII-3 (55/45)	----	----	0.59	----
VII-1 & VII-4 (55/45)	----	----	----	0.59
Total	100.00	100.00	100.00	100.00

[0092] The viscometric properties of the above exemplified materials were evaluated; the results are reported below:

Table 3

Example	VII Treat (polymer mass %)	kv_{100} (cST)	kv loss after 90 cycle KO (%)	MRV @ -25°C (cp)	CCS @ -20°C (cp)
Example 1	0.59	14.18	8.7	21322	7771
Example 2	0.47	14.33	17.0	23251	7262
Example 3	0.59	14.12	5.9	25508	7918
Example 4	0.59	14.22	9.0	26663	7629

[0093] The above VI improvers were used, together with a commercial detergent-inhibitor (DI) package and lubricating oil flow improver (LOFI) to blend a series of 15W40 grade lubricating oil compositions as follows (all amounts reported as mass %):

Table 4

Component	Example 5 (Comparative)	Example 6 (Comparative)	Example 7 (Comparative)	Example 8 (Invention)
DI Package	11.80	11.80	11.80	11.80
LOFI	0.20	0.20	0.20	0.20
Base Oil	87.35	87.66	87.12	87.28
VII-2	0.65	----	----	----
VII-5	----	0.74	----	----
VII-6	----	----	0.88	----
VII-1 & VII-3 (40/60)	----	----	----	0.72
Total	100.00	100.00	100.00	100.00

[0094] The viscometric properties of the above exemplified materials were evaluated; the results are reported below:

Table 5

Example	VII Treat (polymer mass %)	kv_{100} (cST)	kv loss after 90 cycle KO (%)	MRV @ -25°C (cp)	CCS @ -20°C (cp)	Max. Gelation Index**
Example 5	0.65	14.05	19.7	26300	6250	4.1
Example 6	0.74	13.90	10.8	20700	6180	12.2
Example 7	0.88	13.92	9.8	26800	6870	4.7
Example 8	0.72	13.90	10.8	28100	6500	4.0
** Scanning Brookfield maximum gelation index (ASTM 5133)						

[0095] As shown by the comparison of Table 3, the combination of VI improvers in accordance with the present invention, at substantially constant kv_{100}, provided low temperature properties comparable to those provided by the semi-crystalline OCP and the star polymer alone, and improved shear stability relative to the star polymer. Simultaneously, as shown by the comparison of Table 5, the combination of VI improvers, in accordance with the present invention, at substantially constant kv_{100}, provides improved thickening efficiency relative to amorphous OCP and vastly reduced VII/ base stock interaction (indicated by the lower gelation index) relative to the semi-crystalline OCP.

[0096] The disclosures of all patents, articles and other materials described herein are hereby incorporated, in their entirety, into this specification by reference. A description of a composition comprising, consisting of, or consisting essentially of multiple specified components, as presented herein and in the appended claims, should be construed to also encompass compositions made by admixing said multiple specified components. The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. What applicants submit is their invention, however, is not to be construed as limited to the particular embodiments disclosed, since the disclosed embodiments are regarded as illustrative rather than limiting. Changes may be made by those skilled in the art without departing from the spirit of the invention.

Claims

1. A lubricating oil composition comprising a major amount of oil of lubricating viscosity, and a viscosity index (VI) improver composition comprising a first polymer comprising an amorphous ethylene - α olefin copolymer or ethylene - α olefin -diene terpolymer having a crystallinity of not greater than 1.0 %; and a second polymer comprising a star polymer, the arms of which are derived from diene, and optionally vinyl aromatic hydrocarbon monomer, wherein the star polymer has a Shear Stability Index (SSI) of from 1% to 35% (30 cycle).

2. A lubricating oil composition as claimed in claim 1, wherein the first polymer and the second polymer are present in a mass % ratio of from 80:20 to 20:80.

3. A lubricating oil composition, as claimed in claim 1 or 2, wherein said first polymer is an ethylene-propylene copolymer having less than 2% of units derived from diene.

4. A lubricating oil composition, as claimed in claim 3, wherein said ethylene-propylene copolymer is an amorphous copolymer having a shear stability index (SSI) of from 20% to 50%.

5. A lubricating oil composition, as claimed in claim 3 or 4, wherein said ethylene-propylene copolymer is polymerized via Ziegler-Natta catalysis and contains from 40 mass % to 55 mass % ethylene.

6. A lubricating oil composition, as claimed in claim 3 or 4, wherein said ethylene-propylene copolymer is polymerized via single site (metallocene) catalysis and contain from 35 mass % to 50 mass % ethylene.

7. A lubricating oil composition, as claimed in claim 1 or 2, wherein said second polymer is a hydrogenated polymer derived from a polyolefinic linking agent coupled to arms comprising diene units and optionally vinyl aromatic units.

8. A lubricating oil composition, as claimed in claim 7, wherein said diene units comprise butadiene, isoprene, or a mixture thereof.

9. A lubricating oil composition, as claimed in claim 8, wherein said second polymer comprises from 75 to 90 mass% of units derived from isoprene, and from 10 to 25 mass % of units derived from butadiene, wherein greater than 80 mass % of the butadiene derived units are incorporated as 1, 4 addition product.

10. A lubricating oil composition, as claimed in claim 8, wherein said second polymer comprises butadiene wherein from 30 to 80 mass % of the butadiene units are incorporated as 1,2-addition product and from 20 to 70 mass % of the butadiene units are incorporated as 1,4-addition product.

11. A lubricating oil composition, as claimed in claim 8, wherein said second polymer further comprises from 0 to 35 mass % of units derived from styrene.

12. A lubricating oil composition, as claimed in claim 1 or 2, wherein said first polymer is an ethylene-propylene amorphous copolymer having an SSI of from 20% to 50%; and said second polymer comprises from 75 to 90 mass% of units derived from isoprene, and from 10 to 25 mass % of units derived from butadiene; greater than 80 mass % of the butadiene derived units are incorporated as 1, 4 addition product; and said second polymer has an SSI of from 1% to 15%.

13. A lubricating oil composition as claimed in any one of the preceding claims, further comprising a nitrogenous dispersant derived from a polyalkene having a number average molecular weight (M_n) of greater than 1500.

14. A viscosity index (VI) improver concentrate comprising diluent oil; a first polymer that is an amorphous ethylene α-olefin copolymer having a crystallinity of not greater than 1.0 %; and a second polymer comprising a star polymer, the arms of which are derived from diene, and optionally vinyl aromatic hydrocarbon monomer, wherein the star polymer has a Shear Stability Index (SSI) of from 1% to 35% (30 cycle), wherein the total amount of polymer in the concentrate, including at least said first polymer and said second polymer is at least 5 mass%, based on the total mass of the concentrate.

15. A VI improver concentrate, as claimed in claim 14, wherein the first polymer and the second polymer are present in a mass % ratio of from 80:20 to 20:80.

16. A VI improver concentrate, as claimed in claim 14 or 15, wherein said first polymer is an ethylene-propylene copolymer having less than 2% of units derived from diene.

17. A VI improver concentrate, as claimed in claim 16, wherein said ethylene-propylene copolymer is an amorphous copolymer having a shear stability index (SSI) of from 20% to 50%.

18. A VI improver concentrate, as claimed in claim 16 or 17, wherein said ethylene-propylene copolymer is polymerized via Ziegler-Natta catalysis and contains from 40 mass % to 55 mass % ethylene.

19. A VI improver concentrate, as claimed in claim 16 or 17, wherein said ethylene-propylene copolymer is polymerized via single site (metallocene) catalysis and contain from 35 mass % to 55 mass % ethylene.

20. A VI improver concentrate, as claimed in any one of claims 15 to 19, wherein said second polymer is a hydrogenated polymer derived from a polyolefinic linking agent coupled to arms comprising diene units and optionally vinyl aromatic units.

21. A VI improver concentrate, as claimed in claim 20, wherein said diene units comprise butadiene, isoprene, or a mixture thereof.

22. A VI improver concentrate, as claimed in claim 20, wherein said second polymer comprises from 75 to 90 mass% of units derived from isoprene, and from 10 to 25 mass % of units derived from butadiene, wherein greater than 80 mass % of the butadiene derived units are incorporated as 1, 4-addition product.

23. A VI improver concentrate, as claimed in claim 20, wherein said second polymer comprises butadiene units wherein from 30 to 80 mass % of the butadiene units are incorporated as 1,2-addition product and from 20 to 70 mass % of the butadiene units are incorporated as 1,4-addition product.

24. A VI improver concentrate, as claimed in claim 21, wherein said second polymer further comprises from 5 to 35 mass % of units derived from styrene.

25. A VI improver concentrate, as claimed in claim 15, wherein said first polymer is an ethylene-propylene amorphous copolymer having an SSI of from 35% to 50%; and said second polymer comprises from 75 to 90 mass% of units derived from isoprene, and from 10 to 25 mass % of units derived from butadiene; greater than 80 mass % of the butadiene derived units are incorporated as 1, 4 addition product; and said second polymer has an SSI of from 1% to 15%.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 9617041 A **[0008]**
- US 4194057 A **[0009]**
- WO 2004087849 A **[0010]**
- US 4116917 A **[0038]**
- US 3985830 A **[0042]**
- GB 1030306 A **[0048]**
- US 5141996 A **[0055]**
- WO 9813443 A **[0055]**
- WO 9921902 A **[0055]**
- US 4146489 A **[0055]**
- US 4292414 A **[0055]**
- US 4506056 A **[0055]**
- US 3087936 A **[0075]**
- US 3254025 A **[0075]**
- US 5430105 A **[0075]**
- US 4867890 A **[0080]**

Non-patent literature cited in the description

- Shear Stability Index of Viscosity Modifiers - Effect of Polymer Architecture. **HUANG et al.** 8th Annual Fuels and Lubes Asian Conference and Exhibition. 2002 **[0006]**
- **MCGIRK et al.** Evaluation of Polyolefin Elastomers Produced by Constrained Geometry Chemistry as Viscosity Modifiers for Engine Oil. *SAE Paper No. 971696,* 1997 **[0019]**
- *J Polymer Science, Part A: Polymer Chemistry,* 1988, vol. 26, 1189-1198 **[0055]**
- *J. Polymer Science, Polymer Letters,* 1982, vol. 20, 481-486 **[0055]**
- **GAYLORD ; MEHTA.** *J. Polymer Science, Polymer Letters,* 1983, vol. 21, 23-30 **[0055]**
- **GAYLORD ; MEHTA ; MEHTA.** Degradation and Crosslinking of Ethylene-Propylene Copolymer Rubber on Reaction with Maleic Anhydride and/or Peroxides. *J. Applied Polymer Science,* 1987, vol. 33, 2549-2558 **[0055]**
- Engine Oil Licensing and Certification System. American Petroleum Institute (API, December 1996 **[0068]**