TITLE

LUBRICANTS CONTAINING BLENDS OF POLYMERS

BACKGROUND

[0001] The disclosed technology relates to lubricant formulations containing a mixture of viscosity modifying polymers: a (meth)acrylate-containing polymer comprising a multiplicity of arms, and an ethylene/olefin copolymer comprising polymerized propylene monomers.

[0002] Viscosity modifiers including star polymers and other polymers with multiplicity of arms are known in the field of lubricants for providing viscosity index performance, low temperature performance as described by Brookfield viscosity and higher temperature performance as indicated by kinematic viscosity performance at 40°C and 100°C. The viscosity modifier's performance has been observed in a wide variety of mechanical devices including hydraulic systems, driveline systems, and internal combustion engines. Olefin copolymers are also known as viscosity modifiers.

[0003] There is a continuing need to further improve the viscometric properties of lubricating oils in a variety of applications, such as engine lubricants, motorcycle lubricants (which typically lubricate both the engine and the transmission), driveline lubricants (manual and automatic transmissions and gears), greases, and hydraulic applications. It is particularly desirable to provide lubricants that have an increased (improved) viscosity index and reduced kinematic viscosities such as at 40°C, as well as increased (improved) high temperature-high shear rate viscosity, while maintaining good or even improved other lubricant performance characteristics including good antiwear performance or friction performance. In certain embodiments, such as, for examples, lubricants for motorcycle engines, lubricants as described herein may exhibit one or more of good shear stability under operating conditions characteristic of a motorcycle gearbox, good gear protection, and good deposit performance.

[0004] EP 2 610 332, Lubrizol, July 3, 2013, discloses star polymers and lubricating compositions thereof. The star polymer has at least two inner blocks, at least one of which is in turn bonded to one or more outer blocks. The lubricant composition may further comprise a viscosity modifier (typically an olefin copolymer such as an ethylene-propylene copolymer).

[0005] U.S. Patent 8,513,176, Baum et al., August 20, 2013, discloses a process for preparing a polymer, involving a chain transfer agent containing a thiocarbonyl compound. The product may be a star polymer which may be a block-arm star polymer or a hetero-arm star polymer. Optionally other performance additives may be present in a lubricant, including viscosity modifiers.

[0006] U.S. Application 2010/0190671, Stoehr et al., July 29, 2010, discloses use of comb polymers for reducing fuel consumption. Also disclosed is a lubricant oil formulation comprising the comb polymer which contains in the main chain at least one repeat unit obtained from a polyolefin-based macromonomer. It may also contain an additional additive, which may be, among others, a viscosity index improver. Conventional viscosity index improvers may include olefin copolymers, especially of the poly(ethylene-co-propylene) type.

[0007] U.S. Application 2008/0015131, Vinci et al., January 17, 2008, discloses lubricants containing an olefin copolymer and an acrylate copolymer. A disclosed polymer is an ethylene aliphatic olefin copolymer wherein the aliphatic olefin contains from 3 to about 24 carbon atoms, the copolymer having M_n ranging from about 600 to about 5000. In one embodiment the ethylene content may be about 20 mole % to about 85 mole %. Preferably the copolymer is an ethylene-propylene copolymer. The lubricant compositions are said to exhibit good low temperature and shear stability performance. The lubricants include automatic transmission, manual transmission, and gear lubricants.

[0008] U.S. Application 2003-0036488, Yuki et al., February 20, 2003, discloses a viscosity index improver and lubricant oil containing the same. The viscosity index improver may include such monomers as 2-decyl-tetradecyl methacrylate, 2-dodecyl-hexadecyl methacrylate, or 2-decyl-tetradecyloxyethyl methacrylate.

[0009] The disclosed technology, therefore, provides lubricants that may have one or more of various beneficial properties, such as reduced vane and ring wear in a hydraulic fluid formulation, and good viscosity properties such as viscosity index in an engine or motorcycle lubricant.

SUMMARY

[0010] The disclosed technology provides a lubricant composition comprising: (a) an oil of lubricating viscosity; (b) a (meth)acrylate-containing polymer compris-

ing a multiplicity of arms, wherein the arms contain at least 20, or at least 50 or 100 or 200 or 350 or 500 or 1000, carbon atoms, said arms being attached to a multivalent organic moiety; and (c) an ethylene/olefin copolymer having a weight average molecular weight of 5,000 to 250,000 or 10,000 to about 250,000, wherein the copolymer comprises about 40 to about 70 weight percent polymerized ethylene monomers and further comprises one or more polymerized olefin monomers of 3 to 6 carbon atoms (such as α–olefins).

[0011] The disclosed technology further provides a method for lubricating a mechanical device comprising supplying thereto the foregoing lubricant composition.

DETAILED DESCRIPTION

[0012] Various preferred features and embodiments will be described below by way of non-limiting illustration.

Oil of Lubricating Viscosity

[0013] One component of the disclosed lubricants will be an oil of lubricating viscosity. Such oils include natural and synthetic oils, oil derived from hydrocracking, hydrogenation, and hydrofinishing, unrefined, refined, re-refined oils or mixtures thereof. A more detailed description of unrefined, refined, and re-refined oils is provided in International Publication WO2008/147704, paragraphs [0054] to [0056]. A more detailed description of natural and synthetic lubricating oils is described in paragraphs [0058] to [0059] respectively of WO2008/147704. Synthetic oils may also be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0014] Oils of lubricating viscosity may also be defined as specified in April 2008 version of "Appendix E - API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils", section 1.3 Sub-heading 1.3. "Base Stock Categories." The oil of lubricating viscosity may also be an ester. A summary of the API oil classifications is as follows:

Base Oil Category	Sulfur (%)		Saturates(%)	Viscosity Index
Group I	>0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	>120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III or IV			

Groups I, II and III are mineral oil base stocks. In one embodiment the oil of lubricating viscosity may be an API Group I oil. In other embodiment, it may be a Group II or Group III oil, or any one of groups I through V.

[0015] The amount of the oil of lubricating viscosity present is typically the balance remaining after subtracting from 100 wt. % the sum of the amount of the compound of the disclosed technology and the other performance additives.

[0016] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the star polymer of the disclosed technology is in the form of a concentrate (which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of components the star polymer of the disclosed technology to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 80:20 to 10:90 by weight.

(Meth)acrylate polymer with multiple arms

[0017] The disclosed lubricant will also contain a (meth)acrylate-containing polymer comprising a multiplicity of arms containing at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000, carbon atoms, said arms being attached to a multivalent organic moiety. As used herein, the term (meth)acrylate and its cognates means either methacrylate or acrylate, as will be readily understood. The multi-armed polymer may thus be characteristic of a "star" polymer, a "comb" polymer, or a polymer otherwise having multiple arms or branches as described herein.

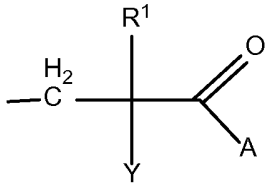
Star polymers

[0018] Star polymers are known. They may be prepared by a number of routes, including atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, nitroxide mediated polymerization, or anionic polymerization. A detailed discussion of ATRP is given in Chapter 11, pages 523 to 628 of the *Handbook of Radical Polymerization,* Edited by Krzyszt-

of Matyjaszewski and Thomas P. Davis, John Wiley and Sons, Inc., 2002 (hereinafter referred to as "Matyjaszewski"). See in particular reaction scheme 11.1 on page 524, 11.4 on page 556, 11.7 on page 571, 11.8 on page 572, and 11.9 on page 575.

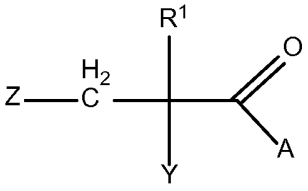
ATRP

[0019] In one embodiment, ATRP may be used to prepare a star polymer having as a core portion a functional group of formula (I):



(I)

wherein R^1 is hydrogen or a linear or branched alkyl group containing 1 to 5 carbon atoms; A is an amino or alkoxy group connected through the nitrogen or oxygen atom thereof to the remainder of the structure (I); and Y is a halogen such as bromine, chlorine, fluorine, or iodine. The halogen may be derived from a suitable halogen-containing compound such as an initiator, including those that contain one or more atoms or groups of atoms which may be transferred by a radical mechanism under the polymerization conditions. In one embodiment, the structure of (I) may be drawn in more detail as structure (Iz):



(Iz)

where Z is a polymeric group such as a crosslinked polymeric group. More detail on ATRP processes is given in US patent 6,391,996 and U.S. Application 2007/0244018, referring therein to paragraphs 0133 to 0144.

[0020] Examples of a halogen containing compound include benzyl halides, such as p-chloromethylstyrene, α-dichloroxylene, α,α-dichloroxylene, α,α-dibromoxylene and hexakis(α-bromomethyl)benzene, benzyl chloride, benzyl bromide, 1-bromo-1-phenylethane and 1-chloro-1-phenylethane; carboxylic acid derivatives which are halogenated at the α-position, such as propyl 2-bromopropionate, methyl 2-chloro-propionate, ethyl 2-chloropropionate, methyl 2-bromopropionate, ethyl 2-bromo-isobutyrate; tosyl halides such as p-toluenesulfonyl chloride; alkyl halides such as

tetrachloromethane, tribromomethane, 1-vinylethyl chloride, 1-vinylethyl bromide; and halogen derivatives of phosphoric acid esters, such as dimethylphosphoric acid.

[0021] In one embodiment when the halogen compound is employed, a transition metal such as copper may also be present. The transition metal may be in the form of a salt. The transition metal is capable of forming a metal to ligand bond and the ratio of ligand to metal depends on the dentate number of the ligand and the coordination number of the metal. The ligand is a nitrogen or phosphorus containing ligand. In one embodiment the ligand is phosphorus-containing with triphenyl phosphene (PPh_3) a common ligand. A suitable transition metal for a triphenyl phosphene ligand includes Rh, Ru, Fe, Re, Ni or Pd.

RAFT

[0022] RAFT polymerization may be employed when the core portion of the polymer contains a functional group of formula (I) above wherein Y is represented by -S-C(=S)-R^5 where R^5 may be an alkyl radical containing 1 to 20 carbon atoms. The Y functionality may be derived from or be a portion of a chain transfer agent. In certain embodiments the core portion comprises a functional group (often from a chain transfer agent) derived from a compound comprising a thiocarbonyl thio group and a free radical leaving groups, such as those disclosed in paragraph 0146 of U.S. Application 2007/0244018.

[0023] Examples of RAFT chain transfer agents include benzyl 1-(2-pyrrolidinone)carbodithioate, benzyl (1,2-benzenedicarboximido)carbodithioate, 2-cyanoprop-2-yl 1-pyrrolecarbodithioate, 2-cyanobut-2-yl 1-pyrrolecarbodithioate, benzyl 1-imidazolecarbodithioate, N,N-dimethyl-S-(2-cyanoprop-2-yl)dithiocarbamate, N,N-diethyl-S-benzyl dithiocarbamate, cyanomethyl 1-(2-pyrrolidone)carbodithoate, cumyl dithiobenzoate, N,N-diethyl S-(2-ethoxy-carbonylprop-2-yl)dithiocarbamate, O-ethyl-S-(1-phenylethyl)xanthtate, O-ethyl-S-(2-(ethoxycarbonyl)prop-2-yl)xanthate, O-ethyl-S-(2-cyanoprop-2-yl)xanthate, O-ethyl-S-(2-cyanoprop-2-yl)xanthate, O-ethyl-S-cyanomethyl xanthate, O-phenyl-S-benzyl xanthate, O-pentafluorophenyl-S-benzyl xanthate, 3-benzylthio-5,5-dimethylcyclohex-2-ene-1-thione or benzyl 3,3-di(benzylthio)prop-2-enedithioate, S,S'-bis-(α,α'-disubstituted-α''-acetic acid)-trithiocarbonate, S,S'-bis-(α,α'-disubstituted-α''-acetic acid)-trithiocarbonate or S-alkyl-S'-(-(α,α'-disubstituted-

α"-acetic acid)-trithiocarbonates, dithiobenzoic acid, 4-chlorodithiobenzoic acid, benzyl dithiobenzoate, 1-phenylethyl dithiobenzoate, 2-phenylprop-2-yl dithiobenzoate, 1-acetoxyethyl dithiobenzoate, hexakis(thiobenzoylthiomethyl)benzene, 1,4-bis(thiobenzoylthiomethyl)benzene, 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene, 1,4-bis-(2-(thiobenzoylthio)prop-2-yl)benzene, 1-(4-methoxyphenyl)ethyl dithiobenzoate, benzyl dithioacetate, ethoxycarbonylmethyl dithioacetate, 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate, 2,4,4-trimethylpent-2-yl dithiobenzoate, 2-(4-chlorophenyl)prop-2-yl dithiobenzoate, 3-vinylbenzyl dithiobenzoate, 4-vinylbenzyl dithiobenzoate, S-benzyl diethoxyphosphinyldithioformate, tert-butyl trithioperbenzoate, 2-phenylprop-2-yl 4-chlorodithiobenzoate, 2-phenylprop-2-yl 1-dithionaphthalate, 4-cyanopentanoic acid dithiobenzoate, dibenzyl tetrathiotereph-thalate, dibenzyl trithiocarbonate, carboxymethyl dithiobenzoate or poly(ethylene oxide) with dithiobenzoate end group or mixtures thereof.

[0024] RAFT polymerization is also described in greater detail in Chapter 12, pages 629 to 690 of Matyjaszewski, especially pages 664 to 665.

Nitroxide mediated

[0025] In the case of nitroxide-mediated polymerization, the core portion of a polymer may comprise a functional group of formula (I) above, wherein Y is an alkyl nitroxide group, $-O-N(R^6)(R^7)$ where R^6 and R^7 may be alkyl groups of 1 to 8 carbon atoms or wherein R^6 and R^7 may be joined together to form a ring. When nitroxide-mediated techniques are employed, in some instances a portion of styrene may be desirable (for instance, the amount of (meth)acrylate may be less than 50 wt % of the star polymer) to allow for a satisfactory polymer to be prepared using TEMPO based derivatives, for the reasons stated in Matyjaszewski, page 477, section 10.4. Alternatively, if non-TEMPO based nitroxide mediated techniques are employed using an alicyclic nitroxide or nonquaternary nitroxide, the presence of styrene is not essential. A list of compounds suitable for nitroxide-mediated techniques is given in Table 10.1, pages 479-481 of Matyjaszewski. Nitroxide-mediated polymerization is also described in paragraphs 016-to 0163 of U.S. Application 2007/0244018.

[0026] The amount of the compound employed to impart halogen, nitroxide group, or dithioether functionality into the core portion in one embodiment is 0.001 to 0.10 moles per mole of monomer, in another embodiment 0.001 to 0.05 moles per

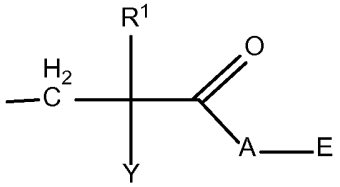
mole of monomer, and in yet another embodiment 0.001 to 0.03 moles per mole of monomer in the arms of the polymer.

Anionic

[0027] Anionic polymerization techniques have also been reported for preparation of star polymers; see for instance WO 96/23012. It is generally recognized that anionic polymerization processes require carefully controlled conditions to be able to prepare star polymers, such as highly pure solvents, inert atmosphere substantially free from water, low reaction temperatures, and use of alkali metal carbanioinic initiators.

Star polymer, details

[0028] When the (meth)acrylate-containing polymer comprising a multiplicity of arms is a star polymer, the polymer may comprise (i) a core portion comprising a polyvalent (meth) acrylic monomer, oligomer or polymer thereof or a polyvalent divinyl non-acrylic monomer, oligomer or polymer thereof; and (ii) at least two arms of polymerized alkyl (meth)acrylate ester. The core portion will further comprise a functional group of formula (Ia):



(Ia)

wherein E is independently another part of the core, a polymeric arm or to a monomeric species, or another structural unit as defined by formula (Ia); R^1 is hydrogen or a linear or branched alkyl group containing 1 to 5 carbon atoms; A is nitrogen or oxygen; and Y is a free radical leaving group selected from the group consisting of one or more atoms or groups of atoms which may be transferred by a radical mechanism under the polymerization conditions, a halogen, a nitroxide group,, or a dithio ester group. Analogous to structure (Iz), the bond shown at the left of structure (Ia) may typically be attached to a Z group, where Z is a polymeric group such as a crosslinked polymeric group.

Arms

[0029] The arms of the star polymer will themselves be (meth)acrylate-containing polymer or oligomer moieties, comprising (meth)acrylic moieties condensed with alcohol moieties to provide alkyl groups. In certain embodiments, the arms of the star

polymer may be formed from alkyl (meth)acrylate esters containing up to 40 carbon atoms in the alkyl group, or up to 30 carbon atoms, or 1 to 18 carbon atoms, or 1 to 15 carbon atoms, or 8 to 15, or 10 to 15, or 12 to 15 carbon atoms. In certain embodiments, one or more of the arms comprises units derived from alkyl acrylate monomers.

[0030] In one embodiment the (meth)acrylate ester contains 98% to 100% of the alkyl groups in the polymerized alkyl (meth)acrylate ester arms which contain 1 to 18 or 1 to 15 carbon atoms; and 0% to 2% of alkyl groups in the polymerized alkyl (meth)acrylate ester arms which contain 19 to 30 or 16 to 30 carbon atoms.

[0031] In one embodiment the polymeric arms comprise an alkyl ester group containing 10 to 15 carbon atoms present in at least 50 % to 100% of the alkyl groups; an alkyl ester group containing 6 to 9 carbon atoms present at 0 % to 20 %, 30 % or 40 % of the alkyl groups; an alkyl ester group containing 1 to 5 carbon atoms present at 0 % to 18 % or 20 % or 30 % of the alkyl groups; an alkyl ester group containing 16 to 30 (or 16 to 18) carbon atoms present at 0 % to 2 % of the alkyl groups; and a nitrogen containing monomer present at 0 wt % to 10 wt % of the polymeric arms.

[0032] In one embodiment the polymeric arms comprise an alkyl ester group containing 10 to 18 carbon atoms present in at least 50 % to 100% of the alkyl groups; an alkyl ester alkyl group containing 6 to 9 carbon atoms present at 0 % to 20 %, 30 % or 40 % of the alkyl groups; an alkyl ester alkyl group containing 1 to 5 carbon atoms present at 0 % to 18 % or 20 % or 30 % of the alkyl groups; an alkyl ester group containing 19 to 30 carbon atoms present at 0 % to 2 % of the alkyl groups; and a nitrogen containing monomer present at 0 wt % to 10 wt % of the polymeric arms.

[0033] The amount of the ester alkyl group containing 10 to 15 carbon atoms present on the star polymer in one embodiment may be at least 50 % of the alkyl groups, in another embodiment at least 60 % of the alkyl groups, in another embodiment at least 70 % of the alkyl groups and in another embodiment at least 80 % of the alkyl groups. In one embodiment the amount of the ester alkyl group containing 10 to 15 carbon atoms may be at least 95 % or 98 %.

[0034] The amount of an ester alkyl group containing 6 to 9 carbon atoms present on the star polymer in one embodiment is from 0 % to 15 % or 20 % or 30 % of the alkyl groups, in another embodiment 0 % to 10 % of the alkyl groups and in another embodiment 0 % to 5 % of the alkyl groups.

[0035] The amount of an ester alkyl group containing 1 to 5 carbon atoms present on the star polymer in one embodiment is from 0 % to 13 % or 20 % or 30 % of the alkyl groups, in another embodiment 0 % to 8 % of the alkyl groups and in another embodiment 0 % to 3 % of the alkyl groups.

[0036] The amount of an ester alkyl group containing 16 to 30 carbon atoms present on the star polymer in one embodiment is from 0 % to 1 % of the alkyl groups and in another embodiment 0 % of the alkyl groups.

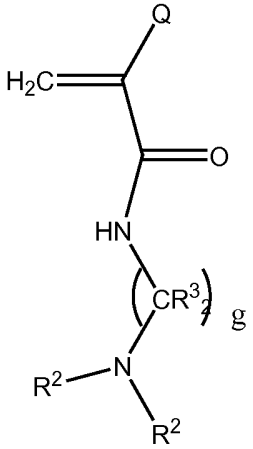
[0037] Examples of the alkyl portion of a (meth)acrylate ester include those derived from saturated alcohols, such as methyl methacrylate, butyl methacrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate, 3 iso-propylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5 methylundecyl (meth)acrylate, dodecyl(meth)acrylate, 2 methyl-dodecyl(meth)acrylate, tridecyl (meth)acrylate, 5- methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 2 methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, 5-isopropylheptadecyl (meth)acrylate, 4-tert-butyloctadecyl (meth)acrylate, 5-ethyloctadecyl (meth)acrylate, 3-isopropyloctadecyl (meth)acrylate, octadecyl(meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetyleicosyl (meth)acrylate, stearyleicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetratriacontyl (meth)acrylate; (meth)acrylates derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 3 vinyl-2-butylcyclohexyl (meth)acrylate or bornyl (meth)acrylate. In certain embodiments the alkyl portion of the ester may be derived from a β-branched alcohol having up to 30 carbon atoms.

[0038] The ester compounds with long-chain alcohol-derived groups may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl methacrylate (by transesterification) with long-chain fatty alcohols, in which

reaction a mixture of esters such as (meth)acrylate with alcohol groups of various chain lengths is generally obtained.

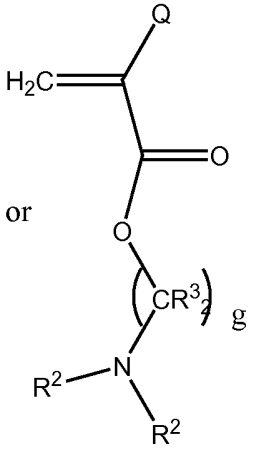
[0039] In one embodiment the star polymer is further functionalized in the core or the polymeric arms with a nitrogen containing monomer. The nitrogen containing monomer may include a vinyl substituted nitrogen heterocyclic monomer, a dialkylaminealkyl (meth)acrylate monomer, a dialkylaminoalkyl (meth)acrylamide monomer, a tertiary-(meth)acrylamide monomer, or mixtures thereof.

[0040] In one embodiment the core or polymeric arms may comprise a (meth)acrylamide or (meth)acrylate monomer of formula (IIa) or (IIb) respectively:



(IIa)

or



(IIb)

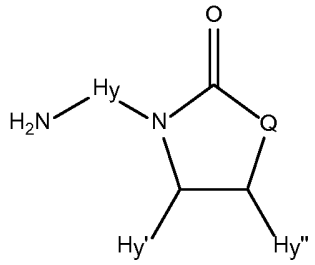
wherein each Q is independently hydrogen or methyl and, in one embodiment, Q is methyl; each R^2 is independently hydrogen or hydrocarbyl group containing 1 to 8 or 1 to 4 carbon atoms; each R^3 is independently hydrogen or hydrocarbyl group containing 1 to 2 carbon atoms and, in one embodiment, each R^3 is hydrogen; and g is an integer from 1 to 6 and, in one embodiment, g is 1 to 3.

[0041] Examples of a suitable nitrogen containing monomer include vinyl pyridine, N-vinyl imidazole, N-vinyl pyrrolidinone, and N-vinyl caprolactam, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, dimethylaminobutyl acrylamide, dimethylaminopropyl methacrylate, dimethylaminopropyl acrylamide, dimethylaminopropyl ethacrylamide, dimethylaminoethyl acrylamide or mixtures thereof.

[0042] In one embodiment the polymer is reacted by copolymerization or grafting onto or into the arms or core with an acylating agent and an amine to form a dispersant viscosity modifier (often referred to as a DVM), thus named because such materials exhibit both dispersant and viscosity modifying properties.

[0043] In one embodiment of the invention the polymeric arms or core (described below) are functionalized by copolymerization or grafting, onto or into the arms or core, with an acylating agent, an amine, or mixtures thereof. Examples of a grafting acylating agent include an unsaturated carboxylic acid or anhydride or derivatives thereof such as maleic anhydride, (meth) acrylic acid, or itaconic acid, which may then, be reacted with a nitrogen compound such as an amine. In one embodiment the acylating agent is a dicarboxylic acid or anhydride. Examples of a dicarboxylic acid or anhydride thereof include itaconic anhydride, maleic anhydride, methyl maleic anhydride, ethyl maleic anhydride, dimethyl maleic anhydride, or mixtures thereof.

[0044] In one embodiment the polymer, b, is further reacted with an amine to form a condensed species such as an amide group. a species with dispersant properties. Examples of an amine include an amino hydrocarbyl substituted amine, such as 4-aminodiphenylamine, a hydrocarbyl substituted morpholine, such as 4 (3-aminopropyl) morpholine or 4-(2-aminoethyl) morpholine or a dialkyl amino alkyl (meth)acrylate such as a dimethyl amino alkyl (meth)acrylate or N-vinyl pyrrolidinone. In one embodiment the alkyl group of dimethyl amino alkyl (meth)acrylate is propyl and in another embodiment ethyl. In certain embodiments the amine compound may comprise an imidazolidinone, cyclic carbamate, or pyrroldininone represented by the structure



wherein Hy is a hydrocarbylene group such as alkylene, or C1-4 alkylene or C2 alkylene, and Hy' and Hy" are each independently hydrogen or hydrocarbyl groups such as alkyl or C1-4 alkyl or C2 alkyl, and Q is >NH, >NR, $>CH_2$, >CHR, $>CR_2$, or -O-, where R is C1-4 alkyl and " > " represents two bonds. Typically Q may be >NH or >NR. In one embodiment the amine compound may be an imidazolinone which may include 1-(2-amino-ethyl)-imidazolidin-2-one (may also be called aminoethylethyleneurea), 1-(3-amino-propyl)-imidazolidin-2-one, 1-(2-hydroxy-ethyl)-

imidazolidin-2-one, 1-(3-amino-propyl)-pyrrolidin-2-one, 1-(3-amino-ethyl)-pyrrolidin-2-one, or mixtures thereof.

[0045] In one embodiment the polymeric arms of the star polymer have a polydispersity of 2 or less, in another embodiment 1.7 or less, in another embodiment 1.5 or less, for instance, 1 to 1.4. In one embodiment the star polymer has polydispersity with a bimodal or higher modal distribution. The bimodal or higher distribution is believed to be partially due to the presence of varying amounts of uncoupled polymer chains and/or uncoupled star-polymers or star-to-star coupling formed as the polymer is prepared.

[0046] In one embodiment the star polymer has at least 3 arms, in another embodiment greater than 5 arms, in another embodiment greater than 7 arms, in another embodiment greater than 10 arms, for instance 12 to 100, 14 to 50, or 16 to 40 arms. In one embodiment the star polymer has 120 arms or less, in another embodiment 80 arms or less, in another embodiment 60 arms or less. In certain embodiments there may be 3 to 20, 5 to 20, or 6 to 15, or 7 to 8 arms per star.

[0047] The star polymer moiety when formed may have uncoupled polymeric arms present (also referred to as a polymer chain or linear polymer). The percentage conversion of a polymer chain to star polymer in one embodiment is at least 10 %, in another embodiment at least 20 %, in another embodiment at least 40 % and in another embodiment at least 55 %, for instance 70 %, 75 % or 80%. In one embodiment the conversion of polymer chain to star polymer is about 90 %, 95 %, or 100%. In one embodiment a portion of the polymer chains does not form a star polymer and remains as a linear polymer. In one embodiment the linear polymer is substantially free of or free of a halogen, a nitroxide group or a dithioether group. In one embodiment the linear polymer has a substantially similar or identical composition and weight average molecular weight as the star polymer arms containing a polymerized alkyl (meth)acrylate ester.

[0048] In one embodiment one or more of the arms of the star polymer are di-block AB type copolymers, in another embodiment tri-block ABA type copolymers, in another embodiment tapered block polymers, and in another embodiment alternating polymers.

[0049] The star polymer described above in one embodiment is a block-arm star (co)polymer (where "(co)polymer" is used to mean "polymer or copolymer"), in another embodiment a hetero-arm star (co)polymer (as described below) and in another embodiment the star polymer is a tapered arm copolymer. A tapered arm copolymer has a variable composition across the length of a polymer chain. For example, the tapered arm copolymer will be composed of, at one end, a relatively pure first monomer and, at the other end, a relatively pure second monomer. The middle of the polymer arm is more of a gradient composition of the two monomers. Tapered block copolymers may be coupled to form block-arm star polymers.

[0050] The block-arm star (co)polymer contains one or more polymer arms derived from two or more monomers within the same arm. A more detailed description of the block-arm star polymer is given in Chapter 13 (pp. 333-368) of "Anionic Polymerization, Principles and Practical Applications" by Henry Hsieh and Roderic Quirk (Marcel Dekker, Inc., New York, 1996) (hereinafter referred to as Hsieh et al.).

[0051] The hetero-arm, or "mikto-arm," star polymer contains arms which may vary from one another either in molecular weight, composition, or both, as defined in Hsieh et al. For example, a portion of the arms of a given star polymer can be of one polymeric type and a portion of a second polymeric type. More complex hetero-arm star polymers may be formed by combining portions of three or more polymeric arms with a coupling agent.

[0052] In certain embodiments the arms may be random copolymers. In certain embodiments they may be copolymers of 73 to 85, or 78 to 84, percent by weight of alkyl methacrylates having predominantly or exclusively 12 to 25 carbon atoms in the alkyl group, 14 to 25, or 16 to 20, percent by weight methyl methacrylate monomers, and 0.05 to 10, or 0.1 to 3, or 0.5 to 2, percent by weight alkyl methacrylate monomers having C6 to C10 carbon atoms in the alkyl groups, such as 2-ethylhexyl methacrylate.

Core

[0053] In a star polymer, the polymeric arms will be attached to (or radiate from) a core which itself will typically have a polymeric or oligomeric structure. The core portion may be a polyvalent (meth) acrylic monomer, oligomer or polymer thereof or

a polyvalent divinyl non-acrylic monomer oligomer or polymer thereof. The polyvalent monomer, oligomer or polymer thereof may be used alone or as a mixture.

[0054] In one embodiment the polyvalent divinyl non-acrylic monomer is a divinyl benzene. In one embodiment the polyvalent (meth) acrylic monomer is an acrylate or methacrylate ester of a polyol or a methacrylamide of a polyamine, such as an amide of a polyamine, for instance a methacrylamide or an acrylamide. In one embodiment the polyvalent (meth) acrylic monomer is an acrylic or methacrylic acid polyol or a condensation product of a polyamine.

[0055] The polyol in one embodiment contains 2 to 20 carbon atoms, or in other embodiments 3 to 15 or 4 to 12; and the number of hydroxyl groups present in one embodiment is 2 to 10, in another embodiment 2 to 4 and in another embodiment 2. Examples of polyols include ethylene glycol, poly (ethylene glycols), alkane diols such as 1,6-hexanene diol or triols such as trimethylolpropane, or oligomerized trimethylolpropanes. Examples of a polyamine include polyalkylenepolyamines, such as, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylene pentamine, pentaethylenehexamine and mixtures thereof.

[0056] Examples of the polyvalent unsaturated (meth) acrylic monomer include ethylene glycol diacrylate, ethylene glycol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, glycerol diacrylate, glycerol triacrylate, mannitol hexaacrylate, 4-cyclohexanediol diacrylate, 1,4-benzenediol dimethacrylate, pentaerythritol tetraacrylate, 1,3-propanediol diacrylate, 1,5-pentanediol dimethacrylate, bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200-4000, polycaprolactonediol diacrylate, pentaerythritol triacrylate, 1,1,1-trimethylolpropane triacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,1,1-trimethylolpropane trimethacrylate, hexamethylenediol diacrylate or hexamethylenediol dimethacrylate or an alkylene bis-(meth)acrylamide.

[0057] The amount of polyvalent coupling agent may be an amount suitable to provide coupling of polymer previously prepared as arms onto a core comprising the coupling agent in monomeric, oligomeric, or polymeric form, to provide a star polymer. As described above, suitable amounts may be determined readily by the person skilled in the art with minimal experimentation, even though several variables

may be involved. For example, if an excessive amount of coupling agent is employed, or if excessive unreacted monomer from the formation of the polymeric arms remains in the system, crosslinking rather than star formation may occur. Typically the mole ratio of polymer arms to coupling agent may be 50:1 to 1.5:1 (or 1:1), or 30:1 to 2:1, or 10:1 to 3:1, or 7:1 to 4:1, or 4:1 to 1:1. In other embodiments the mole ratio of polymer arms to coupling agent may be 50:1 to 0.5:1, or 30:1 to 1:1, or 7:1 to 2:1. The desired ratio may also be adjusted to take into account the length of the arms, longer arms sometimes tolerating or requiring more coupling agent than shorter arms. In certain embodiments, 1 to 5 parts by weight, or 2 to 4, or 2.5 to 3, parts by weight of a coupling agent such as ethylene glycol dimethacrylate may be used to react with pre-formed arms prepared with 100 parts by weight of (meth)acrylate monomers. If desired, the polymer prepared by coupling arms with a coupling agent, may be further treated or reacted with various monomers such as additional acrylate or methacrylate monomers, e.g., methyl methacrylate, methyl acrylate, ethylhexyl methacrylate, ethylhexyl acrylate, or lauryl methacrylate. Such further treatment may be with a relatively minor amount of such monomer, e.g., 0.05 to 2 of 0.5 to 1.5 weight percent. Typically the material prepared will be soluble in an oil of lubricating viscosity.

[0058] In certain embodiments the arms of the star polymer may each independently have a number average molecular weight of 4,000 to 200,000, or 10,000 to 100,000, or 15,000 to 50,000, or 10,000 to 200,000, or 20,000 to 100,000, or 35,000 to 50,000.

[0059] In one embodiment the star polymer overall has a weight average molecular weight (M_w) of 5000 to 1,000,000, in another embodiment 10,000 to 1,000,000, in another embodiment 10,000 to 600,000 and in another embodiment 15,000 to 500,000 or 8,000 to 1,000,000 or 8,000 to 700,000. Examples of a suitable M_w include 15,000 to 350,000, 15,000 to 50,000, 150,000 to 280,000, or 25,000 to 140,000, or to 280,000, or to 600,000.

[0060] In one embodiment the star polymer overall has a polydispersity (M_w/M_n) greater than 1.3 or 2, in one embodiment 3 or more, in another embodiment 4 or more and in another embodiment 5 or more. An upper range on the polydispersity may include 30 or 20 or 15 or 10. Examples of suitable ranges include 1.3 to 30, 3 to 15 or 1.3 to 10. In one embodiment the star polymer comprises a mixture of star and linear

polymers. The polydispersity of said mixtures is the same as, or similar to, or slightly larger than the ranges described immediately above.

Comb polymer

[0061] In another embodiment, the (meth)acrylate-containing polymer comprising a multiplicity of arms may be a comb polymer, as described in greater detail in U.S. patent 8,067,349. Such as material may comprise a main chain from which arms emanate. The main chain may comprise repeat units derived from low molecular weight monomers such as styrene or substituted styrene, alkyl(meth)acrylates having 1 to 10 carbon atoms in the alcohol (alkyl) group, vinyl esters, vinyl ethers, and other such as described in claim 1 of US 8,067,349. There will also be a multiplicity of polyolefin-based macromonomers which may have a number average molecular weight in the range of 700 to 10,000, and which may also contain non-olefinic monomers. The macromonomer will typically have exactly one polymerizable double bond which may be a terminal bond. For example, a cationic polymerization of isobutylene may form a polyisobutylene which has a terminal double bond. Typical macromonomers may be prepared by reacting a macroamine (long chain amine) or a macroalcohol (long chain alcohol), each based on a polyolefin, with methyl methacrylate by an aminolysis or transesterification reaction. Further details of their synthesis are reported in the aforementioned US 8,067,349. The molecular weights and compositions of the branches described above for the star polymers may also be applied to the branches of the comb polymer.

[0062] Other polymers having a multiplicity of arms include those described in U.S. Application 2003-0036488, Yuki et al., February 20, 2003. The materials disclosed therein may include polymers prepared from monomers such as 2-decyl-tetradecyl methacrylate, 2-dodecyl-hexadecyl methacrylate, or 2-decyl-tetradecyloxyethyl methacrylate. Those particular monomers may have arms with 20 to 30 or 24 to 28 carbon atoms and may also contain ether functionality. In some embodiments these arms have a branch at the β-position. In some embodiments the alcohols from which they are derived are referred to as Guerbet alcohols. Guerbet alcohols typically have one or more carbon chains with branching at the β- or higher position. The Guerbet alcohols in general may contain, in various embodiments, 10 to 60, or 12 to 60, or 16 to 40, or 20 to 30 carbon atoms. Methods to

prepare Guerbet alcohols are disclosed in US Patent 4,767,815 (see column 5, line 39 to column 6, line 32). Correspondingly longer arms may also be used.

[0063] In some embodiments, for instance (but not exclusively) when the (meth)acrylate-containing polymer with multiple arms is in the form of a comb polymer, the arms may comprise hydrocarbyl groups or may comprise hydrocarbyl monomer units. In one embodiment, the arms may be polymeric entities comprising conjugated diene monomer units (optionally hydrogenated) or isobutylene monomer units. In one embodiment, the conjugated diene may comprise butadiene, that is, 1,3-butadiene or isoprene. (The expression "comprising [certain] monomer units" as used herein is intended to refer to polymerized monomer units or "units derived from" the indicated monomers by way of polymerization. It is understood that the monomer units in their original, unpolymerized form, are not normally present in any significant amount, and there is no intention to suggest the contrary.)

[0064] The amount of the (meth)acrylate-containing polymer comprising a multiplicity of arms is present in a lubricating composition in an amount of 0.1 to 5 percent by weight or 0.1 to 2.5 percent by weight, or 0.25 to 5 percent by weight, or 0.25 to 2.5 percent by weight, or 0.5 to 4, or 1 to 3.5, or 1.3 to 3.4, percent by weight. It may also be provided as a concentrate in an oil or other medium, in which case its amount within the concentrate will be correspondingly greater, such as 1 to 25 or 2.5 to 25 or to 50 percent by weight.

Olefin copolymer

[0065] The lubricant composition will also contain a second polymer which is an ethylene/olefin copolymer having a weight average molecular weight of 5,000 to 250,000, or 10,000 to 250,000, or alternatively 10,000 to 200,000, or 20,000 to 180,000, or 15,000 to 150,000, or 20,000 to 100,000, or 20,000 to 80,000 or, alternatively, 100,000 to 200,000 or 100,000 to 180,000. This polymer may also be of a form having long arms, although it may also be of a more conventional linear or branched structure.

[0066] The second copolymer itself, the ethylene-olefin copolymer, will comprise 40 to 75 or 40 to 70 weight percent polymerized ethylene monomers and will further comprise one or more polymerized olefin monomers of 3 to 6 carbon atoms. In certain embodiments the olefin monomers may comprise at least one of propylene or

butylene monomer units, and in one embodiment may comprise propylene monomer units. In certain embodiments the second polymer may comprise 40 to 50 percent by weight ethylene monomer units and 50 to 60 percent by weight of the other olefin monomer units such as propylene monomer units. Other monomers may also be present, such as non-conjugated diene units, optionally hydrogenated, typically in an amount of 0-10 percent by weight, or 1 to 5 percent.

[0067] The amount of the ethylene/olefin copolymer in a fully formulated lubricant may be 0.03 to 1, or 0.05 to 0.5, or 0.1 to 0.4, or 0.1 to 10, or 0.1 to 2.5 percent by weight. It may also be provided as a concentrate in an oil or other medium, in which case its amount within the concentrate will be correspondingly greater, such as 5 to 15 percent by weight. Both polymers may be present in the same concentrate at the identified amounts.

[0068] Suitable olefin copolymers are well known and are described, for instance, in U.S. Application 2008/0015131, Vinci et al. Such polymers are commercially available as Lucant™ polymer, Trilene™ polymers, Nordel™ polymers, Paratone™ polymers, Lubrizol® 70XY series polymers, and Royalene™ polymers.

[0069] Copolymers of aliphatic olefins may thus comprise an ethylene-aliphatic olefin copolymer wherein the aliphatic olefins, typically alpha olefins, contain 3 to 24 carbon atoms, said copolymers having an Mn from 500 to 5000, such as 800 to 4000 or 2000 to 4000. At least some propylene monomer will typically be present. The polydispersity (M_w/M_n) may be from 1.1 to 3, such as 1.3 to 2.5 or 2.0 to 2.4. Such polymers may be formed by copolymerization of ethylene and one or more aliphatic olefins under conditions known in the art. Examples include polymerizations conducted using Ziegler-Natta or metallocene catalysts.

[0070] Other Components Other components that are commonly used in lubricants may also be present. One such material may be an overbased detergent. Overbased materials, otherwise referred to as overbased or superbased salts, are generally single phase, homogeneous Newtonian systems characterized by a metal content in excess of that which would be present for neutralization according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. The overbased materials may be prepared by reacting an acidic material (typically an inorganic acid or lower carboxylic acid such as carbon dioxide) with a mixture

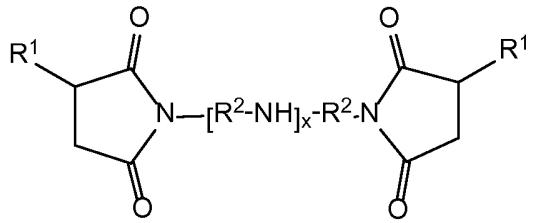
comprising an acidic organic compound, a reaction medium comprising at least one inert, organic solvent (such as mineral oil, naphtha, toluene, xylene) for said acidic organic material, a stoichiometric excess of a metal base, and a promoter such as a phenol or alcohol. The acidic organic material will normally have a sufficient number of carbon atoms to provide a degree of solubility in oil. The amount of excess metal is commonly expressed in terms of metal ratio. The term "metal ratio" is the ratio of the total equivalents of the metal to the equivalents of the acidic organic compound. A neutral metal salt has a metal ratio of one. A salt having 4.5 times as much metal as present in a normal salt will have metal excess of 3.5 equivalents, or a ratio of 4.5.

[0071] Such overbased materials are well known to those skilled in the art. They are useful for a variety of purposes, including cleanliness and neutralization of acidic by-products of combustion when used in engine lubricants; they may also provide control of friction or control of corrosion. Patents describing techniques for making basic salts of sulfonic acids, carboxylic acids, phenols, phosphonic acids, and mixtures of any two or more of these include U.S. Patents 2,501,731; 2,616,905; 2,616,911; 2,616,925; 2,777,874; 3,256,186; 3,384,585; 3,365,396; 3,320,162; 3,318,809; 3,488,284; and 3,629,109. Other detergents include salixarate detergents; they and methods for their preparation are described in greater detail in U.S. patent number 6,200,936 and PCT Publication WO 01/56968. Also known are salicylate detergents, described in greater detail in U.S. Patents 4,710,023 and 3,372,116. In one embodiment the lubricant comprises an overbased sulfonate detergent, an overbased phenol-containing detergent, or mixtures there.

[0072] The amount of detergent in a fully formulated lubricant, if present, may be 0.01 to 15 percent by weight, or 0.1 to 5 , or 0.5 to 2, or 1 to 3 percent.

[0073] Dispersants are also well known additives in the field of lubricants and include primarily what is known as ashless dispersants and polymeric dispersants. Ashless dispersants are so-called because, as supplied, they do not contain metal and thus do not normally contribute to sulfated ash when added to a lubricant. However they may, of course, interact with ambient metals once they are added to a lubricant which includes metal-containing species. Ashless dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typi-

cal ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures including typically



where each R^1 is independently an alkyl group, frequently a polyisobutylene group with a molecular weight (Mn) of 500-5000 based on the polyisobutylene precursor, and R^2 are alkylene groups, commonly ethylene (C_2H_4) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. In the above structure, the amine portion is shown as an alkylene polyamine such as polyethylene polyamine, although other aliphatic and aromatic mono- and polyamines may also be used, such as amino diphenylamine. Also, a variety of modes of linkage of the R^1 groups onto the imide structure are possible, including various cyclic linkages. The dispersant may be formed by a process involving the use of chlorine or by a thermal "ene" process or a free radical process. The average number of succinic acid groups attached to an R^1 group (e.g., polyisobutylene group) may be, in certain embodiments, 1.1 to 2.0, or 1.15 to 1.35, 1.30 to 1.8, or 1.4 to 1.7. The ratio of the carbonyl groups of the acylating agent to the nitrogen atoms of the amine may be 1:0.5 to 1:3, and in other instances 1:1 to 1:2.75 or 1:1.5 to 1:2.5. Succinimide dispersants are more fully described in U.S. Patents 4,234,435 and 3,172,892 and in EP 0355895.

[0074] Another class of ashless dispersant is high molecular weight esters. These materials are similar to the above-described succinimides except that they may be seen as having been prepared by reaction of a hydrocarbyl acylating agent and a polyhydric aliphatic alcohol such as glycerol, pentaerythritol, or sorbitol. Such materials are described in more detail in U.S. Patent 3,381,022.

[0075] Another class of ashless dispersant is Mannich bases. These are materials which are formed by the condensation of a higher molecular weight, alkyl substituted

phenol, an alkylene polyamine, and an aldehyde such as formaldehyde. Such materials are described in more detail in U.S. Patent 3,634,515.

[0076] Other dispersants include polymeric dispersant additives, which are generally hydrocarbon-based polymers which contain polar functionality to impart dispersancy characteristics to the polymer.

[0077] Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds. References detailing such treatment are listed in U.S. Patent 4,654,403. In one embodiment the lubricant composition comprises at least one boron-containing dispersant.

[0078] The amount of the dispersant in a fully formulated lubricant of the present technology may be at least 0.1% of the lubricant composition, or at least 0.3% or 0.5% or 1%, and in certain embodiments at most 9% or 8% or 6% or 4% or 3% or 2% by weight.

[0079] The lubricant may also contain a metal salt of a phosphorus acid. Metal salts of the formula

$$[(R^8O)(R^9O)P(=S)\text{-}S]_n\text{-}M$$

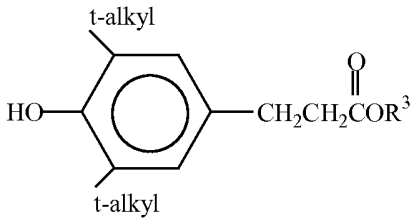
where R^8 and R^9 are independently hydrocarbyl groups containing 3 to 30 carbon atoms, are readily obtainable by heating phosphorus pentasulfide (P_2S_5) and an alcohol or phenol to form an O,O-dihydrocarbyl phosphorodithioic acid. The alcohol which reacts to provide the R^8 and R^9 groups may be a mixture of alcohols, for instance, a mixture of isopropanol and 4-methyl-2-pentanol, and in some embodiments a mixture of a secondary alcohol and a primary alcohol, such as isopropanol and 2-ethylhexanol. Other alcohols may include secondary-butyl alcohol or iso-octyl alcohol. The resulting acid may be reacted with a basic metal compound to form the salt. The metal M, having a valence n, generally is aluminum, lead, tin, manganese, cobalt, nickel, zinc, or copper, and in many cases, zinc, to form zinc dialkyldithiophosphates. Such materials are well known and readily available to those skilled in the art of lubricant formulation. Suitable variations to provide good phosphorus retention in an engine are disclosed, for instance, in US published application 2008-0015129, see, e.g., claims.

[0080] The amount of the metal salt of a phosphorus acid in a completely formulated lubricant, if present, will typically be 0.1 to 4 percent by weight, such as 0.5 to 2 percent by weight or 0.75 to 1.25 percent by weight. The amount may be, in some embodiments, an amount which delivers phosphorus to the lubricant at 0.01 to 0.15 percent by weight, or 0.03 to 0.08, or 0.03 to 0.06 percent by weight.

[0081] Another component that may be used is a supplemental viscosity modifier, which would be in addition to the combination of polymeric viscosity modifiers of the disclosed technology, presented above. Viscosity modifiers (VM) and dispersant viscosity modifiers (DVM) are well known. Examples of VMs and DVMs may include polymethacrylates, polyacrylates, polyolefins, hydrogenated vinyl aromatic-diene copolymers (e.g., styrene-butadiene, styrene-isoprene), styrene-maleic ester copolymers, and similar polymeric substances including homopolymers, copolymers, and graft copolymers. The DVM may comprise a nitrogen-containing methacrylate polymer, for example, a nitrogen-containing methacrylate polymer derived from methyl methacrylate and dimethylaminopropyl amine.

[0082] Examples of commercially available VMs, DVMs and their chemical types may include the following: polyisobutylenes (such as Indopol™ from BP Amoco or Parapol™ from ExxonMobil); olefin copolymers (such as Lubrizol™ 7060, 7065, and 7067 from Lubrizol and Lucant™ HC-2000L and HC-600 from Mitsui); hydrogenated styrene-diene copolymers (such as Shellvis™ 40 and 50, from Shell and LZ® 7308, and 7318 from Lubrizol); styrene/maleate copolymers, which are dispersant copolymers (such as LZ® 3702 and 3715 from Lubrizol); polymethacrylates, some of which have dispersant properties (such as those in the Viscoplex™ series from RohMax, the Hitec™ series of viscosity index improvers from Afton, and LZ® 7702, LZ® 7727, LZ® 7725 and LZ® 7720C from Lubrizol); olefin-graft-polymethacrylate polymers (such as Viscoplex™ 2-500 and 2-600 from RohMax); and hydrogenated polyisoprene star polymers (such as Shellvis™ 200 and 260, from Shell). Viscosity modifiers that may be used are described in U.S. patents 5,157,088, 5,256,752 and 5,395,539. The VMs and/or DVMs may be used in the functional fluid at a concentration of up to 20% by weight. Concentrations of 1 to 12%, or 3 to 10% by weight may be used.

[0083] Another component may be an antioxidant. Antioxidants encompass phenolic antioxidants, which may be hindered phenolic antioxidants, onr or both orthopositions on a phenolic ring being occupied by bulky groups such as t-butyl. The para position may also be occupied by a hydrocarbyl group or a group bridging two aromatic rings. In certain embodiments the para position is occupied by an ester-containing group, such as, for example, an antioxidant of the formula



wherein R^3 is a hydrocarbyl group such as an alkyl group containing, e.g., 1 to 18 or 2 to 12 or 2 to 8 or 2 to 6 carbon atoms; and t-alkyl can be t-butyl. Such antioxidants are described in greater detail in U.S. Patent 6,559,105.

[0084] Antioxidants also include aromatic amines. In one embodiment, an aromatic amine antioxidant can comprise an alkylated diphenylamine such as nonylated diphenylamine or a mixture of a di-nonylated and a mono-nonylated diphenylamine. Other amine antioxidants include phenylnaphthylamine and alkylated phenylnaphthylamines.

[0085] Antioxidants also include sulfurized olefins such as mono- or disulfides or mixtures thereof, for instance, sulfurized diisobutylene, or sulfurized α-olefins. These materials generally have sulfide linkages of 1 to 10 sulfur atoms, e.g., 1 to 4, or 1 or 2. Materials which can be sulfurized to form the sulfurized organic compositions of the present invention include oils, fatty acids and esters, olefins and polyolefins made thereof, terpenes, or Diels-Alder adducts. Details of methods of preparing some such sulfurized materials can be found in U.S. Pat. Nos. 3,471,404 and 4,191,659.

[0086] Molybdenum compounds can also serve as antioxidants, and these materials can also serve in various other functions, such as antiwear agents or friction modifiers. U.S. Pat. No. 4,285,822 discloses lubricating oil compositions containing a molybdenum- and sulfur-containing composition prepared by combining a polar solvent, an acidic molybdenum compound and an oil-soluble basic nitrogen compound to form a molybdenum-containing complex and contacting the complex with carbon disulfide to form the molybdenum- and sulfur-containing composition. Mo-

lybdenum dithiocarbamates and other molybdenum compounds are commercially available. Additionally, titanium compounds such as titanium alkoxides such as titanium 2-ethylhexoxide, or titanium carboxylates such as the neodecanoate can provide a variety of benefits, including antioxidancy and antiwear performance.

[0087] Dithiocarbamates may also serve as antioxidants.

[0088] Typical amounts of antioxidants will, of course, depend on the specific antioxidant and its individual effectiveness, but illustrative total amounts can be 0.01 to 5 percent by weight or 0.15 to 4.5 percent or 0.2 to 4 percent or 0.5 to 2 percent or 0.05 to 0.1 percent.

[0089] Another additive is an antiwear agent. Examples of anti-wear agents include phosphorus-containing antiwear/extreme pressure agents such as metal thiophosphates, phosphoric acid esters and salts thereof, phosphorus-containing carboxylic acids, esters, ethers, and amides; and phosphites. In certain embodiments a phosphorus antiwear agent may be present in an amount to deliver 0.01 to 0.2 or 0.015 to 0.15 or 0.02 to 0.1 or 0.025 to 0.08 percent phosphorus. In some embodiments, the antiwear agent may comprise an ashless (non-metal-containing) dithiophosphate. Often the antiwear agent is a zinc dialkyldithiophosphate (ZDP), as described above. For a typical ZDP, which may contain 11 percent P (calculated on an oil free basis), suitable amounts may include 0.09 to 0.82 percent. Non-phosphorus-containing anti-wear agents include borate esters (including borated epoxides), dithiocarbamate compounds, molybdenum-containing compounds, and sulfurized olefins.

[0090] Other materials that may be used as antiwear agents (also referred to as ashless antiwear agents) include tartrate esters, tartramides, and tartrimides. Examples include oleyl tartrimide (the imide formed from oleylamine and tartaric acid) and oleyl diesters (from, e.g, mixed C12-16 alcohols). Other related materials that may be useful include esters, amides, and imides of other hydroxy-carboxylic acids in general, including hydroxy-polycarboxylic acids, for instance, acids such as tartaric acid, malic acid, citric acid, lactic acid, glycolic acid, hydroxy-propionic acid, hydroxyglutaric acid, and mixtures thereof. These materials may also impart additional functionality to a lubricant beyond antiwear performance. These materials are described in greater detail in US Publication 2006-0079413 and PCT publication

WO2010/077630. Such derivatives of (or compounds derived from) a hydroxy-carboxylic acid, if present, may typically be present in the lubricating composition in an amount of 0.1 weight % to 5 weight %, or 0.2 weight % to 3 weight %, or greater than 0.2 weight % to 3 weight %.

[0091] Another component that may be used in the composition used in the present technology is a friction modifier. Friction modifiers are well known to those skilled in the art. A list of friction modifiers that may be used is included in U.S. Patents 4,792,410, 5,395,539, 5,484,543 and 6,660,695. U.S. Patent 5,110,488 discloses metal salts of fatty acids and especially zinc salts, useful as friction modifiers. A list of friction modifiers that may be useful may include:

fatty phosphites	borated alkoxylated fatty amines
fatty acid amides	metal salts of fatty acids
fatty epoxides	sulfurized olefins
borated fatty epoxides	fatty imidazolines

fatty amines other than the fatty amines discussed above
condensation products of carboxylic acids and polyalkylene-polyamines
glycerol esters such as glycerol monooleate
metal salts of alkyl salicylates

borated glycerol esters	amine salts of alkylphosphoric acids
alkoxylated fatty amines	ethoxylated alcohols
oxazolines	imidazolines
hydroxyalkyl amides	polyhydroxy tertiary amines
dialkyl tartrates	molybdenum compounds

—— and mixtures of two or more thereof. If a lubricant is to be used to lubricate a device that encompasses a wet (lubricated) clutch, additives may be present which control the amount of slip between the components of the clutch, that is, provide a relatively high, stable coefficient of friction between the clutch components, such as at a friction plate-steel plate interface. Among such materials may be borated dispersants, certain phosphorus-containing compounds, and certain amide compounds. Other materials that may be useful in providing such performance may include branched-alkyl calcium sulfonate detergents and calcium alkylphenate detergents.

[0092] Other additives that may optionally be used in lubricating oils include one or more of pour point depressing agents, extreme pressure agents, anti-wear agents, color stabilizers, demulsifiers, rust inhibitors, metal deactivators, and anti-foam agents.

[0093] Anti-foam agents, also known as foam inhibitors are known in the art and include but are not limited to organic silicones and non-silicon foam inhibitors. Some examples of organic silicones include dimethyl silicone and polysiloxanes. Some examples of non-silicon foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexylacrylate, copolymers of ethyl acrylate, 2-ethylhexyl acrylate, and vinyl acetate, polyethers, polyacrylates, and mixtures thereof. In some embodiments the antifoam agent may be a polyacrylate. Antifoam agents may be present in a lubricant composition in amounts of 0.001 to 0.012 percent by weight or to 0.004 percent, or 0.001 to 0.003 percent by weight.

[0094] Demulsifiers are known in the art and include but are not limited to derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines, or polyamines, reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include polyethylene glycols, polyethylene oxides, polypropylene oxides such as ethylene oxide-propyelene oxide polymers, and mixtures thereof. In some embodiments the demulsifier may be a polyether. Demulsifiers may be present in a lubricant at 0.002 to 0.012 weight percent.

[0095] Pour point depressants are known in the art and include but are not limited to esters of maleic anhydride-styrene copolymers; polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; copolymers comprising dialkyl fumarates; polyalphaolefins, vinyl esters of fatty acids; ethylene-vinyl acetate copolymers; alkyl phenol formaldehyde condensation resins; alkyl vinyl ethers; and mixtures thereof.

[0096] Rust inhibitors may include hydrocarbyl amine salts of alkylphosphoric acid, hydrocarbyl amine salts of dialkyldithiophosphoric acid, hydrocarbyl amine salts of hydrocarbyl aryl sulfonic acids, fatty carboxylic acids or esters thereof (including alkyl substituted succinic acids and salts, esters, amide, or imides thereof), esters of nitrogen-containing carboxylic acids, ammonium sulfonates, imidazolines,

or combinations or mixtures thereof. A rust inhibitor may be present in a lubricant in an amount of 0.02 to 0.2 percent by weight, or 0.03 to 0.15, or 0.04 to 0.12, or 0.05 to 0.10 percent by weight.

[0097] Metal deactivators may be used to neutralize the catalytic effect of metals for promoting oxidation in lubricating oils. Suitable metal deactivators include but are not limited to triazoles, tolyltriazoles, thiadiazoles, and combinations or derivatives thereof. Examples include derivatives of benzotriazoles, benzimidazoles, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N'-dialkyldithiocarbamoyl)benzothiazoles, 2,5-bis(alkyldithio)-1,3,4-thiadiazoles, 2,5-bis-(N,N'-dialkyldithiocarbamoyl-1,3,4-thiadiazoles, 2-alkyldithio-5-mercaptothiadaizoles, and mixtures thereof. A metal deactivator may be present in an amount of 0.001 to 0.1, or 0.1 to 0.04, or 0.15 to 0.03 percent by weight.

[0098] In one embodiment a lubricant further comprises (in addition to the polymers disclosed herein) at least one of a detergent, a dispersant, an antioxidant, an anti-wear agent, a friction modifier, a pour point depressant, a corrosion inhibitor, and antifoam agent, a demulsifier, a metal deactivator, or a metal salt of a phosphorus acid; in one embodiment a lubricant composition further comprises an overbased detergent in an amount of 0.5 to 2.0 weight percent and an ashless dispersant in an amount of 0.5 to 3 weight percent.

[0099] Method for lubricating. The additives and the lubricant compositions described above may be used for lubricating a mechanical device, and such lubrication may comprise supplying to the device, or to that part of the device that admits the lubricant, the lubricant as described herein. Examples of suitable devices may include internal combustion engines such spark-ignited engines, passenger car engines, or motorcycle engines; gears, clutches, transmissions, hydraulic devices, and turbines. The lubricant may be a liquid lubricant or a grease.

[0100] Engines may include internal combustion engines such as a gasoline or spark-ignited engine such as a passenger car engine, a diesel or compression-ignited engine such as a passenger car diesel engine, heavy duty diesel truck engine, a natural gas fueled engine such as a stationary power engine, an alcohol-fueled engine, a mixed gasoline/alcohol fueled engine, a bio-diesel fueled engine, a hydrogen-fueled engine, a two-cycle engine, an aviation piston or turbine engine, or a marine or railroad diesel

engine. In one embodiment the internal combustion engine may be a diesel fueled engine and in another embodiment a gasoline fueled engine or a hydrogen-fueled engine. The internal combustion engine may be fitted with an emission control system or a turbocharger. Examples of emission control systems include diesel particulate filters (DPF), exhaust gas recirculation (EGR), and systems employing selective catalytic reduction (SCR).

[0101] The engine may also be a motorcycle engine and the lubricant may be considered a motorcycle lubricant. Lubricants for motorcycles typically provide lubrication for the engine (a crankcase) as well as a wet clutch. These two devices, although often lubricated by the same fluid, often have different lubrication requirements. For example, the lubrication of the engine desirably provides low metal-on-metal friction, to promote good fuel economy. (Typically, the "metal" referred to is steel.) However, the friction coefficient for the metal-on-composition interfaces located within the wet clutch may desirably be relatively high, to assure good engagement and power transmission. Additionally, motorcycle lubricants will also lubricate other devices such as gears or bearings, each having their own lubricating requirement. In one embodiment, the lubricant as described herein may lubricate both the engine and the wet clutch of a motorcycle.

[0102] Hydraulic fluids may be more generally described as, or may be considered a species of, industrial fluids, which may include hydraulic fluids, turbine oils, circulating oils, or combinations thereof. A hydraulic fluid may be considered to a fluid that transfers force through a device by virtue of its fluid properties. The hydraulic system may comprise a hydraulic pump such as a piston pump, vane pump, gear pump, or a combination of these. It may also contain hydraulic motors or hydraulic pistons used to actuate wheels or tracks for locomotion and/or operation of implements, such as buckets, diggers, or rams. Mobile hydraulic systems include those used on wheel loaders, backhoes, excavators, rollers, and farm equipment. Hydraulic fluids and hydraulic equipment may be used in transportation vehicles systems, such as hydraulic launch assists or hydraulic braking systems, as well as in stationary devices. In one embodiment, the hydraulic system may be capable of transferring rotational energy into a stored energy reservoir for later reconversion into

rotational energy. The hydraulic fluid may optionally be zinc free, metal free, or ashless or may optionally contain any of the aforesaid features.

[0103] As used herein, the term "condensation product" and its cognates (e.g., "condensed") is intended to encompass esters, amides, imides and other such materials that may be prepared by a condensation reaction of an acid or a reactive equivalent of an acid (e.g., an acid halide, anhydride, or ester) with an alcohol or amine, irrespective of whether a condensation reaction is actually performed to lead directly to the product. Thus, for example, a particular ester may be prepared by a transesterification reaction rather than directly by a condensation reaction. The resulting product is still considered a condensation product.

[0104] The amount of each chemical component described is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, that is, on an active chemical basis, unless otherwise indicated. However, 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.

[0105] As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term "hydrocarbyl substituent" or "hydrocarbyl group" is found in paragraphs [0137] to [0141] of published application US 2010-0197536.

[0106] 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 or anionic 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.

[0107] The invention herein is useful for application in hydraulic systems and engines, which may be better understood with reference to the following examples.

EXAMPLES

[0108] Examples 1-5. Lubricants are prepared in a formulation to have a viscosity index of about 140 with a variety of ISO grades (represented by kinematic viscosity at 40 °C, mm^2/s). The lubricants are prepared from the base oils indicated, and each formulation contains about 0.85% of a commercial dispersant/inhibitor ("DI") package which in turn comprises a zinc dialkyldithiophosphate, a phenolic antioxidant, calcium detergents (alkylsulfonate(s) and phenate(s)), an alkyl-substituted carboxylic anhydride, and small amounts of other inhibitor(s) and other conventional materials, as well as diluent oil. Formulations can be made in various viscosity grades, as illustrated in Table I:

Table I.

Example	1	2	3	4	5
ISO viscosity grade target	22	32	46	68	100
Base oil composition[a]					
80 N Group III	40				
100 N Group I	60	74.1			
150 N Group I		25.9	100	80	55
600 N Group I				20	45
DI Package, %	0.85	0.85	0.85	0.85	0.85
Star polymer[b], %	0.31	0.42	0.47	0.65	0.80
Ethylene/olefin copolymer[c], %	0.34	0.47	0.52	0.72	0.88
Viscosity properties:					
KV @ 40 °C (mm^2/s)	22.3	33.3	47.8	69.2	102.0
KV @ 100 °C (mm^2/s)	4.79	6.32	8.02	10.6	14.0
Viscosity Index (VI)	140	143	140	140	139

a. Relative amounts, totaling 100% oil; API Groups I or III as indicated.

b. Oil-free amount. As supplied, contains 53% oil. Polymer is a star polymer with 6-15 arms on average, the arms having a M_n of about 35,000 to 50,000. The arms are random copolymers comprising C10-18 alkyl methacrylate monomer(s) and C1-9 alkyl methacrylate monomer(s), linked to a core prepared from an alkylene glycol dimethacrylate.

c. Oil-free amount. As supplied, contains 87% oil. Polymer is a commercial ethylene/propylene copolymer, about 45 percent by weight ethylene monomer units, having a M_w of about 150,000.

[0109] Examples 6-11. Lubricants are prepared targeting an ISO 46 viscosity grade, using varying amounts and various relative ratios of star polymer and ethylene/olefin copolymer. The DI package is the same commercial package that is used in Examples 1-5. Footnotes a, b, and c from Table I apply.

Table II

Example	6	7	8	9	10	11
ISO viscosity grade target	46	46	46	46	46	46
Base oil composition[a]						
150 N Group II	100	99	94.4	90.5	88	85
500 N Group II		1	5.6	9.5	12	15
DI Package, %	0.85	0.85	0.85	0.85	0.85	0.85
Star polymer[b], %	0.11	0.23	0.31	0.38	0.44	0.49
Ethylene/olefin copolymer[c], %	0.58	0.56	0.48	0.51	0.37	0.32
Viscosity properties:						
KV @ 40 °C (mm^2/s)	46.8	46.8	46.7	46.8	46.8	46.8
KV @ 100 °C (mm^2/s)	7.89	7.94	7.87	7.85	7.84	7.82
Viscosity Index (VI)	139	141	139	137	137	136

[0110] The results illustrate ease of formulation of lubricants of a variety of viscosity grades with high viscosity index, using varying ratios of the polymers of the disclosed technology.

[0111] Examples 12 and 13. Lubricants are prepared with formulations as set forth in Table III (footnotes a, b, and c from Table I apply):

Table III

Example	12	13 (ref.)
Base oil composition[a]		
100 N Group I	74	76
500 N Group I	26	24
DI Package, %	0.85	0.85
Conventional methacrylate pour point depressant/ viscosity modifier (oil-free, excl. 40% oil), %	0.12	0.12
Star polymer[b]	0.42	—
Ethylene/olefin copolymer[c]	0.47	—
Conventional linear methacrylate copolymer; 86% C12-15, 14% C1, (oil-free, excl. 21.4% oil), %	—	5.1
Viscosity properties:		
KV @ 40 °C (mm^2/s)	33.3	32.2
KV @ 100 °C (mm^2/s)	6.32	6.30
Viscosity Index (VI)	143	150
104c pump test; weight loss, mg		
Ring	36.1	81.9
Vane	0.5	2.2
Total	36.6	84.1

[0112] The lubricants are also subjected to the 104c ("Conestoga") pump test, as described in greater detail in ISO20763, and the results are also reported in Table III. In this test, a pump cam ring and vanes are weighed before and after the test, and the weight loss from the ring and vanes is measured. The test length is 250 hours, the temperature 69 °C, pressure of 14 MPa (140 bar) and 1440 r.p.m. The lubricant sample size is 70 L with a flow rate of about 25 L/min. The results show that the material of the disclosed technology provides dramatically reduced wear compared with a similar formulation using a conventional linear methacrylate copolymer viscosity modifier.

[0113] Examples 14-17. Formulations are prepared as shown in Table IV, below, using comb polymers identified as d or e in the footnotes or, for reference, a linear methacrylate polymer.

Table IV

Example	14	15	16	17(ref)
ISO viscosity grade target	46	46	46	46
Base oil composition[a]				
150 N Group II	100	100	100	100
DI Package, %	0.85	0.85	0.85	0.85
Pour point depressant as in Table III	0.12	0.12	0.12	0.12
Comb polymer[d], %		0.44		
Comb polymer[e], %			0.44	
Star polymer[b], %	0.47			
Ethylene/olefin copolymer[c], %	0.52	0.56	0.56	
Linear methacrylate polymer[j]				6.1
Viscosity properties:				
KV @ 40 °C (mm^2/s)	47.8	46.6	46.3	46.2
KV @ 100 °C (mm^2/s)	8.02	7.87	7.88	8.33
Viscosity Index (VI)	140	139	141	157
Wear scar (μm), 4-ball wear test ASTM D 4172	not determined	0.25	0.25	0.27

a. Relative amount, totaling 100% base oil

b. See footnote to Table I

c. See footnote to Table I.

d. Oil free amount; as supplied contains 60% oil. A comb polymer comprising 5% by weight C12-15 alkyl methacrylate, 83% by weight C4 methacrylate, and 12% by weight macromonomer comprising an alkyl methacrylate where the alkyl group is derived from polybutadiene (hydrogenated) having about 355 carbon atoms. M_w 182,000.

e. Oil free amount; as supplied contains 60% oil. A comb polymer comprising 14% by weight styrene, 58% by weight C4 alkyl methacrylate, and 28% by weight macromonomer as listed in footnote d. Mw 140,000.

j. Oil free amount; as in Table III.

[0114] Examples 18 (reference) and 19. Lubricant formulations are prepared as shown in Table V. (Amount of base oil is given as percentage of the lubricant formulation.)

Table V

Example	18 (ref)	19
Base oil composition		
3 cSt Group III, %	85.0	86.4
DI Package[f], %	9.18	9.18
Pour point depressant[g]	0.1	0.2
Star polymer[b], %	2.64	1.85
Ethylene/olefin copolymer[c], %	0	0.2
Viscosity properties:		
KV @ 40 °C (mm^2/s)	36.2	37.2
KV @ 100 °C (mm^2/s)	8.30	8.12
Viscosity Index (VI)	216	201

b. As defined in Table I; except containing 54% oil (amount presented in table on oil-free basis).

c. Ethylene/propylene copolymer as defined for Table I, except provided here as an oil-free solid material.

f. A commercial passenger car engine oil dispersant/inhibitor package containing about 17% Na and Ca overbased detergents, 44% dispersant(s), 9% zinc dialkyldithiophosphates, 17% antioxidants, and 8% alkyl tartrimide, each of the foregoing containing conventional amounts (if any) of diluent oil, plus further diluent oil and smaller amounts of other conventional components.

g. A methacrylate copolymer; amount includes about 50% diluent oil

[0115] The lubricants of Ex. 18 (reference) and Ex 19, formulated as SAE 0W-20 grade lubricants, are tested by an externally driven engine assembly friction test rig, measuring torque at speeds from 500 to 2,500 r.p.m. at 88, 60, and 25 °C. The per-

cent reduction in torque for the candidate fluids is compared to that of a baseline SAE 0W-20 fluid. While both fluids exhibit reduced torque compared to the baseline lubricant at 60 and 88 °C, the formulation containing the mixture of star polymer and ethylene-propylene copolymer (Ex. 19) exhibits a greater reduction in torque. Results at 60 and 88 °C are shown in the following Table Va

Table Va

% Reduction in Torque	Ref Ex. 18	Ex. 19
500 rpm/88°C	6.61	8.89
1000 rpm/88°C	4.76	6.06
1500 rpm/88°C	4.06	4.80
2000 rpm/88°C	3.09	6.42
2500 rpm/88°C	1.82	3.03
average @ 88°C	4.07	5.84
500 rpm/60°C	2.21	2.76
1000 rpm/60°C	-0.34	1.45
1500 rpm/60°C	-0.41	1.24
2000 rpm/60°C	0.26	1.37
2500 rpm/60°C	0.71	1.36
average @ 60°C	0.49	1.64

(Results at 25 °C show little change over the baseline; average torque reduction: +0.42% for Ref. Ex. 18 and -0.57% for Ex. 19.)

[0116] Examples 20 through 26. Lubricants are prepared and tested as shown in Table VI:

Table VI

Example	20	21	22	23	24	25	26 (ref)
Base oil composition							
6 cSt API Group III oil,%	60.2	60.2	60.2	60.1	60.1	60.1	61.5
7 cSt API Group I oil, %	20.1	20.0	20.0	20.0	20.0	20.0	18.5
DI Package[m], %	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Succinimide dispersant[h]	2.5	2.5	2.5	2.5	2.5	2.5	0.3

Aminic antioxidant	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pour point depressant[g]	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Star polymer[b], %	1.3	1.2	0.99	0.61	0.47	0.24	0
Ethylene/olefin copolymer[c], %	0.60	0.63	0.70	0.81	0.84	0.90	0.98
Viscosity properties:							
KV @ 40 °C (mm^2/s)	90.7	90.2	91.6	94.5	95.7	96.6	97.0
KV @ 100 °C (mm^2/s)	14.7	14.6	14.6	14.8	14.8	14.7	14.7
Viscosity Index (VI)	170	169	167	163	161	159	158
MRV viscometry, -30°C, Pa-s (ASTM D4684)	17.4	18.0	18.5	19.8	19.9	21.4	22.8
After-Shear KV@100 °C (ASTM D7109)	13.6	13.4	13.5	13.2	13.2	13.2	13.1

b. As in Table I, oil-free amount

c. As in Table I, oil-free amount

g. As in Table V

h. Including about 33% diluent oil. A borated dispersant, in addition to dispersant(s) present in the DI package.

m. A multipurpose commercial additive package containing 21% overbased detergent(s), 54% dispersant(s), 12% antioxidants, and 10% zinc dialkyldithiophosphate, each of the foregoing containing conventional amounts (if any) of diluent oil, plus further diluent oil and smaller amounts of other conventional components.

[0117] Lubricants which contain the mixture of Star polymer and olefin copolymer exhibit reduced MRV viscosity and increased viscosity index with good retention of viscosity after shear as measured according to ASTM D7109 (90-pass "Orbahn" shear stability test, in which polymer-containing fluid is passed through a Bosch™ diesel injector nozzle at high pressure. This treatment causes degradation of polymer molecules. Kinematic viscosity at 100°C before and after shear is determined).

[0118] Each of the documents referred to above is incorporated herein by reference, including any prior applications, whether or not specifically listed above, from which priority is claimed. The mention of any document is not an admission that such document qualifies as prior art or constitutes the general knowledge of the skilled person in any jurisdiction. 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 optionally modified by the word "about." It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention can be used together with ranges or amounts for any of the other elements.

[0119] As used herein, the transitional term “comprising,” which is synonymous with “including,” “containing,” or “characterized by,” is inclusive or open-ended and does not exclude additional, un-recited elements or method steps. However, in each recitation of “comprising” herein, it is intended that the term also encompass, as alternative embodiments, the phrases “consisting essentially of” and “consisting of,” where “consisting of” excludes any element or step not specified and “consisting essentially of” permits the inclusion of additional un-recited elements or steps that do not materially affect the essential or basic and novel characteristics of the composition or method under consideration. The expression “consisting of” or “consisting essentially of,” when applied to an element of a claim, is intended to restrict all species of the type represented by that element, notwithstanding the presence of the term “comprising” elsewhere in the claim.

[0120] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention. In this regard, the scope of the invention is to be limited only by the following claims. In certain jurisdictions, recitation of one or more of narrower values for a numerical range or recitation of a narrower selection of elements from a broader list means that such recitations represent preferred embodiments.

The Claims defining the Invention are as follows:

1. A lubricant composition comprising:

(a) an oil of lubricating viscosity;

(b) a (meth)acrylate-containing polymer comprising a multiplicity of arms wherein the arms contain at least about 20, or at least 50 or 100 or 200 or 350 or 500 or 1000, carbon atoms, said arms being attached to a multivalent organic moiety; and

(c) an ethylene/olefin copolymer having a weight average molecular weight of about 5000 to about 250,000, or about 10,000 to about 250,000, wherein the copolymer comprises about 40 to about 70 weight percent polymerized ethylene monomer and further comprises one or more polymerized olefin monomers of 3 to 6 carbon atoms.

2. The lubricant composition of claim 1 wherein said arms are polymeric entities comprising non-olefinic monomer units.

3. The lubricant composition of claim 1 or claim 2 wherein said arms are polymeric entities comprising alkyl (meth)acrylate monomer units.

4. The lubricant composition of any of claims 1 through 3 wherein said arms are polymeric entities comprising comonomers of C10-C18 alkyl methacrylate groups and C1-C9 alkyl methacrylate groups.

5. The lubricant composition of any of claims 1 through 4 wherein the arms comprise random copolymers.

6. The lubricant composition of any of claims 1 through 5 wherein the arms comprise block copolymers.

7. The lubricant composition of any of claims 1 through 6 wherein the number of arms attached to the multivalent organic moiety is 3 to 20, or 5 to 20, or 6 to 15, or 7 to 8.

8. The lubricant composition of any of claims 1 through 7 wherein the number average molecular weight of the arms is about 10,000 to about 200,000, or 20,000 to 100,000, or 35,000 to 50,000 .

9. The lubricant composition of any of claims 1 through 8 wherein one or more of the arms comprises a unit derived from an alkyl acrylate monomer.

10. The lubricant composition of any of claims 1 through 9 wherein the (meth)-acrylate-containing polymer comprises a star polymer with multiple arms linked to a core.

11. The lubricant composition of claim 10 wherein the core comprises polymerized monomers of an alkylene glycol dimethacrylate.

12. The lubricant composition of claim 1 wherein said arms comprise hydrocarbyl groups.

13. The lubricant composition of any of claims 1 through 12 wherein the (meth)acrylate-containing polymer comprises a comb polymer.

14. The lubricant composition of claim 13 wherein said arms are polymeric entities comprising conjugated diene monomer units (optionally hydrogenated) or isobutylene monomer units.

15. The lubricant composition of claim 14 wherein the conjugated diene comprises butadiene or isoprene.

16. The lubricant composition of any of claims 1 through 15 wherein the amount of the (meth)acrylate-containing polymer comprising a multiplicity of arms is present in an amount of about 0.1 to 2.5 or 0.25 to about 2.5 percent by weight.

17. The lubricant composition of any of claims 1 through 16 wherein the ethylene/olefin copolymer comprises at least one of propylene or butylene monomer units.

18. The lubricant composition of any of claims 1 through 17 wherein the ethylene/olefin copolymer comprises propylene monomer units.

19. The lubricant composition of any of claims 1 through 18 wherein the ethylene/olefin copolymer comprises about 40 to about 50 percent by weight ethylene monomer units and about 50 to about 60 percent by weight propylene monomer units.

20. The lubricant composition of any of claims 1 through 19 wherein the ethylene/olefin copolymer has a weight average molecular weight of about 20,000 to about 180,000.

21. The lubricant composition of any of claims 1 through 20 wherein the amount of the ethylene/olefin copolymer is about 0.1 to about 10 or about 0.1 to about 2.5 or about 0.1 to about 1 percent by weight.

22. The lubricant composition of any of claims 1 through 21 further comprising at least one of a detergent, a dispersant, an antioxidant, an anti-wear agent, a friction modifier, a pour point depressant, a corrosion inhibitor, and antifoam agent, a demulsifier, a metal deactivator, or a metal salt of a phosphorus acid.

23. The lubricant composition of any of claims 1 through 22 wherein the composition further comprises an overbased detergent in an amount of about 0.5 to about 2.0 weight percent and an ashless dispersant in an amount of about 0.5 to about 3 weight percent.

24. A lubricant composition of any one of claims 1 through 23 suitable for lubricating a motorcycle crankcase and wet clutch, further comprising an overbased calcium detergent in an amount of 0.2 to 1.8 weight percent of the composition, an ashless dispersant in an amount of 0.8 to 3.2 weight percent of the composition, and a friction modifying additive that increases static friction at a friction plate-steel plate interface in an amount of 0.05 to 1.85 weight percent of the composition.

25. A method for lubricating a mechanical device comprising supplying thereto the lubricant composition of any of claims 1 through 24.

26. The method of claim 25 wherein the mechanical device comprises a hydraulic system.

27. The method of claim 25 wherein the mechanical device comprises an internal combustion engine.

28. The method of claim 27 wherein the internal combustion engine is a passenger car engine.

29. The method of claim 27 or claim 28 wherein the internal combustion engine is a spark-ignited engine.

30. The method of claim 27 wherein the internal combustion engine comprises a motorcycle engine.