



- (51) International Patent Classification:
C10M 169/04 (2006.01)
- (21) International Application Number:
PCT/US2014/037774
- (22) International Filing Date:
13 May 2014 (13.05.2014)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
61/822,953 14 May 2013 (14.05.2013) US
- (71) Applicant: THE LUBRIZOL CORPORATION
[US/US]; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).
- (72) Inventors: ABRAHAM, William D.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US). STRECK, Kevin J.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US). RUSSO, Gary A.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US). SCHIFERL, Elizabeth A.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).
- (74) Agents: ESPOSITO, Michael F. et al.; 29400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



WO 2014/186318 A1

(54) Title: LUBRICATING COMPOSITION AND METHOD OF LUBRICATING A TRANSMISSION

(57) Abstract: The present invention relates to a lubricating composition comprising: (a) an oil of lubricating viscosity having a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 104 to 130; (b) 1.2 to 5.0 wt % of at least one borated dispersant, wherein at least one borated dispersant is further functionalised with a sulphur or phosphorus moiety; (c) a calcium-containing detergent present in an amount to deliver at least 110 ppm to 700 ppm of calcium; (d) at least two phosphorus-containing compounds present in an amount to deliver 360 to 950 ppm of phosphorus; and (e) 0.1 wt % to 5 wt % of a linear polymer viscosity modifier having dispersant functionality. The invention further provides a method of lubricating a transmission with the lubricating composition disclosed wherein.

TITLE

Lubricating Composition and Method of Lubricating a Transmission

FIELD OF INVENTION

5 The present invention relates to a lubricating composition comprising:(a) an oil of lubricating viscosity having a kinematic viscosity at 100°C of 2.8 to 3.6 cSt and a viscosity index of 104 to 130; (b) 1.2 to 5.0 wt % of at least one borated dispersant, wherein at least one borated dispersant is further functionalised with a sulphur or phosphorus moiety; (c) a calcium-containing
10 detergent present in an amount to deliver at least 110 ppm to 700 ppm of calcium; (d) at least two phosphorus-containing compounds, wherein the phosphorus-containing compounds are present in an amount to deliver 360 to 950 ppm of phosphorus to the lubricating composition, wherein at least 150 ppm of the phosphorus is delivered by a C₄₋₆ hydrocarbyl phosphite; and (e) 0.1 wt % to
15 5 wt % of a linear polymer viscosity modifier having dispersant functionality. The invention further provides a method of lubricating a transmission with the lubricating composition disclosed wherein.

BACKGROUND OF THE INVENTION

[0001] Driveline transmissions especially automatic transmission fluids
20 (ATFs), present highly challenging technological problems and solutions for satisfying the multiple and often conflicting lubricating and power transmitting requirements of modern automatic transmissions (including continuously variable transmissions of various types). Many additive components are typically included in an ATF, providing such performance characteristics as lubrication, dispersancy,
25 friction control (for clutches), anti-wear durability (e.g., gear wear) and pump durability, fuel economy, anti-shudder performance, anti-corrosion and anti-oxidation performance. However, over periods of use, the additive components are consumed which may detrimentally damage transmissions.

[0002] US 5,578,236 (Srinivasan, published 26 November 1996) discloses a
30 power transmission fluid composition wherein said composition has on a weight basis an oil-soluble boron content of about 0.001 to about 0.1%, an oil-soluble phosphorus content of about 0.005 to about 0.2%, and either no metal

additive content or an oil-soluble metal content as one or more metal-containing additives of no more than about 100 ppm; wherein said composition comprises: a) at least about 50 wt % based on the total weight of said composition of one or more hydrotreated mineral oils in the range of about 55N
5 to about 125N; b) about 5 to about 40 wt % based on the total weight of said composition of hydrogenated poly- α -olefin oligomer fluid having a viscosity in the range of about 2 to about 6 cSt at 100 °C; c) on an active ingredient basis, about 5 to about 20 wt % based on the total weight of said composition of an acrylic viscosity index improver having a permanent shear
10 stability index of 30 or less in the form of a solution in an inert solvent; d) an effective seal-swelling amount of at least one seal swell agent selected from oil-soluble dialkyl esters, oil-soluble sulfones, and mixtures thereof; e) a dispersant amount of at least one oil-soluble ashless dispersant; f) a friction modifying amount of at least one oil-soluble friction modifier; and g) oil-
15 soluble inhibitors selected from the group consisting of foam inhibitors, copper corrosion inhibitors, rust inhibitors, and oxidation inhibitors; with the proviso that said composition has (i) a Brookfield viscosity of 13,000 cP or less at -40 °C, (ii) a viscosity of at least 2.6 mPa.s at 150 °C in the ASTM D-4683 method, and (iii) a viscosity of at least 6.8 cSt at 100 °C after 40 cycles in the FISST of
20 ASTM D-5275.

[0003] US 2011-0239971 (Nelson, published 6 October, 2011) discloses a method for improving copper corrosion performance of a lubricating oil composition comprising (a) a major amount of a base oil of lubricating viscosity; and (b) one or more dispersants containing one or more basic
25 nitrogen atoms, the method comprising adding to the lubricating oil composition an effective amount of one or more copper corrosion performance improving agents of the general formula Si-X₄ or a hydrolysis product thereof, wherein each X is independently a hydroxyl-containing group, hydrocarbyloxy-containing group, acyloxy-containing group, amino-containing group, monoalkyl amino-containing group or dialkyl amino-containing group.
30

[0004] EP 1 705 235 (Ozbalik, published 22 March 2006) discloses an automatic transmission fluid composition comprising: (a) a major amount of a

base oil; (b) one or more friction modifiers, wherein total nitrogen content provided by the one or more friction modifiers is greater than or equal to about 300 ppm; and (c) one or more ashless dispersants, wherein the total nitrogen content provided by the one or more ashless dispersants is greater than or equal
5 to about 500 ppm; wherein the automatic transmission fluid has a kinematic viscosity at 100 °C of from about 4 cSt to about 6.5 cSt and a Brookfield viscosity at -40 °C of from about 4,000 cP to about 20,000 cP.

[0005] International Publication WO 2005/010134 (Sumiejski *et al.*, 3 February 2005) discloses a lubricating composition containing (a) a
10 hydrocarbyl phosphite; (b) the condensation product of at least one fatty acid with a polyamine; (c) a borate ester; (d) a borated dispersant; and (e) an oil of lubricating viscosity. The invention further relates to the use of the composition in automotive transmissions.

[0006] International Publication WO 2007/127615 (Tipton *et al.*, 8 November
15 2007) discloses a lubricating composition containing a polymer such as a star polymer, a phosphorus-containing compound and a dispersant. The invention further provides a method for lubricating a mechanical device using the lubricating composition.

[0007] International Publication WO 00/70001 (Ward, 23 November 2000)
20 discloses a method for lubricating a continuously variable transmission, comprising supply thereto a composition comprising (a) an oil of lubricating viscosity; (b) a dispersant; a detergent; or mixtures of (b) and (c) wherein at least one of the dispersant (b) and the detergent (c) is a borated species and wherein the amount of boron is at least 250 parts per million, based on the
25 composition, and is present in an amount sufficient to impart improved friction and anti-seizure properties to said composition when employed in said transmission. The composition is also noted as useful for automatic transmissions.

[0008] US 5,840,663 (Nibert *et al.*, published 24 November 1998) discloses
30 a composition and method of improving the anti-shudder durability of a power transmitting fluid comprising: a major amount of a lubricating oil; and an anti-shudder improving effective amount of an additive combination comprising: a

reaction product of an isomerized alkenyl substituted succinic anhydride and a polyamine, an oil-soluble alkyl phosphite, an ashless dispersant with alkyl side chains of greater than 1500 molecular weight; a nitrogen containing corrosion inhibitor, and optionally, a metallic detergent which is a salt of an alkali, or
5 alkaline earth metal. The anti-shudder durability of these fluids can be further improved by optionally incorporating overbased metallic detergents.

[0009] US 7,737,092 (Ward *et al.*, published 11 August 2005) discloses a composition suitable for use as a lubricant for a transmission, comprising: (a) an oil of lubricating viscosity; (b) a dispersant; (c) a calcium detergent; (d) a
10 magnesium detergent; and (e) an inorganic phosphorus compound; wherein at least one of (b), (c), and (d) is borated. The formulations of Ward are suitable for use as fluids for transmissions, especially continuously variable transmissions. Ward also discloses that continuously variable transmissions (CVT) represent a radical departure from conventional automatic transmissions.

[0010] US 20020151441 (Srinivasan *et al.*, published 17 October 2002) discloses an automatic transmission fluid, comprising: a major amount of a base oil, and a minor amount of an additive comprising at least about 0.10 weight % of a metal-containing detergent, a dispersant, and a mixture of at
15 least two different friction modifiers. The automatic transmission fluid has anti-shudder durability, and friction durability.

[0011] US 20090305922 (Cha *et al.*, published 10 December 2009) discloses an automatic transmission lubricating oil composition, and particularly to an automatic transmission lubricating oil composition comprising an oil of lubricating viscosity, an ashless dispersant, an anti-
25 oxidant, a phosphorus-based anti-wear agent and a friction-modifier, wherein more than 310 ppm of phosphorus is contained, thereby being useful for lubricating or operating an automatic transmission comprising a transmission clutch using a slip lock-up torque converter and a paper based clutch material and a planetary gear system, especially six-speed automatic transmission.

[0012] US 20120277134 (Deshimaru, published 1 November 2012) discloses a lubricating oil composition contains: at least one lubricating base oil selected from the group consisting of a mineral lubricating base oil and a
30

synthetic lubricating base oil; (a) a neutral phosphorus compound; (b) at least one acid phosphorus compound selected from the group consisting of a specific acid phosphate amine salt and a specific acid phosphite; and (c) a sulphur compound. The lubricating oil composition may be an automatic transmission fluid with a kinematic viscosity at 100-°C of 5 mm²/s.

SUMMARY OF THE INVENTION

[0013] An objective of the present invention is to provide a lubricating composition capable of lubricating an automatic transmission. The lubricating composition may be capable of providing at least one property including friction control (for clutches), improved fuel economy, anti-wear durability (*e.g.*, gear wear) and pump durability, and anti-shudder performance. The lubricating composition may for instance, be capable of providing improved fuel economy, and anti-wear durability.

[0014] 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 basic and novel characteristics of the composition or method under consideration.

[0015] As used herein the term “C₄₋₆ hydrocarbyl phosphite” is intended to include both a mono- C₄₋₆ hydrocarbyl phosphite and di- C₄₋₆ hydrocarbyl phosphite. Typically the C₄₋₆ hydrocarbyl phosphite comprises a di- C₄₋₆ hydrocarbyl phosphite.

[0016] As used herein the expression “(meth)acrylic”, (meth)arylate” and related terms is intended to encompass both acrylic functionality as well as methacrylic functionality. Typically the (meth)acrylic”, (meth)arylate” and related terms is intended to include a methacrylic or methacrylate.

[0017] The present invention in one embodiment may be a lubricating composition comprising:

(a) an oil of lubricating viscosity having a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 104 to 130;

(b) 1.2 to 5.0 wt % of at least one borated dispersant, wherein at least one borated dispersant is further functionalised with a sulphur or phosphorus moiety;

5 (c) a calcium-containing detergent, wherein the detergent is present in an amount to deliver at least 110 ppm to 700 ppm of calcium;

(d) at least two phosphorus-containing compounds, wherein the phosphorus-containing compounds are present in an amount to deliver 360 to 950 ppm of phosphorus to the lubricating composition, wherein at least 150 ppm of
10 the phosphorus is delivered by a C₄₋₆ hydrocarbyl phosphite; and

(e) 0.1 wt % to 5 wt % of a linear polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of 5,000 to 25,000.

[0018] The present invention in a different embodiment may be a
15 lubricating composition comprising:

(a) an oil of lubricating viscosity having a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 104 to 130;

(b) 1.2 to 5.0 wt % of at least one borated dispersant, wherein at least one borated dispersant is further functionalised with a sulphur or phosphorus moiety;

20 (c) a calcium-containing detergent, wherein the detergent is present in an amount to deliver at least 160 ppm to 400 ppm of calcium;

(d) a at least two phosphorus-containing compounds, wherein the phosphorus-containing compounds are present in an amount to deliver 525 to 800 ppm of phosphorus to the lubricating composition, wherein at least 150 ppm of
25 the phosphorus is delivered by a C₄₋₆ hydrocarbyl phosphite; and

(e) 0.1 wt % to 5 wt % of a linear polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of 5,000 to 25,000.

[0019] The lubricating composition of the present invention may further
30 comprise 0.1 wt % to 5 wt % of a (meth)acrylic polymer having star architecture.

[0020] The lubricating composition of the present invention may further comprise 0.1 wt % to 5 wt % of a linear (meth)acrylic polymer viscosity

modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of greater than 25,000 to 400,000 (or to 350,000).

[0021] The amount of boron in the lubricant composition disclosed herein may be 150 to 400 parts per million by weight.

5 [0022] In one embodiment, the lubricating composition disclosed herein further comprises 0.3 wt % to 1.2 wt % of an amine antioxidant.

[0023] In one embodiment, the lubricating composition disclosed herein further comprises 0.5 wt % to 3.5 wt % of a friction modifier component comprising at least two ashless friction modifiers.

10 [0024] In one embodiment, the lubricating composition disclosed herein further comprises 0.3 wt % to 1.2 wt % of an amine antioxidant; and 0.5 wt % to 3.5 wt % of a friction modifier component comprising at least two ashless friction modifiers.

[0025] The lubricating composition disclosed herein may in one
15 embodiment of the invention have a kinematic viscosity at 100°C of 3.6 to 4.8 cSt (mm²/s); and a Brookfield viscosity at -40°C may be at most 6,800 cP (mPa·s).

[0026] In one embodiment the invention provides a method of lubricating an automatic transmission comprising supplying to the automatic transmission a
20 lubricating composition disclosed herein.

[0027] In one embodiment the invention provides for the use of the lubricating composition disclosed herein to provide at least one of friction control (for clutches), improved fuel economy, anti-wear durability (e.g., gear wear) and pump durability, and anti-shudder performance for an automatic transmission.

25 [0028] The automatic transmission includes continuously variable transmissions (CVT), infinitely variable transmissions (IVT), Toroidal transmissions, continuously slipping torque converted clutches (CSTCC), stepped automatic transmissions or dual clutch transmissions (DCT).

DETAILED DESCRIPTION OF THE INVENTION

30 [0029] The present invention provides a method of lubricating an automatic transmission and a lubricating composition as disclosed above.

[0030] As used herein, the viscosity index is determined by employing ASTM method D2270-10e1.

[0031] As used herein, the kinematic viscosity at 100°C is measured by the methodology of ASTM D445-12.

5 [0032] As used herein, the Brookfield viscosity is measured by ASTM D2983-09 at -40°C (Brookfield viscosity at -40°C).

Lubricating Composition

[0033] The lubricating composition may have a kinematic viscosity at 100°C of 3.6 to 4.8 cSt (mm²/s), or 4.0 to 4.6 cSt (mm²/s), or 4.0 to 4.4 cSt (mm²/s), or
10 4.0 to 4.2 cSt (mm²/s).

[0034] The lubricating composition may have a Brookfield viscosity at -40 C of at most 6,800 cP (mPa·s). The Brookfield viscosity at -40°C may be 3,000 to 6,800 cP (mPa·s).

[0035] The lubricating composition may have a kinematic viscosity at 100°C of 3.6 to less than 4.5 cSt (mm²/s); and a Brookfield viscosity at -40°C may be
15 3000 to at most 6,800 cP (mPa·s).

[0036] The lubricating composition may have a kinematic viscosity at 100°C of 4.0 to 4.4 cSt (mm²/s); and a Brookfield viscosity at -40°C may be 3,000 to 6,800 cP (mPa·s).

20 Oils of Lubricating Viscosity

[0037] The oil of lubricating viscosity of the invention has a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s), or 2.9 to 3.5 cSt (mm²/s), or 3.0 to 3.4 cSt (mm²/s). The kinematic viscosity at 100°C is measured by the methodology of ASTM D445-12. The oil of lubricating viscosity of the
25 invention may also be defined as an API Group II+ base oil. API Group II+ base oils are known and described for example in SAE publication entitled “Design Practice: Passenger Car Automatic Transmissions”, fourth Edition, AE-29, published 2012, page 12-9. US 8,216,448 also defines a API Group II+ as a
30 “Group II plus base oil” having a viscosity index greater than or equal to 110 and less than 120.

[0038] The oil of lubricating viscosity of the invention may have a viscosity index (VI) of at 104 to 130, or least 105, or at least 110, or at least 115 to 130. The viscosity index may be in the range of 104 to 125, or 110 to less than 120. In one particular embodiment the oil of lubricating viscosity has a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 110 to less than 120;

[0039] Examples of an oil of lubricating viscosity of the present invention include base oils sold under the registered trade names of S-Oil, Nexbase, Yubase, Petrocanada, and Chevron neutral oil 110RLV.

[0040] The oil of lubricating viscosity of the invention may be present at 60 wt % to 97.5 wt %, or 70 wt % to 95 wt %, or 80 wt % to 95 wt % of the lubricating composition.

[0041] The oil of lubricating viscosity of the invention with a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) may also be blended with a conventional oil of lubricating viscosity (*i.e.*, an oil of lubricating viscosity other than that defined by the present invention). The conventional oil of lubricating viscosity may be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows: Group I (sulphur content >0.03 wt %, and/or <90 wt % saturates, viscosity index 80-120); Group II (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index 80-120); Group III (sulphur content ≤0.03 wt %, and ≥90 wt % saturates, viscosity index ≥120); Group IV (all polyalphaolefins (PAOs)); and Group V (all others not included in Groups I, II, III, or IV). The oil of lubricating viscosity comprises an API Group I, Group II (other than the oil of lubricating viscosity defined by the present invention), Group III, Group IV, Group V oil or mixtures thereof.

[0042] Often the conventional oil of lubricating viscosity is an API Group I, Group II (other than the oil of lubricating viscosity defined by the present invention), Group III, Group IV oil or mixtures thereof. Alternatively the conventional oil of lubricating viscosity is often an API Group II (other than the oil of lubricating viscosity defined by the present invention), Group III or Group IV oil or mixtures thereof.

[0043] In one embodiment the conventional oil of lubricating viscosity may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

5 [0044] In one embodiment the conventional oil of lubricating viscosity may be an API Group IV oil. The amount of Group IV oil may be 0 wt % to 20 wt %, or 0.1 wt % to 20 wt %, or 1 wt % to 15 wt %, or 5 to 10 wt % of the lubricating composition.

[0045] 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 performance additives of the present invention.

[0046] The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the performance additives of this invention are 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 performance additives 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.

Detergent

[0047] The lubricating composition includes a calcium-containing detergent. The calcium-containing detergent is present in an amount to deliver 130 ppm to 600 ppm, or 160 ppm to 400 ppm of calcium.

[0048] The calcium-containing detergent may be an overbased detergent, a non-overbased detergent, or mixtures thereof. Typically the detergent may be overbased.

[0049] The preparation of the calcium-containing detergent is known in the art. Patents describing the preparation of overbased calcium-containing detergents 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.

[0050] As used herein the TBN values quoted and associated range of TBN is on “an as is basis,” i.e., containing conventional amounts of diluent oil. Conventional amounts of diluent oil typically range from 30 wt % to 60 wt % (often 40 wt % to 55 wt %) of the detergent component.

[0051] A more detailed description of the expressions “metal ratio”, TBN and “soap content” are known to a person skilled in the art and explained in standard textbook entitled “Chemistry and Technology of Lubricants”, Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, pages 219
5 to 220 under the sub-heading 7.2.5. Detergent Classification.

[0052] The calcium-containing detergent may be a non-overbased detergent (may also be referred to as a neutral detergent). The TBN of a non-overbased may be 20 to less than 200, or 30 to 100, or 35 to 50 mg KOH/g. The TBN of a non-overbased calcium-containing detergent may also be 20 to 175, or 30 to
10 100 mg KOH/g. When a non-overbased calcium-containing detergent is prepared from a strong acid such as a hydrocarbyl-substituted sulphonic acid, the TBN may be lower (for example 0 to 50 mg KOH/g, or 10 to 20 mg KOH/g).

[0053] The calcium-containing detergent may be an overbased detergent,
15 which may have a TBN of greater than 200 mg KOH/g (typically 250 to 600, or 300 to 500 mg KOH/g).

[0054] The calcium-containing detergent may be formed by the reaction of a basic calcium compound and an acidic detergent substrate. The acidic detergent substrate may include an alkyl phenol, an aldehyde-coupled alkyl phenol, a
20 sulphurised alkyl phenol, an alkyl aromatic sulphonic acid (such as, alkyl naphthalene sulphonic acid, alkyl toluene sulphonic acid or alkyl benzene sulphonic acid), an aliphatic carboxylic acid, a calixarene, a salixarene, an alkyl salicylic acid, or mixtures thereof.

[0055] The metal basic compound is used to supply basicity to the
25 detergent. The basic calcium compound is a compound of a hydroxide or oxide of the metal.

[0056] The oxides and/or hydroxides may be used alone or in combination. The oxides or hydroxides may be hydrated or dehydrated, although hydrated is typical. In one embodiment the basic calcium compound may be calcium
30 hydroxide, which may be used alone or mixtures thereof with other metal basic compounds. Calcium hydroxide is often referred to as lime. In one

embodiment the metal basic compound may be calcium oxide which may be used alone or mixtures thereof with other metal basic compounds.

5 [0057] Collectively, when the alkyl phenol, the aldehyde-coupled alkyl phenol, and the sulphurised alkyl phenol are used to prepare a calcium-containing detergent, the detergent may be referred to as a calcium phenate. The calcium phenate may be an alkyl phenate, an aldehyde-coupled alkyl phenate, a sulphurised alkyl phenate, or mixtures thereof.

10 [0058] The TBN of a calcium phenate may vary from less 200, or 30 to 175 typically 150 to 175) mg KOH/g for a neutral phenate to 200 or more to 500, or 210 to 400 (typically 230 to 270) mg KOH/g for an overbased phenate.

[0059] The alkyl group of a phenate (i.e., an alkyl phenate) may contain 4 to 80, or 6 to 45, or 8 to 20, or 9 to 15 carbon atoms.

15 [0060] In one embodiment the calcium-containing detergent may be a sulphonate, or mixtures thereof. The sulphonate may be prepared from a mono- or di- hydrocarbyl-substituted benzene (or naphthalene, indenyl, indanyl, or bicyclopentadienyl) sulphonic acid, wherein the hydrocarbyl group may contain 6 to 40, or 8 to 35 or 9 to 30 carbon atoms.

20 [0061] The hydrocarbyl group may be derived from polypropylene or a linear or branched alkyl group containing at least 10 carbon atoms. Examples of a suitable alkyl group include branched and/or linear decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl, un-eicosyl, do-eicosyl, tri-eicosyl, tetra-eicosyl, penta-eicosyl, hexa-eicosyl or mixtures thereof.

25 [0062] In one embodiment the hydrocarbyl-substituted sulphonic acid may include polypropene benzenesulphonic acid and/or C₁₆-C₂₄ alkyl benzenesulphonic acid, or mixtures thereof.

30 [0063] In one embodiment a calcium sulphonate detergent may be a predominantly linear alkylbenzene sulphonate detergent having a metal ratio of at least 8 as is described in paragraphs [0026] to [0037] of US Patent Application 2005065045 (and granted as US 7,407,919). In some embodiments the linear alkyl group may be attached to the benzene ring anywhere along the linear chain of the

alkyl group, but often in the 2, 3 or 4 position of the linear chain, and in some instances predominantly in the 2 position.

[0064] When neutral or slightly basic, a calcium sulphonate detergent may have TBN of less than 100, or less than 75, typically 20 to 50 mg KOH/g, or 0 to 20 mg KOH/g.

[0065] When overbased, a calcium sulphonate detergent may have a TBN greater than 200, or 300 to 550, or 350 to 450 mg KOH/g.

[0066] The detergent may be borated or non-borated.

[0067] Chemical structures for sulphonates, and phenates detergents are known to a person skilled in the art. The standard textbook entitled "Chemistry and Technology of Lubricants", Third Edition, Edited by R. M. Mortier and S. T. Orszulik, Copyright 2010, pages 220 to 223 under the sub-heading 7.2.6 provide general disclosures of said detergents and their structures.

[0068] In one embodiment the calcium-containing detergent may be an overbased calcium sulphonate, an overbased calcium phenate, or mixtures thereof. Typically the detergent may be an overbased calcium sulphonate.

[0069] In one embodiment the calcium-containing detergent may be in a mixture with a having zinc-, barium-, sodium-, or magnesium- containing detergent. The zinc-, barium-, sodium-, or magnesium- containing detergent is also well known in the art and described in the same references describing a calcium-containing detergent. The TBN and metal ratios may however, differ slightly. The zinc-, barium-, sodium-, or magnesium- containing detergent may be a phenate, a sulphur-containing phenate, sulphonate, salixarate or salicylate. Typically a zinc-, barium-, sodium-, or magnesium- containing detergent may be a magnesium phenate, a magnesium sulphur-containing phenate, or a magnesium sulphonate.

Phosphorus-containing compound

[0070] The phosphorus-containing compounds may be an acid, salt or ester; and may be a friction modifier, an antiwear agent, an extreme pressure agent or mixtures thereof. In one embodiment the phosphorus-containing compounds are in the form of a mixture of two or three, or two to four (typically two or three) phosphorus-containing compounds.

[0071] The phosphorus-containing compound may be metal-containing or metal free (prior to being mixed with other components).

[0072] The phosphorus-containing compound may be present in an amount to deliver 400 ppm to 900 ppm, or 500 ppm to 850 ppm, or 525 ppm to 800 ppm of phosphorus.

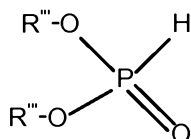
[0073] The phosphorus-containing compound may be derived from a phosphoric acid, phosphorous acid, thiophosphoric acid, thiophosphorous acid, or mixtures thereof.

[0074] The phosphorus-containing compound may be a non-ionic phosphorus compound.

[0075] In one embodiment the phosphorus-containing compounds comprise two or more (possibly up to four) non-ionic phosphorus compounds. Typically the non-ionic phosphorus compound may have an oxidation of +3 or +5. The different embodiments comprise phosphite ester, phosphate esters, or mixtures thereof.

[0076] In one embodiment the phosphorus-containing compound comprises a non-ionic phosphorus compound (a C₄₋₆ hydrocarbyl phosphite) and an amine salt of a phosphorus acid or ester.

[0077] The phosphorus-containing compound comprises a non-ionic phosphorus compound that is a C₄₋₆ hydrocarbyl phosphite, or mixtures thereof. The C₄₋₆ hydrocarbyl phosphite of the invention includes those represented by the formula:



wherein each R''' may be independently hydrogen or a hydrocarbyl group having 4 to 6 carbon atoms, typically 4 carbon atoms, with the proviso that at least one of the R''' groups is hydrocarbyl. Typically the C₄₋₆ hydrocarbyl phosphite comprises dibutyl phosphite.

[0078] The C₄₋₆ hydrocarbyl phosphite may deliver at least 175 ppm, or at least 200 ppm of the total amount of phosphorus delivered by the phosphorus-containing compounds.

[0079] The C₄₋₆ hydrocarbyl phosphite may deliver at least 45 wt %, or 50 wt % to 100 wt %, or 50 wt % to 90 wt % or 60 wt % to 80 wt % of the total amount of phosphorus from the phosphorus-containing compound.

5 [0080] The phosphorus-containing compounds may comprise a second phosphite whose formula is similar to that disclosed above, except R¹ may contain 2 to 40, 8 to 24 or 11 to 20 carbon atoms, with the proviso that the second phosphite is not a C₄₋₆ hydrocarbyl phosphite. Examples of suitable hydrocarbyl groups include propyl, dodecyl, butadecyl, hexadecyl, octadecyl, propenyl, dodecenyl, butadecenyl, hexadeenyl, or octadecenyl groups.

10 [0081] As used herein the term “alk(en)yl” is intended to include moieties that have an alkyl and/or alkenyl group.

[0082] In one embodiment the phosphorus-containing compounds include a mixture of a C₄₋₆ hydrocarbyl phosphite (typically dibutyl phosphite) and a C₁₂₋₁₈ alk(en)yl hydrogen phosphite and optionally phosphoric acid. In different
15 embodiments the phosphoric acid is present or absent.

[0083] In one embodiment the phosphorus-containing compounds include a mixture of a C₄₋₆ hydrocarbyl phosphite (typically dibutyl phosphite) and a C₁₆₋₁₈ alk(en)yl hydrogen phosphite. The alk(en)yl hydrogen phosphite be may an alkyl hydrogen phosphite, and alkenyl hydrogen phosphite, or a mixture of
20 alkenyl hydrogen phosphite and alkyl hydrogen phosphite. In one embodiment the alk(en)yl hydrogen phosphite be may a mixture of alkenyl hydrogen phosphite and alkyl hydrogen phosphite and optionally phosphoric acid. The phosphoric acid may be present or absent.

[0084] In one embodiment the phosphorus-containing compounds include a mixture of a C₄₋₆ hydrocarbyl phosphite (typically dibutyl phosphite) and a C₁₁₋₁₄ alk(en)yl hydrogen phosphite. The alk(en)yl hydrogen phosphite be may an
25 alkyl hydrogen phosphite, and alkenyl hydrogen phosphite, or a mixture of alkenyl hydrogen phosphite and alkyl hydrogen phosphite. In one embodiment the alk(en)yl hydrogen phosphite may be a mixture of alkenyl hydrogen
30 phosphite and alkyl hydrogen phosphite and optionally phosphoric acid.

[0085] In one embodiment the phosphorus-containing compounds include a mixture of a C₄₋₆ hydrocarbyl phosphite (typically dibutyl phosphite) and phosphoric acid.

5 [0086] The lubricating composition of the invention in one embodiment includes a package that comprises a phosphorus-containing compound and a non-ionic phosphorus compound that is a hydrocarbyl phosphite.

[0087] In one embodiment the lubricating composition further comprises a C₈₋₂₀ hydrocarbyl phosphite, or a C₁₂₋₁₈ hydrocarbyl phosphite, or C₁₆₋₁₈ hydrocarbyl phosphite.

10 [0088] In different embodiments the lubricating composition of the invention may or may not contain phosphoric acid. In one embodiment the lubricating composition further includes phosphoric acid.

Dispersant

15 [0089] The borated dispersant of the invention may be a succinimide dispersant, a Mannich dispersant, a polyolefin succinic acid ester, amide, or ester-amide, or mixtures thereof. In one embodiment the non-borated dispersant may be a borated succinimide dispersant.

20 [0090] The borated dispersant may be based upon a borated polyisobutylene succinimide dispersant, wherein the polyisobutylene of the borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.

[0091] The borated dispersant may be used alone or as part of a mixture of borated dispersants. If a mixture of borated dispersants is used, there may be two to five, or two to three or two borated dispersants.

25 [0092] A second borated dispersant may also be a borated polyisobutylene succinimide dispersant (provided it is chemically different from the first borated dispersant), wherein the polyisobutylene of the borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.

30 [0093] The lubricating composition containing one or more borated dispersant may also further comprise a non-borated dispersant. The non-borated may be a polyisobutylene succinimide, wherein the polyisobutylene of the

borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.

5 [0094] The borated and non-borated polyisobutylene succinimide are known in the art and may be prepared with a polyisobutylene having a number average molecular weight of 950.

[0095] The borated and non-borated dispersant may be formed by reaction of a substituted acylating agent with a polyamine (typically having two or more reactive sites). For example, the substituted acylating agent may be a polyisobutylene succinic anhydride and the polyamine.

10 [0096] The polyamine may be an alkylene-polyamine. The alkylene-polyamine may include an ethylene-polyamine, a propylene-polyamine, a butylene-polyamine, or mixtures thereof. Examples of propylene-polyamine include propylenediamine, dipropylenetriamine and mixtures thereof.

15 [0097] In one embodiment the polyamine is selected from the group consisting of ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyamine still bottoms and mixtures thereof.

20 [0098] The borated and non-borated dispersant may be obtained/obtainable from reaction of succinic anhydride by an "ene" or "thermal" reaction, by what is referred to as a "direct alkylation process." The "ene" reaction mechanism and general reaction conditions are summarised in "Maleic Anhydride", pages, 147-149, Edited by B.C. Trivedi and B.C. Culbertson and Published by Plenum Press in 1982. The non-borated dispersant prepared by a process that includes an "ene" reaction may be a polyisobutylene succinimide having a carbocyclic ring present on less than 50 mole %, or 0 to less than 30 mole %, or 0 to less than 20 mole %, or 0 mole % of the dispersant molecules. The "ene" reaction may have a reaction temperature of 180°C to less than 300°C, or 200 °C to 250°C, or 200°C to 220°C.

25 [0099] The borated and non-borated dispersant may also be obtained/obtainable from a chlorine-assisted process, often involving Diels-Alder chemistry, leading to formation of carbocyclic linkages. The process is known to a person skilled in the art. The chlorine-assisted process may

produce a non-borated dispersant that is a polyisobutylene succinimide having a carbocyclic ring present on 50 mole % or more, or 60 to 100 mole % (typically 100 mole %) of the dispersant molecules. Both the thermal and chlorine-assisted processes are described in greater detail in U.S. Patent 5 7,615,521, columns 4-5 and preparative examples A and B.

[00100] The borated dispersant(s) of the present invention may be prepared in such a way to have a N:CO ratio of 0.9:1 to 1.6:1, or 0.95:1 to 1.5:1, or 1:1 to 1:4.

10 **[00101]** The non-borated dispersant may have a carbonyl to nitrogen ratio (CO:N ratio) of 5:1 to 1:10, 2:1 to 1:10, or 1:1 to 1:10, or 1:1 to 1:5, or 1:1 to 1:2. In one embodiment the non-borated dispersant may have a CO:N ratio of 1:1 to 1:10, or 1:1 to 1:5, or 1:1 to 1:2.

15 **[00102]** The borated and non-borated dispersant may also be post-treated by conventional methods by a reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulphide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, maleic anhydride, nitriles, epoxides, and phosphorus compounds.

20 **[00103]** The non-borated dispersant is typically present at 0.1 wt % to 10 wt %, or 0.5 wt % to 7 wt %, or 1 wt % to 4 wt %, or 1.5 wt % to 3 wt % of the lubricating oil composition.

25 **[00104]** The dispersant may be a reaction product prepared by heating together: (a) a dispersant (such as a polyisobutylene succinimide) and (b) 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole which is substantially insoluble in a hydrocarbon oil of lubricating viscosity at 25°C, and further either (c) a borating agent or (d) an inorganic phosphorus compound, or both (c) and (d), said heating being sufficient to provide a reaction product of (a), (b), and (c) or (d) which is soluble in said hydrocarbon oil at 25°C.

30 **[00105]** The reaction product can typically contain 0.5 to 2.5 weight percent sulfur derived from component (b), or 1 to 2 weight percent, or 1.25 to 1.5 weight percent sulfur. It can likewise contain 0.2 to 0.6 weight percent boron

from component (c), or 0.3 to 1.1 percent phosphorus from component (d), or such amounts from both components (c) and (d).

5 [00106] Borated dispersants may be prepared by borating using a variety of agents selected from the group consisting of the various forms of boric acid (including metaboric acid, HBO_2 , orthoboric acid, H_3BO_3 , and tetraboric acid, $\text{H}_2\text{B}_4\text{O}_7$), boric oxide, boron trioxide, and alkyl borates. These agents are described in more detail above. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents.

10 [00107] The borated dispersant may be prepared by blending the boron compound and a N-substituted long chain alkenyl succinimide and heating them at a suitable temperature, typically $80\text{ }^\circ\text{C}$ to $250\text{ }^\circ\text{C}$, $90\text{ }^\circ\text{C}$ to $230\text{ }^\circ\text{C}$, or $100\text{ }^\circ\text{C}$ to $210\text{ }^\circ\text{C}$, until the desired reaction has occurred. An inert liquid may be used in performing the reaction. The liquid may include but are not limited to toluene, xylene, chlorobenzene, dimethylformamide and mixtures thereof.

15 [00108] The borated dispersant may also be a product prepared by heating together:

- (i) a dispersant substrate;
- (ii) 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof;
- 20 (iii) a borating agent; and
- (iv) optionally a dicarboxylic acid of an aromatic compound selected from the group consisting of 1,3 diacids and 1,4 diacids; or
- (v) optionally a phosphorus acid compound,

25 said heating being sufficient to provide a product of (i), (ii), (iii) and optionally (iv) or (v), which is soluble in an oil of lubricating viscosity.

[00109] The mixture of dispersant substrate, dicarboxylic acid of an aromatic compound and the mercaptothiadiazole is treated with a borating agent and optionally also with a phosphorus acid or anhydride. The components may be combined and reacted in any order. In particular, the borating agent may be a
30 pre-treatment process or a post-treatment process. Thus, for instance, boric acid (and optionally also phosphoric acid) may be reacted with a dispersant substrate in one step, and thereafter the intermediate borated dispersant may be

reacted with the mercapthothiadiazole and the dicarboxylic acid of an aromatic compound. Alternatively, the dispersant substrate, dicarboxylic acid of an aromatic compound and mercapthothiadiazole may be first reacted, and then the product treated with a borating agent (and optionally with phosphoric acid, a phosphorus acid). In yet another variation, a phosphorylated succinimide dispersant may be prepared by reacting a phosphorus acid with a hydrocarbyl-substituted succinic anhydride to prepare a mixed anhydride-acid precursor, and then reacting the precursor with a polyamine to form a phosphorus-containing dispersant. The phosphorus-containing dispersant may thereafter be reacted with the dicarboxylic acid of an aromatic compound and mercapthothiadiazole; and with the borating agent.

[00110] The components are typically reacted by heating the borating agent and optionally the phosphorus acid compound (together or sequentially) with the remaining components, that is, with the dispersant substrate, dicarboxylic acid of an aromatic compound and the dimercapthothiadiazole, although other orders of reaction are possible, as described above. The heating will be at a sufficient time and temperature to assure solubility of resulting product, typically 80-200°C, or 90-180°C, or 120-170°C, or 150-170°C. The time of reaction is typically at least 0.5 hours, for instance, 1-24 hours, 2-12 hours, 4-10 hours, or 6-8 hours. The length of time required for the reaction is determined in part by the temperature of the reaction, as will be apparent to one skilled in the art. Progress of the reaction is generally evidenced by the evolution of H₂S or water from the reaction mixture. Typically, the H₂S is derived from one or more of the sulphur atoms in the dimercapthothiadiazole.

[00111] The reaction product may typically contain 0.5 to 2.5 weight percent sulphur derived from component (iii), or 1 to 2 weight percent, or 1.25 to 1.5 weight percent sulphur. It may likewise contain 0.2 to 0.6 weight percent boron from component (iv), or 0.3 to 1.1 percent phosphorus from component (e), or such amounts from both components (iv) and (v).

[00112] The reaction may be conducted in a hydrophobic medium such as an oil of lubricating viscosity which may, if desired, be retained in the final product. The oil, however, should typically be an oil which does not itself

react or decompose under conditions of the reaction. Thus, oils containing reactive ester functionality are typically not used as diluent. Oils of lubricating viscosity are described in greater detail above.

5 [00113] In the absence of the dicarboxylic acid, the relative amounts of the components which are reacted are, expressed as parts by weight prior to reaction are typically 100 parts of (i) the dispersant, per 0.75 to 6 parts of (ii) the dimercaptiothiadiazole or substituted dimercaptiothiadiazole, and 0 or 0.01 to 7.5 parts of (iii) the borating agent, and 0.01 to 7.5 parts of (v) the phosphorus acid compound, provided that the relative amount of (iii) + (v) is at least 0.075 parts. In one embodiment the relative amounts are 100 parts of (i), 1.5 to 3 parts of (ii), 0 to 4.5 parts of (iii), and 0 to 4.5 parts of (v), provided that (iii) + (v) is at least 1.5 parts. In another embodiment, the relative amounts are 100 parts (i) : 1.5 to 2.2 parts (ii) : 3.7 to 4.4 parts (iii) : 1.5 to 4.4 parts (v). The amounts and ranges of the various components, in particular, (iii) and (v), may be independently combined so that there may be, for instance, 3.7 to 4.4 parts of (iii) whether or not any of (v) is present, and likewise there may be 1.5 to 4.4 parts (v) whether or not any of (iii) is present.

15 [00114] When the dicarboxylic acid is present, relative amounts of the components which are reacted are, expressed as parts by weight prior to reaction are typically 100 parts of (i) the dispersant, per 5-5000 parts per million of (ii) the dicarboxylic acid of an aromatic compound, 0.75 to 6 parts of (iii) the dimercaptiothiadiazole or substituted dimercaptiothiadiazole, and 0 to 7.5 parts of (iv) the borating agent and 0 to 7.5 parts of (v) the phosphorus acid compound, provided that the relative amount of (ii) + (iii) + (iv) + (v) is at least 1.5 parts. In a one embodiment the relative amounts are 100 parts of (i), 1.5 to 6 parts of (ii), 5-1000 parts per million of (iii), 0 or 0.01 to 4.5 parts of (iv), and 0 to 4.5 parts of (v), provided that (iii) + (iv) + (v) is at least 1.5 parts. In another embodiment, the relative amounts are 100 parts (i) : 1.5 to 5.0 parts (ii) : 25-500 parts per million (iii) : 3.7 to 4.4 parts (iv) : 0 to 4.4 parts (v). The amounts and ranges of the various components, in particular, (iv) and (v), may be independently combined so that there may be, for instance, 3.7 to 4.4 parts

of (iv) whether or not any of (v) is present, and likewise there may be 1.5 to 4.4 parts (v) whether or not any of (iv) is present.

The Dispersant Substrate

[00115] The product prepared by heating comprises a dispersant substrate. The dispersant of the invention is well known and include a succinimide dispersant (for example N-substituted long chain alkenyl succinimides), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl monocarboxylic acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant, a polyetheramine dispersant, a viscosity modifier containing dispersant functionality (for example polymeric viscosity index modifiers (VMs) containing dispersant functionality), or mixtures thereof. Typically the dispersant substrate is a succinimide, or mixtures thereof. The dispersant substrate may be a polyisobutylene succinimide.

[00116] In one embodiment the borated dispersant is prepared by reaction in the presence of a 1,3-dicarboxylic acid or 1,4-dicarboxylic acid of an aromatic compound, or reactive equivalents thereof, or mixtures thereof, which is reacted or complexed with the dispersant. The term "reactive equivalents thereof" include acid halides, esters, amides or mixtures thereof. The "aromatic component" is typically a benzene (phenylene) ring or a substituted benzene ring, although other aromatic materials such as fused ring compounds or heterocyclic compounds are also contemplated. It is believed (without intending to be bound by any theory) that the dicarboxylic acid aromatic compound may be bound to the dispersant by salt formation or complexation, rather than formation of covalently bonded structures such as amides, which may also be formed but may play a less important role. Typically the presence of the dicarboxylic acid aromatic compound within the present invention is believed to impart corrosion inhibition properties to the composition. Examples of suitable dicarboxylic acids include 1,3-dicarboxylic acids such as isophthalic acid and alkyl homologues such as 2-methyl isophthalic acid, 4-methyl isophthalic acid or 5-methyl isophthalic acid; and 1,4-dicarboxylic acids such as terephthalic acid and alkyl homologues such as 2-methyl terephthalic acid. Other ring

substituents such as hydroxy or alkoxy (e.g., methoxy) groups may also be present in certain embodiments. In one embodiment the aromatic compound is terephthalic acid.

5 [00117] In one embodiment the borated dispersant is prepared by reaction in the presence of a dimercaptothiadiazoole which is reacted as a part of the “product prepared by heating.” This is in addition to any dimercaptothiadiazoole which may be present within a lubricating composition as a separate corrosion inhibitor. Examples include 2,5-dimercapto-1,3-4-thiadiazoole or a hydrocarbyl-substituted 2,5-dimercapto-1,3-4-thiadiazoole, or oligomers thereof. The
10 oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3-4-thiadiazoole typically form by forming a sulphur-sulphur bond between 2,5-dimercapto-1,3-4-thiadiazoole units to form oligomers of two or more of said thiadiazoole units.

[00118] In one embodiment the borated dispersant is prepared by reaction in the presence of a phosphorus acid compound. The phosphorus acid compound
15 may contain an oxygen atom and/or a sulphur atom as its constituent elements, and is typically a phosphorus acid or anhydride. This component includes the following examples: phosphorous acid, phosphoric acid, hypophosphoric acid, polyphosphoric acid, phosphorus trioxide, phosphorus tetroxide, phosphorous pentoxide (P_2O_5), phosphorotetrathionic acid (H_3PS_4), phosphoromonothionic acid (H_3PO_3S),
20 phosphorodithionic acid ($H_3PO_2S_2$), phosphorotrithionic acid ($H_3PO_2S_3$), and P_2S_5 . Among these, phosphorous acid and phosphoric acid or their anhydrides are typically used. A salt, such as an amine salt of a phosphorus acid compound may also be used. It is also possible to use a plurality of these phosphorus acid compounds together. The phosphorus acid
25 compound is often phosphoric acid or phosphorous acid or their anhydride.

[00119] The phosphorus acid compound may also include phosphorus compounds with a phosphorus oxidation of +3 or +5, such as, phosphates, phosphonates, phosphinates, or phosphine oxides. A more detailed description for these suitable phosphorus acid compounds is described in US Patent
30 6,103,673, column 9, line 64 to column 11, line 8.

[00120] In one embodiment the phosphorus acid compound is an inorganic phosphorus compound.

[00121] The borated dispersant is typically present at 0.1 wt % to 10 wt %, or 0.5 wt % to 7 wt %, or 1 wt % to 4 wt % of the lubricating oil composition.

[00122] In one embodiment the dispersant package may comprise

5 (i) a non-borated dispersant that comprises a polyisobutylene succinimide, wherein the polyisobutylene used to prepare the non-borated dispersant has a number average molecular weight of 550 to 1150, or 750 to 1150, or 900 to 1000 (often commercially available with a number average molecular weight of about 950); and

10 (ii) a borated dispersant that comprises a polyisobutylene succinimide, wherein the polyisobutylene used to prepare the non-borated dispersant has a number average molecular weight of 550 to 1150, or 750 to 1150, or 900 to 1000 (often commercially available with a number average molecular weight of about 950).

[00123] In one embodiment the dispersant package may comprise:

15 (a) a non-borated dispersant that comprises a polyisobutylene succinimide, wherein the polyisobutylene used to prepare the non-borated dispersant has a number average molecular weight of 550 to 1150, or 750 to 1150, or 900 to 1000 (often commercially available with a number average molecular weight of about 950); and

20 (b) the borated dispersant may also be a product prepared by heating together:

(i) a dispersant substrate;

(ii) 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof;

25 (iii) a borating agent; and

(iv) optionally a dicarboxylic acid of an aromatic compound selected from the group consisting of 1,3 diacids and 1,4 diacids; or

(v) optionally a phosphorus acid compound,
said heating being sufficient to provide a product of (i), (ii), (iii) and optionally
30 (iv) or (v), which is soluble in an oil of lubricating viscosity.

Viscosity Modifier

[00124] As used herein ranges below for the viscosity modifier are measured by GPC using polystyrene standards with a weight average molecular weight ranging from 350 to 2,000,000.

5 [00125] The lubricating composition contains 0.1 wt % to 5 wt % (or 0.5 wt % to 4 wt %) of a linear polymer having dispersant functionality. Compounds of this type are known in the art and are considered different from dispersants and the molecular weights are lower than that of the linear polymer of the present invention.

Linear Polymer

10 [00126] The lubricating composition of the invention in one embodiment includes a linear polymer with a weight average molecular weight of 5,000 to 25,000, or 8000 to 20,000.

[00127] In one embodiment the linear polymer includes a poly(meth)acrylate, or mixtures thereof. The linear polymer may be present in the compositions
15 described herein at 0.1 wt % to 5 wt %, or 0.1 wt % to 4 wt %, or 0.2 wt % to 3 wt %, or 0.5 wt % to 3 wt %, 0.5 wt % to 4 wt % of the lubricating composition.

[00128] The linear polymer may have a composition that comprises a poly(meth)acrylate polymer derived from a monomer composition comprising:(a) 50 wt % to 95 wt %, or 60 wt % to 80 wt % of an alkyl
20 (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 10 to 15 carbon atoms; (b) 1 wt % to 40 wt %, or 4 wt % to 35 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 1 to 9 carbon atoms; (c) 1 wt % to 10 wt %, or 1 wt % to 8 wt % of a dispersant monomer,
25 (d) 0 wt % to 4 wt %, or 0 wt % to 2 wt %, or 0 wt % of a vinyl aromatic monomer (typically styrene); and (e) 0 wt % to 9 wt %, or 0 wt % to 6 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 16 to 18 carbon atoms. In one embodiment the linear polymer may contain 0 wt % to 20 wt % of 16 to 18 alkyl (meth)acrylate.

[00129] The Star polymer may be derived from a monomer composition
30 comprising C₁₂₋₁₅ alkyl (meth)acrylate (about 80 wt %), and about 20 wt % of a mixture of monomers composed of methyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and ethylene glycol di(meth)acrylate. a difunctional The

linear polymer may be derived from a monomer composition comprising 2-ethylhexyl (meth)acrylate (30 wt %), C₁₂₋₁₅ alkyl (meth)acrylate (68.2 wt %), and dimethylaminopropyl (meth)acrylate (1.8 wt %).

5 [00130] In one embodiment the linear polymer includes a poly(meth)acrylate (typically a polymethacrylate) with units derived from a mixture of alkyl (meth)acrylate ester monomers containing, (a) 8 to 24, or 10 to 18, or 12 to 15 carbon atoms in the alcohol-derived portion of the ester group and (b) 6 to 11, or 8 to 11, or 8 carbon atoms in the alcohol-derived portion of the ester group, and which have 2-(C₁₋₄ alkyl)-substituents, and optionally, at least one monomer
10 selected from the group consisting of (meth)acrylic acid esters containing 1 to 7 carbon atoms in the alcohol-derived portion of the ester group and which are different from (meth)acrylic acid esters (a) and (b), vinyl aromatic compounds (or vinyl aromatic monomers); and nitrogen-containing vinyl monomer; provided that no more than 60% by weight, or no more than 50% by weight, or no more
15 than 35% by weight of the esters contain not more than 10 carbon atoms in the alcohol-derived portion of the ester group. The linear polymer of this type is described in more detail in US 6,124,249, or EP 0 937 769 A1 paragraphs [0019] and [0031] to [0067]. (The “alcohol-derived portion” refers to the “-OR” portion of an ester, when written as R'C(=O)-OR, whether or not it is actually prepared
20 by reaction with an alcohol.) Optionally, the linear polymer may further contain a third monomer. The third monomer may be styrene, or mixtures thereof. The third monomer may be present in an amount 0% to 25% of the polymer composition, or from 1% to 15% of the composition, 2% to 10% of the composition, or even from 1% to 3% of the composition.

25 [00131] Typically, the mole ratio of esters (a) to esters (b) in the copolymer ranges from 95:5 to 35:65, or 90:10 to 60:40, or 80:20 to 50:50.

[00132] The esters are usually aliphatic esters, typically alkyl esters. In one embodiment the ester of (a) may be a C₁₂₋₁₅ alkyl (meth)acrylate and the ester of (b) may be 2-ethylhexyl (meth)acrylate.

30 [00133] In one embodiment, the ester groups in ester (a) contain branched alkyl groups. The ester groups may contain 2 to 65%, or 5 to 60% of the ester groups having branched alkyl groups. The branched alkyl groups may be

β -branched and may contain 8 to 60, or 8 to 30, or 8 to 16 carbon atoms. For examples branched alkyl groups may be derived from 2-ethylhexanol, 2-butyloctanol, 2-hexyldecanol, 2-octyldodecanol, 2-decyltetradecanol, or mixtures thereof, or commercially available alcohols such as Isofol® branched
5 Guerbet alcohols available from Sasol.

[00134] The C₁₋₄ alkyl substituents may be methyl, ethyl, and any isomers of propyl and butyl.

[00135] The weight average molecular weight of the linear poly(meth)acrylate may be 45,000 or less, or 35,000 or less, or 25,000 or less, or
10 8000 to 25,000, or, 10,000 to 35,000, or 12,000 to 20,000.

[00136] The linear polymer viscosity modifier having dispersant functionality may be used as a sole dispersant viscosity modifier present at 0.5 wt % to 4 wt % of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight
15 of 5,000 to 25,000, or 10,000 to 20,000, and wherein oil the of lubricating viscosity has a kinematic viscosity at 100°C of 2.8 to 3.1 cSt (mm²/s) and a viscosity index of 104 to 130.

[00137] The lubricating composition in one embodiment may contain only two linear polymer viscosity modifiers having dispersant functionality, wherein the
20 linear polymer has a weight average molecular weight of 5,000 to 25,000, or 10,000 to 20,000,

[00138] In one embodiment the lubricating composition of the invention includes a viscosity modifier comprises a star polymer and linear polymer described herein.

[00139] In one embodiment the lubricating composition may comprise 0.1 wt% to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of greater than 25,000 to 400,000 (or to 350,000) or 30,000 to 150,000. The linear (meth)acrylic polymer a weight
25 average molecular weight of greater than 25,000 to 400,000 (or to 350,000) may
30 be considered chemically similar to the linear (meth)acrylic polymer a weight

average molecular weight of 5,000 to 25,000 except the weight average molecular weight is different.

5 [00140] The lubricating composition may comprise a linear polymer viscosity modifier having dispersant functionality comprises: 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of 10,000 to 20,000; and 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight
10 of greater than 20,000 to 250,000 (or 30,000 to 150,000).

[00141] The lubricating composition may comprise a linear polymer viscosity modifier having dispersant functionality comprises 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer having dispersant functionality wherein the linear polymer has a weight average molecular weight of 5,000 to
15 25,000 or 10,000 to 20,000, and the composition further comprises 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a (meth)acrylic polymer having star architecture.

[00142] A detailed description of the star polymer disclosed herein may also be described in WO 2007/127660 (published on 8 November 2007, by Baker *et al.* and assigned to The Lubrizol Corporation), paragraphs [0021] to [0061].
20 Baker discloses composition and methods of preparation of a variety of star polymers.

[00143] In different embodiments the star polymer may contain greater than 50 wt %, or 55 wt % or more, or 70 wt % or more, or 90 wt % or more, or 95 wt % or more, or 100 wt % of a non-diene monomer (that is to say, non-diene monomer units or units derived from polymerisation of one of more non-diene monomers).
25 Examples of diene monomers include 1,3-butadiene or isoprene. In contrast, examples of a non-diene of the present invention may include styrene, (meth)acrylates, acrylates, or mixtures thereof. In one embodiment the star polymer may be a polymer derived from (meth)acrylates, or mixtures thereof, and
30 is free of styrene.

[00144] As described hereinafter the molecular weight of the viscosity modifier has been determined using known methods, such as GPC analysis

using polystyrene standards. Methods for determining molecular weights of polymers are well known. The methods are described for instance: (i) P.J. Flory, "Principles of star polymer Chemistry", Cornell University Press 91953), Chapter VII, pp 266-315; or (ii) "Macromolecules, an Introduction to star polymer Science", F. A. Bovey and F. H. Winslow, Editors, Academic Press (1979), pp 296-312. As used herein the weight average and number average molecular weights of the polymers of the invention are obtained by integrating the area under the peak corresponding to the star polymer of the invention, which is normally the major high molecular weight peak, excluding peaks associated with diluents, impurities, uncoupled star polymer chains and other additives.

[00145] The (meth)acrylic polymer having star architecture has three or more arms that comprise a poly(meth)acrylate polymer is derived from a monomer composition comprising: (a) 50 wt % to 100 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 12 to 15 carbon atoms;(b) 0 wt % to 40 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 1 to 9 carbon atoms; (c) 0 wt % to 10 wt % of a dispersant monomer, (d) 0 wt % to 5 wt %, or 0 wt % to 2 wt %, or 0 wt % of a vinyl aromatic monomer (typically styrene); and (e) 0 wt % to 20 wt %, or 0 wt % to 10 wt %, or 0 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 16 to 18 carbon atoms.

[00146] The (meth)acrylic polymer having star architecture may have three or more arms that comprise a poly(meth)acrylate polymer is derived from a monomer composition comprising:(a) 60 wt % to 95 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 12 to 15 carbon atoms;(b) 5 wt % to 30 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 1 to 9 carbon atoms; (c) 0 wt % to 10 wt % of a dispersant monomer, (d) 0 wt % to 5 wt %, or 0 wt % to 2 wt %, or 0 wt % of a vinyl aromatic monomer (typically styrene); and(e) 0 wt % to 20 wt %, or 0 wt % to 10 wt %, or 0 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 16 to 18 carbon atoms.

[00147] The star polymer may have a weight average molecular weight of 100,000 to 1,300,000, or 125,000 to 1,000,000, or 150,000 to 950,000, or 200,000 to

800,000. As used herein the shear stability index (SSI) of the star polymer may be determined by a 20 hour KRL test (Volkswagen Tapered Bearing Roller Test). The test procedure is set out in both CEC-L-45-99 or equivalent test method DIN 51350-6-KRL/C.

5 [00148] The star polymer SSI may be in the range of 0 to 100, or 0 to 80, or 0 to 60, or 0 to 50, 0 to 20, or 0 to 15, or 0 to 10, or 0 to 5. An example of a suitable range for the SSI includes 1 to 5, 10 to 25, or 25 to 65.

[00149] The star polymer may be a homopolymer or a copolymer, that is, its arms may be homopolymeric or copolymeric (i.e., containing two or more
10 monomer types). In one embodiment the star polymer may be a copolymer. The star polymer may be a star polymer having a random, tapered, di-block, tri-block or multi-block architecture. Typically the star polymer has random or tapered architecture.

[00150] The star polymer may have arms that may have a block-arm
15 architecture, or hetero-arm architecture, or tapered-arm architecture. Tapered-arm architecture has a variable composition across the length of a star polymer arm. For example, the tapered arm may 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 arm is more of a gradient composition of the two
20 monomers.

[00151] The hetero-arm, or “mikto-arm,” star polymers contain arms which may vary from one another either in molecular weight, composition, or both, as described in Hsieh et al. (Chapter 13 (pp. 333-368) of “Anionic Polymerization, Principles and Practical Applications” by Henry Hsieh and Roderic
25 Quirk (Marcel Dekker, Inc, New York, 1996) (hereinafter referred to as Hsieh et al.). For example, a portion of the arms of a given star polymer may 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. In one embodiment hetero-arm
30 stars may be prepared by combining several batches of polymers with living characteristics prior to linkage and core formation.

[00152] The above-described monomers, as used in the disclosed technology for formation of the “arm” portion of the polymers, are based on methacrylic acid rather than acrylic acid. In certain embodiments, methacrylic polymers have better low temperature properties than do acrylic polymers. In general, the amount of acrylic monomers present in the reaction mixture to form the polymer arms or in the resulting polymer arms themselves may be 0 to 5 mole % , or 0.001 to 2 mole % or 0.01 to 1 mole percent or 0.05 to 0.5 mole percent, or less than 0.1 mole percent.

[00153] The star polymer with branched, comb-like, radial or star architecture may have 2 or more arms, or 5 or more arms, or 7 or more arms, or 10 or more arms, for instance 12 to 100, or 14 to 50, or 16 to 40 arms. The star polymer with branched, comb-like, radial or star architecture may have 120 arms or less, or 80 arms or less, or 60 arms or less.

[00154] The star polymer may be obtained/obtainable from a controlled radical polymerisation technique. Examples of a controlled radical polymerisation technique include RAFT, ATRP or nitroxide mediated processes. The star polymer may also be obtained/obtainable from anionic polymerisation processes. In one embodiment the star polymer may be obtained/obtainable from RAFT, ATRP or anionic polymerisation process. In one embodiment the star polymer may be obtained/obtainable from RAFT or ATRP polymerisation process. In one embodiment the star polymer may be obtained/obtainable from a RAFT polymerisation process.

[00155] RAFT or ATRP polymerization process are preferred to other polymerization techniques when preparing star polymers because polar vinyl monomers, including (meth)acrylates and (meth)acrylamides may be prone to side reactions during anionic polymerisation, making anionic polymerization less desirable.

[00156] Methods of preparing polymers using ATRP, RAFT or nitroxide-mediated techniques are disclosed in the example section of International Publication WO 2006/047398, see examples 1 to 47.

[00157] More detailed descriptions of polymerisation mechanisms and related chemistry is discussed for nitroxide-mediated polymerisation (Chapter

10, pages 463 to 522), ATRP (Chapter 11, pages 523 to 628) and RAFT (Chapter 12, pages 629 to 690) in the Handbook of Radical Polymerization, edited by Krzysztof Matyjaszewski and Thomas P. Davis, 2002, published by John Wiley and Sons Inc (hereinafter referred to as “Matyjaszewski *et al.*”).

5 [00158] The discussion of the star polymer mechanism of ATRP polymerisation is shown on page 524 in reaction scheme 11.1, page 566 reaction scheme 11.4, reaction scheme 11.7 on page 571, reaction scheme 11.8 on page 572 and reaction scheme 11.9 on page 575 of Matyjaszewski *et al.* In ATRP polymerisation, groups that may be transferred by a radical mechanism
10 include halogens (from a halogen-containing compound) or various ligands. A more detailed review of groups that may be transferred is described in US 6,391,996, or paragraphs 61 to 65 of International Publication WO 2006/047398.

[00159] In RAFT polymerisation, chain transfer agents are important. A
15 more detailed review of suitable chain transfer agents is found in paragraphs [0066] to [0071] of International Publication WO 2006/047398. In one embodiment a suitable RAFT chain transfer agent includes 2-dodecylsulphanyl-thiocarbonylsulphanyl-2-methyl-propionic acid butyl ester, cumyl dithiobenzoate or mixtures thereof. A discussion of the star polymer mechanism of RAFT
20 polymerisation is shown on page 664 to 665 in section 12.4.4 of Matyjaszewski *et al.*

[00160] The star polymers may be prepared by techniques known in the art to prepare either core-first or arm-first approaches. Typically the star polymer is prepared by an “arm-first” approach using RAFT or ATRP (typically RAFT)
25 polymerization techniques.

[00161] The (meth)acrylic polymer having star architecture may be prepared from known monomers such as alkyl (meth)acrylate. Alkyl (meth)acrylates include, for example, compounds derived from saturated alcohols, such as methyl (meth)acrylate, butyl (meth)acrylate, 2-methylpentyl (meth)acrylate, 2-propylheptyl (meth)acrylate, 2-butyloctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, nonyl (meth)acrylate, isooctyl (meth)acrylate, isononyl (meth)acrylate, 2-tert-butylheptyl (meth)acrylate,
30

3-isopropylheptyl (meth)acrylate, decyl (meth)acrylate, undecyl (meth)acrylate, 5-methylundecyl (meth)acrylate, dodecyl (meth)acrylate, 2-methyldodecyl (meth)acrylate, tridecyl (meth)acrylate, 5-methyltridecyl (meth)acrylate, tetradecyl (meth)acrylate, pentadecyl (meth)acrylate, hexadecyl (meth)acrylate, 5 2-methylhexadecyl (meth)acrylate, heptadecyl (meth)acrylate, octadecyl (meth)acrylate, nonadecyl (meth)acrylate, eicosyl (meth)acrylate, cetylcicosyl (meth)acrylate, stearylcicosyl (meth)acrylate, docosyl (meth)acrylate and/or eicosyltetracontyl (meth)acrylate; (meth)acrylates derived from unsaturated alcohols, such as oleyl (meth)acrylate; and cycloalkyl (meth)acrylates, such as 10 3-vinyl-2-butylcyclohexyl (meth)acrylate or bornyl (meth)acrylate.

[00162] The alkyl (meth)acrylates with long-chain alcohol-derived groups may be obtained, for example, by reaction of a (meth)acrylic acid (by direct esterification) or methyl (meth)acrylate (by transesterification) with long-chain fatty alcohols, in which reaction a mixture of esters such as (meth)acrylate with 15 alkyl groups of various chain lengths is generally obtained. These fatty alcohols include Oxo Alcohol® 7911, Oxo Alcohol® 7900 and Oxo Alcohol® 1100 of Monsanto; Alphanol® 79 of ICI; Nafol® 1620, Alfol® 610 and Alfol® 810 of Condea (now Sasol); Epal® 610 and Epal® 810 of Ethyl Corporation; Linevol® 79, Linevol® 911 and Dobanol® 25 L of Shell AG; Lial® 125 of 20 Condea Augusta, Milan; Dehydad® and Lorol® of Henkel KGaA (now Cognis) as well as Linopol® 7-11 and Acropol® 91 of Uguine Kuhlmann, as well as Isofol® branched Guerbet alcohols from Sasol.

[00163] In one embodiment the star polymer may be further functionalised in the core or the polymeric arms with a nitrogen-containing monomer. The 25 nitrogen-containing monomer may be referred to as a dispersant monomer. The nitrogen-containing monomer may include a vinyl-substituted nitrogen heterocyclic monomer, a dialkylaminoalkyl (meth)acrylate monomer, a dialkylaminoalkyl (meth)acrylamide monomer, a tertiary-(meth)acrylamide monomer, ureido (meth)acrylate, or mixtures thereof.

[00164] In one embodiment the core or polymeric arms further comprise a 30 (meth)acrylamide or a nitrogen containing (meth)acrylate monomer. Examples of a suitable nitrogen-containing vinyl monomer include

N,N-dimethylacrylamide, N-vinyl carbonamides such as N-vinyl-formamide, vinyl pyridine, N-vinylacetoamide, N-vinyl-n-propionamides, N-vinyl hydroxyacetoamide, N-vinyl imidazole, N-vinyl pyrrolidinone, N-vinyl caprolactam, dimethylaminoethyl acrylate (DMAEA), dimethylaminoethyl-
5 (meth)acrylate (DMAEMA), dimethylaminobutylacrylamide, dimethylamine-propyl(meth)acrylate (DMAPMA), dimethylamine-propyl-acrylamide, dimethylaminopropylmethacrylamide, dimethylaminoethyl-acrylamide, or mixtures thereof. A dispersant monomer may also be oxygen-containing compound. The oxygen-containing compound may include hydroxyalkyl
10 (meth)acrylates such as 3-hydroxypropyl (meth)acrylate, 3,4-dihydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2,5-dimethyl-1,6-hexanediol (meth)acrylate, 1,10-decanediol (meth)acrylate, carbonyl-containing (meth)acrylates such as 2-carboxyethyl (meth)acrylate, carboxymethyl (meth)acrylate, oxazolidinylethyl
15 (meth)acrylate, N-(methacryloyloxy)formamide, acetyl (meth)acrylate, N-methacryloylmorpholine, N-methacryloyl-2-pyrrolidinone, N-(2-methacryloyloxyethyl)-2-pyrrolidinone, N-(3-methacryloyloxypropyl)-2-pyrrolidinone, N-(2-methacryloyloxy-pentadecyl)-2-pyrrolidinone, N-(3-methacryloyloxyheptadecyl)-2-pyrrolidinone; glycol di(meth)acrylates such as
20 ethylene glycol di(meth)acrylate, 1,4-butanediol (meth)acrylate, 2-butoxyethyl (meth)acrylate, 2-ethoxyethoxymethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, or mixtures thereof.

[00165] Other examples of suitable non-carbonyl oxygen containing compounds capable of being incorporated into the copolymer include
25 (meth)acrylates of ether alcohols, such as tetrahydrofurfuryl (meth)acrylate, vinyloxyethoxyethyl (meth)acrylate, methoxyethoxyethyl (meth)acrylate, 1-butoxypropyl (meth)acrylate, 1-methyl-(2-vinyloxy)ethyl (meth)acrylate, cyclohexyloxymethyl (meth)acrylate, methoxymethoxyethyl (meth)acrylate, benzyloxymethyl (meth)acrylate, furfuryl (meth)acrylate, 2-butoxyethyl
30 (meth)acrylate, 2-ethoxyethoxymethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, allyloxymethyl (meth)acrylate, 1-ethoxybutyl (meth)acrylate, methoxymethyl (meth)acrylate, 1-ethoxyethyl (meth)acrylate, ethoxymethyl

(meth)acrylate and ethoxylated (meth)acrylates which typically have 1 to 20, or 2 to 8, ethoxy groups, or mixtures thereof.

[00166] The star polymer may be prepared from a bifunctional monomer divinylbenzene, dipentaerythritol hexamethacrylate, dipentaerythritol
5 hexaacrylate, tripentaerythritol octamethacrylate, tripentaerythritol octaacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, bis-acrylates and methacrylates of polyethylene glycols of molecular weight 200-4000, polycaprolactonediol diacrylate, pentaerythritol triacrylate, pentaerythritol trimethacrylate, 1,1,1-trimethylolpropane triacrylate,
10 pentaerythritol diacrylate, pentaerythritol tetraacrylate, ethylene glycol dimethacrylate, triethylene glycol diacrylate, triethylene glycol dimethacrylate, 1,1,1-trimethylolpropane trimethacrylate, hexamethylenediol diacrylate or hexamethylenediol dimethacrylate or an alkylene bis-(meth)acrylamide. Typically the bifunctional monomer comprises a bifunctional methacrylate
15 monomer.

[00167] The linear or star (meth)acrylate may contain 0 wt % to 30 wt % or 0 wt % to 20 wt % of a C₁-C₁₀, or C₁-C₈ acrylate group. The acrylate groups may for instance be ethyl acrylate or 2-ethylhexyl acrylate.

[00168] The lubricating composition of the present invention may further
20 comprise 0.1 wt % to 5 wt % (0.1 wt % to 4 wt % or 0.2 wt % to 3 wt %) of a polymer having comb architecture.

[00169] The polymer having comb architecture may be a comb polymer comprising, in the main chain, repeat units which are derived from polyolefin-based macromonomers, and repeat units which are derived from low molecular
25 weight monomers selected from the group consisting of styrene monomers having from 8 to 17 carbon atoms, alkyl(meth)acrylates having from 1 to 15 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having from 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumarates having from 1 to 10 carbon atoms in the
30 alcohol group, (di)alkyl maleates having from 1 to 10 carbon atoms in the alcohol group, and mixtures of these monomers, wherein the molar degree of branching is in the range from 0.1 to 10 mol % and the comb polymer

comprises a total of at least 80% by weight, based on the weight of the repeat units, which are derived from polyolefin-based macromonomers, and repeat units which are derived from low molecular weight monomers selected from the group consisting of styrene monomers having from 8 to 17 carbon atoms, 5 alkyl(meth)acrylates having from 1 to 15 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having from 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumarates having from 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having from 1 to 10 carbon atoms in the alcohol group, and mixtures of these 10 monomers.

[00170] In one embodiment the polymer having comb architecture may have a glass transition temperature in the range from -30 to 100 °C.

[00171] The polymer having comb architecture may have repeat units which are derived from polyolefin-based macromonomers have a number-average 15 molecular weight in the range from 500 to 10 000 g/mol.

[00172] The polymer having comb architecture may have at least 90% by weight of repeat units which are derived from polyolefin-based macromonomers and repeat units which are derived from low molecular weight monomers selected from the group consisting of styrene monomers having from 20 8 to 17 carbon atoms, alkyl(meth)acrylates having from 1 to 15 carbon atoms in the alcohol group, vinyl esters having from 1 to 11 carbon atoms in the acyl group, vinyl ethers having from 1 to 10 carbon atoms in the alcohol group, (di)alkyl fumarates having from 1 to 10 carbon atoms in the alcohol group, (di)alkyl maleates having from 1 to 10 carbon atoms in the alcohol group, and 25 mixtures of these monomers.

[00173] The polymer having comb architecture may have a molar degree of branching is in the range from 0.8% to 6.0%, or 0.8% to 3.4%.

[00174] The polymer having comb architecture may have the iodine number of less than or equal to 0.2 g per g of comb polymer.

30 [00175] The polymer having comb architecture may have the repeat units derived from polyolefin-based macromonomers which are derived from

monomers selected from the group consisting of C2-C10-alkenes and/or C4-C10-alkadienes.

5 [00176] The repeat units may be derived from polyolefin-based macromonomers which comprise at least 80% by weight of groups which are derived from monomers selected from the group consisting of C2-C10-alkenes and/or C4-C10-alkadienes, based on the weight of the repeat units derived from polyolefin-based macromonomers.

10 [00177] The polymer having comb architecture may have the repeat units derived from polyolefin-based macromonomers comprising groups which are derived from non-olefinic monomers selected from the group of styrenes, (meth)acrylates, vinyl esters, vinyl ethers, fumarates and maleates.

15 [00178] The repeat units may be derived ~~are~~ from polyolefin-based macromonomers comprising at most 20% by weight of groups which are derived from non-olefinic monomers selected from the group of styrenes, (meth)acrylates, vinyl esters, vinyl ethers, fumarates and maleates, based on the weight of the repeat units.

[00179] The polymer having comb architecture may have repeat units derived from polyolefin-based macromonomers having a melting point of less than or equal to -10 °C.

20 [00180] The polymer having comb architecture may have repeat units which are derived from styrene, and repeat units which are derived from n-butyl methacrylate. The repeat units may be derived from styrene, and repeat units which are derived from n-butyl acrylate.

25 [00181] The polymer having comb architecture may have repeat units which are derived from methyl methacrylate and repeat units which are derived from n-butyl methacrylate.

[00182] The polymer having comb architecture may have a weight-average molecular weight in the range from 50,000 to 500,000 g/mol.

30 [00183] The process to prepare the polymer having comb architecture may be continuous or batch-wise, typically batch-wise.

[00184] The process to prepare the polymer having comb architecture may be carried out in the absence or presence of a solubilizing carrier medium,

typically in the presence of a solubilizing carrier medium. When present, the carrier medium is selected from the group of the base oil and/or the aromatic hydrocarbons.

[00185] A more detailed description of the comb polymer is described in US2008/194443. The comb polymer may also be prepared as is disclosed in paragraphs [0142] to [0160] of US2008/194443. A more detailed description of the comb polymer is described in US2008/194443. The comb polymer may also be prepared as is disclosed in paragraphs [0142] to [0160] of US2008/194443.

10 Friction Modifier

[00186] The lubricating composition of the present invention may optionally contain at least two friction modifiers. Useful friction modifiers for the present invention are described below.

[00187] In one embodiment the friction modifier may be formed by the condensation of the hydroxyalkyl compound with an acylating agent or an amine. A more detailed description of the hydroxyalkyl compound is described in US Patent Application 60/725360 (filed on October 11, 2005, inventors Bartley, Lahiri, Baker and Tipton) in paragraphs 8, 19-21. The friction modifier disclosed in US Patent Application 60/725360 may be an amide represented by the formula $R^1R^2N-C(O)R^3$, wherein R^1 and R^2 are each independently hydrocarbyl groups of at least 6 carbon atoms and R^3 is a hydroxyalkyl group of 1 to 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent. Preparative Examples are disclosed in Examples 1 and 2 (paragraphs 68 and 69). In one embodiment the amide of a hydroxylalkyl compound is prepared by reacting glycolic acid, that is, hydroxyacetic acid, HO-CH₂-COOH with an amine.

[00188] In one embodiment the friction modifier may be a secondary or tertiary amine being represented by the formula $R^4R^5NR^6$, wherein R^4 and R^5 are each independently an alkyl group of at least 6 carbon atoms and R^6 is hydrogen, a hydrocarbyl group, a hydroxyl-containing alkyl group, or an amine-containing alkyl group. A more detailed description of the friction

modifier is described in US Patent Application 05/037897 in paragraphs 8 and 19 to 22.

[00189] In one embodiment the friction modifier may be derived from the reaction of a carboxylic acid or a reactive equivalent thereof with an aminoalcohol, wherein the friction modifier contains at least two hydrocarbyl groups, each containing at least 6 carbon atoms. An example of such a friction modifier includes the reaction product of isostearic acid or an alkyl succinic anhydride with tris-hydroxymethylaminomethane. A more detailed description of such a friction modifier is disclosed in International Publication WO04/007652) in paragraphs 8 and 9 to 14.

[00190] The friction modifier includes fatty amines, borated glycerol esters, fatty acid amides, non-borated fatty epoxides, borated fatty epoxides, alkoxyated fatty amines, borated alkoxyated fatty amines, metal salts of fatty acids, fatty imidazolines, metal salts of alkyl salicylates (may also be referred to as a detergent), metal salts of sulphonates (may also be referred to as a detergent), condensation products of carboxylic acids or polyalkylene-polyamines, or amides of hydroxyalkyl compounds.

[00191] In one embodiment the friction modifier includes a fatty acid ester of glycerol. The final product may be in the form of a metal salt, an amide, an imidazoline, or mixtures thereof. The fatty acids may contain 6 to 24, or 8 to 18 carbon atoms. The fatty acids may be branched or straight-chain, saturated or unsaturated. Suitable acids include 2-ethylhexanoic, decanoic, oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, and linolenic acids, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, and Neat's foot oil. In one embodiment the fatty acid is oleic acid. When in the form of a metal salt, typically the metal includes zinc or calcium; and the products include overbased and non-overbased products. Examples are overbased calcium salts and basic oleic acid-zinc salt complexes which may be represented by the general formula $Zn_4Oleate_6O$. When in the form of an amide, the condensation product includes those prepared with ammonia, or with primary or secondary amines such as diethylamine and diethanolamine. When in the form of an imidazoline, the condensation product of an acid with a

diamine or polyamine such as a polyethylenepolyamine. In one embodiment the friction modifier is the condensation product of a fatty acid with C8 to C24 atoms, and a polyalkylene polyamine, and in particular, the product of isostearic acid with tetraethylenepentamine.

5 **[00192]** In one embodiment the friction modifier includes those formed by the condensation of the hydroxyalkyl compound with an acylating agent or an amine. A more detailed description of the hydroxyalkyl compound is described in WO 2007/0044820 paragraphs 9, and 20-22. The friction modifier disclosed in WO2007/044820 includes an amide represented by the formula
10 $R^{12}R^{13}N-C(O)R^{14}$, wherein R^{12} and R^{13} are each independently hydrocarbyl groups of at least 6 carbon atoms and R^{14} is a hydroxyalkyl group of 1 to 6 carbon atoms or a group formed by the condensation of said hydroxyalkyl group, through a hydroxyl group thereof, with an acylating agent. Preparative Examples are disclosed in Examples 1 and 2 (paragraphs 72 and 73 of
15 WO2007/044820). In one embodiment the amide of a hydroxylalkyl compound is prepared by reacting glycolic acid, that is, hydroxyacetic acid, HO-CH₂-COOH with an amine.

[00193] In one embodiment the friction modifier includes a secondary or tertiary amine being represented by the formula $R^{15}R^{16}NR^{17}$, wherein R^{15} and
20 R^{16} are each independently an alkyl group of at least 6 carbon atoms and R^{17} is hydrogen, a hydrocarbyl group, a hydroxyl-containing alkyl group, or an amine-containing alkyl group. A more detailed description of the friction modifier is described in US Patent Application 2005/037897 in paragraphs 8 and 19 to 22.

25 **[00194]** In one embodiment the friction modifier includes a reaction product of a di-cocoalkyl amine (or di-cocoamine) with glycolic acid. The friction modifier includes compounds prepared in Preparative Examples 1 and 2 of WO 2008/014319.

[00195] In one embodiment the friction modifier includes those derived from
30 the reaction product of a carboxylic acid or a reactive equivalent thereof with an aminoalcohol, wherein the friction modifier contains at least two hydrocarbyl groups, each containing at least 6 carbon atoms. An example of

such a friction modifier includes the reaction product of isostearic acid or an alkyl succinic anhydride with tris-hydroxymethylaminomethane. A more detailed description of such a friction modifier is disclosed in US Patent Application 2003/22000 (or International Publication WO04/007652) in paragraphs 8 and 9 to 14.

[00196] In one embodiment the friction modifier includes an alkoxyated alcohol. A detailed description of suitable alkoxyated alcohols is described in paragraphs 19 and 20 of US Patent Application 2005/0101497. The alkoxyated amines are also described in US Patent 5,641,732 in column 7, line 15 to column 9, line 25.

[00197] In one embodiment the friction modifier includes a hydroxyl amine compound as defined in column 37, line 19, to column 39, line 38 of US Patent 5,534,170. Optionally the hydroxyl amine includes borated as such products are described in column 39, line 39 to column 40 line 8 of US Patent 5,534,170.

[00198] In one embodiment the friction modifier includes an alkoxyated amine e.g., an ethoxylated amine derived from 1.8 % Ethomeen™ T-12 and 0.90 % Tomah™ PA-1 as described in Example E of US Patent 5,703,023, column 28, lines 30 to 46. Other suitable alkoxyated amine compounds include commercial alkoxyated fatty amines known by the trademark “ETHOMEEN” and available from Akzo Nobel. Representative examples of these ETHOMEEN™ materials is ETHOMEEN™ C/12 (bis[2-hydroxyethyl]-coco-amine); ETHOMEEN™ C/20 (polyoxyethylene[10]cocoamine); ETHOMEEN™ S/12 (bis[2-hydroxyethyl]soyamine); ETHOMEEN™ T/12 (bis[2-hydroxyethyl]-tallow-amine); ETHOMEEN™ T/15 (polyoxyethylene-[5]tallowamine); ETHOMEEN™ 0/12 (bis[2-hydroxyethyl]oleyl-amine); ETHOMEEN™ 18/12 (bis[2—hydroxyethyl]octadecylamine); and ETHOMEEN™ 18/25 (polyoxyethylene[15]octadecylamine). Fatty amines and ethoxylated fatty amines are also described in U.S. Patent 4,741,848.

[00199] In one embodiment the friction modifier includes a polyol ester as described in US Patent 5,750,476 column 8, line 40 to column 9, line 28.

[00200] In one embodiment the friction modifier includes a low potency friction modifier as described in US Patent 5,840,662 in column 2, line 28 to

column 3, line 26. US Patent 5,840,662 further discloses in column 3, line 48 to column 6, line 25 specific materials and methods of preparing the low potency friction modifier.

5 [00201] In one embodiment the friction modifier includes a reaction product of an isomerised alkenyl substituted succinic anhydride and a polyamine as described in US Patent 5,840,663 in column 2, lines 18 to 43. Specific embodiments of the friction modifier described in US Patent 5,840,663 are further disclosed in column 3, line 23 to column 4, line 35. Preparative examples are further disclosed in column 4, line 45 to column 5, line 37 of US
10 Patent 5,840,663.

[00202] In one embodiment the friction modifier includes an alkylphosphonate mono- or di- ester sold commercially by Rhodia under the trademark Duraphos® DMODP.

15 [00203] The condensation of a fatty acid and a polyamine of the invention typically result in the formation of at least one compound selected from hydrocarbyl amides, hydrocarbyl imidazolines and mixtures thereof. In one embodiment the condensation products are hydrocarbyl imidazolines. In one embodiment the condensation products are hydrocarbyl amides. In one embodiment the condensation products are mixtures of hydrocarbyl imidazolines and hydrocarbyl amides. Typically the condensation product is a
20 mixture of hydrocarbyl imidazolines and hydrocarbyl amides.

[00204] The fatty acid of the invention may be derived from a hydrocarbyl carboxylic acid. The hydrocarbyl group may be alkyl, cycloalkyl, or aryl, although alkyl is typical, and the hydrocarbyl groups may be linear or
25 branched. Typically the fatty acid contains 8 or more, 10 or more, more 13 or 14 or more carbon atoms (including the carbon of the carboxy group). Typically the fatty acid contains 8 to 30, 12 to 24, or 16 to 18 carbon atoms. Other suitable carboxylic acids may include the polycarboxylic acids or carboxylic acids or anhydrides having from 2 to 4 carbonyl groups, typically 2.
30 The polycarboxylic acids may include succinic acids and anhydrides and Diels-Alder reaction products of unsaturated monocarboxylic acids with unsaturated carboxylic acids (such as acrylic, methacrylic, maleic, fumaric, crotonic and

itaconic acids). The fatty carboxylic acids include fatty monocarboxylic acids containing 8 to 30, 10 to 26, or 12 to 24 carbon atoms.

[00205] Examples of suitable fatty acids may include caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, eicosic acid and, tall oil acids. In one embodiment the fatty acid is stearic acid, which may be used alone or in combination with other fatty acids.

[00206] The polyamines of the invention may be acyclic or cyclic, preferably acyclic; and linear or branched, preferably linear.

[00207] In one embodiment the polyamines may be alkylene polyamines selected from the group consisting of ethylene polyamines, propylene polyamines, butylene polyamines and mixtures thereof. Examples of propylene polyamines may include propylene diamine and dipropylene triamine.

[00208] Particularly useful ethylene polyamines are selected from the group consisting of ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, N-(2-aminoethyl)-N'-[2-[(2-aminoethyl)amino]ethyl]-1,2-ethanediamine, polyamine still bottoms and mixtures thereof.

[00209] In one embodiment the polyamines may be α,β -diaminoalkanes. Suitable α,β -diaminoalkanes may include diaminopropanes, diaminobutanes or mixtures thereof. Specific diaminoalkanes are selected from the group consisting of N-(2-aminoethyl)-1,3-propane diamine, 3,3'-diamino-N-methyldipropylamine, tris(2-aminoethyl)amine, N,N-bis(3-aminopropyl)-1,3-propane diamine, N,N'-1,2-ethanediylbis-(1,3-propane diamine) and mixtures thereof.

[00210] In one embodiment other polyamines may include di-(trimethylene)triamine, piperazine, diaminocyclohexanes and mixtures thereof.

[00211] One or both friction modifiers may in one embodiment be nitrogen-containing compounds, typically both friction modifiers are nitrogen-containing.

[00212] In one embodiment one of friction modifiers is the condensation product of a fatty acid with C8 to C24 atoms, and a polyalkylene polyamine, and in particular, the product of isostearic acid with tetraethylenepentamine.

5 [00213] The mixture of at least two friction modifiers may be present at 0.1 wt % to 1 wt %, or 0.2 wt % to 0.9 wt % or 0.1 wt % to 0.4 wt %, or 0.4 wt % to 1.0 wt %, of the lubricating composition

Antioxidant

10 [00214] In one embodiment the lubricating composition of the invention includes an amine antioxidant. The amine antioxidant may be a phenyl- α -naphthylamine (PANA) or a hydrocarbyl substituted diphenylamine, or mixtures thereof. The hydrocarbyl substituted diphenylamine may include mono- or di-C₄ to C₁₆-, or C₆ to C₁₂-, or C₉- alkyl diphenylamine. For example the hydrocarbyl substituted diphenylamine may be octyl diphenylamine, or di-octyl diphenylamine, dinonyl diphenylamine, typically dinonyl diphenylamine.

15 [00215] When present the amine antioxidant may be present at 0.2 wt % to 1.2 wt %, or 0.3 wt % to 1.0 wt %, or 0.4 wt % to 0.9 wt % or 0.5 wt % to 0.8 wt %, of the lubricating composition.

20 [00216] The lubricating composition be optionally include at least one other antioxidant that is known and includes sulphurised olefins, hindered phenols, molybdenum dithiocarbamates, and mixtures thereof.

25 [00217] The hindered phenol antioxidant often contains a secondary butyl and/or a tertiary butyl group as a sterically hindering group. The phenol group is often further substituted with a hydrocarbyl group and/or a bridging group linking to a second aromatic group. Examples of suitable hindered phenol antioxidants include 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol or 4-butyl-2,6-di-tert-butylphenol, or 4-dodecyl-2,6-di-tert-butylphenol. In one embodiment the hindered phenol antioxidant may be an ester and may include, e.g., Irganox™ L-135 from Ciba, or butyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate.

30

[00218] If present, the secondary antioxidant may be present at 0.1 wt % to 1 wt %, or 0.2 wt % to 0.9 wt % or 0.1 wt % to 0.4 wt %, or 0.4 wt % to 1.0 wt %, of the lubricating composition.

5 [00219] Optionally the lubricating composition may further contain other performance additives. Other performance additives include corrosion inhibitors, foam inhibitors, pour point depressants, demulsifiers, metal deactivators or seal swell agents.

10 [00220] Corrosion inhibitors include 1-amino-2-propanol, amines, triazole derivatives including tolyl triazole, dimercaptothiadiazole derivatives, octylamine octanoate, condensation products of dodeceny succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine.

15 [00221] Foam inhibitors that may be useful in the compositions of the invention include polysiloxanes, copolymers of ethyl acrylate and 2-ethylhexylacrylate and optionally vinyl acetate; demulsifiers including fluorinated polysiloxanes, trialkyl phosphates, polyethylene glycols, polyethylene oxides, polypropylene oxides and (ethylene oxide-propylene oxide) polymers.

[00222] Pour point depressants that may be useful in the compositions of the invention include polyalphaolefins, esters of maleic anhydride-styrene copolymers, poly(meth)acrylates, polyacrylates or polyacrylamides.

20 [00223] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

25 [00224] Metal deactivators include derivatives of benzotriazoles (typically tolyl triazole), 1,2,4-triazoles, benzimidazoles, 2-alkyldithiobenzimidazoles or 2-alkyldithiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[00225] Seal swell agents include sulfolene derivatives, Exxon Necton-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

30 [00226] The following examples provide illustrations of the invention. These examples are non-exhaustive and are not intended to limit the scope of the invention.

EXAMPLESLubricants: Invention and Reference Lubricating Oil Compositions

5 [00227] Four Inventive fluids (INV1 to INV4) are prepared as summarized below by adding to the named base oil (or oil of lubricating viscosity) 13.85 wt % of an additive package described below. The base oil of each inventive lubricant has a kinematic viscosity at 100°C in the range of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of between 110, and less than 120.

	INV1	INV2	INV3	INV4
Base Oil				
3 mm ² /s Ultra S-3 oil	84	100	100	100
8 mm ² /s Ultra S-8 oil	16	0	0	0
Borated succinimide dispersant (wt %)	1.83	1.83	1.83	1.83
overbased calcium-containing sulphonate detergent (delivering ppm of calcium)	170	170	170	170
A mixture of phosphorus-containing antiwear agents	0.33	0.33	0.33	0.33
Total amount of Phosphorus from dibutyl phosphite (ppm)	356 ppm	356 ppm	356 ppm	356 ppm
Total amount of Phosphorus in lubricant (ppm)	689	689	689	689
Mixture of amine-containing friction modifiers (wt %)	1.17	1.17	1.17	1.17
Star poly(meth)acrylate copolymer having Mw of about 300,000	0.27	0.85	0.25	0
Linear dispersant poly(meth)acrylate copolymer having Mw of about 15,000	0.62	0.94	1.48	0.62
Other additives (wt %)	4.24	4.24	4.24	4.24

Footnote:

Ultra S-3 oil and S-8 oil are both API Group II+ base oils having a viscosity index of between 110 and less than 120.

The mixture of antiwear agents comprises phosphoric acid, dibutyl phosphite, and a dihydrocarbyl C16-18 hydrogen phosphite (wherein the hydrocarbyl groups are a mixture of alkyl and alkenyl groups).

The mixture of friction modifiers includes between 3 and 6 friction modifiers.

The other additives treated at 4.24 wt % include a mixture of phenolic and aminic antioxidants, a carboxylic acid ester, borate esters, corrosion inhibitors, pour point depressants, antifoam agents, seal swell agents, and diluent oil.

The linear polymer may be derived from a monomer composition comprising methyl methacrylate (14.1 wt %), 2-ethylhexyl methacrylate (4.7 wt %), C₁₂₋₁₅ alkyl methacrylate (75.1 wt %), and ethylene glycol dimethacrylate (6.1 wt %).

The weight average molecular weight of the linear polymer is 15,000.

A comparative example is evaluated based upon a Ford Type A MERCON®LV ATF and Shell ATF™134FE

[00228] Each lubricant INV1 to INV4, and the comparative ATF are assessed by comparing CAFE figures using a 2011 Ford Fusion AT (6HP6) using the following procedures described below.

[00229] ASTM D2882 Pump Test: This procedure assesses lubricant antiwear properties using an electric motor driven Vickers 104-C vane pump. The weight loss of the pump vanes and cam rings are recorded after 100 hours of continuous operation, followed by visual inspection for scoring and scuffing.

[00230] The Falex wear/EP test described in ASTM D-3233 is used to assess the friction, wear and extreme pressure (EP) properties of a lubricating fluid. A rotating steel journal is run between two stationary steel V-blocks immersed in the test fluid. Load is applied to V-blocks in 250-lbf (1112 N) increments with the load maintained constant for 1 minute at each load increment until failure to maintain torque or by seizure of the blocks against the pin. The test was conducted with fluid temperatures of 100 & 150°C.

[00231] The results obtained for the Falex EP test and the pump test are:

	Vane Pump Test		
Lubricant	Cam Ring Wear loss (mg)	Vane weight loss (mg)	Total mass loss (mg)
INV1	1.0	0.1	1.1
INV2	1.0	0.4	1.4
INV3	1.8	0.4	2.2
INV4	2.0	0.8	2.8
Mercon LV	835.4	4.6	840
ATF 134FE	2598.6	23.2	2621.8
	Falex EP Test (Result passing load based upon 2 tests)		
	100 °C	150 °C	
INV1	680	510	
INV2	737	510	
INV3	680	567	
INV4	624	454	
Mercon LV	567	340	
ATF 134FE	680	397	

- [00232] The lubricating compositions are then evaluated by determining the kinematic and Brookfield viscosities (by employing ASTM methods D445 at 40 °C and 100 °C (kinematic viscosity at 40 °C, KV40 and 100 °C, KV100) and D2983 at -40°C (Brookfield viscosity at -40 °C, BV-40) respectively). The results obtained are also shown in the table. The results obtained for each lubricant are as follows:

Lubricant	KV40 (mm ² /s)	KV100 (mm ² /s)	BV-40 (mm ² /s)	Base Oil Viscosity at 100 °C (mm ² /s)
INV1	20	4.51	4900	3.55
INV2	18.85	4.5	3710	3.1
INV3	17.61	4.17	3600	3.1
INV4	16.46	3.91	2470	3.1
Mercon®LV	28.91	5.92	9860	Unknown
ATF™ 134FE	17.38	4.19	5070	Unknown

[00233] Overall the data indicates that the lubricating composition of the present invention has reduced wear as measured by Vane pump test, higher passing load as measured by 150 °C Falex wear test, while maintaining a low lubricant viscosity.

- 5 [00234] Inventive Examples 5 to 11 (INV5 to INV12) are prepared in a similar way to INV1, except lubricating composition of each lubricant is summarized as follows:

	INV5	INV6	INV7	INV8	INV9	INV10
Borated succinimide dispersant (wt %)	1.83	1.83	1.83	1.83	1.83	1.83
overbased calcium-containing sulphonate detergent (delivering ppm of calcium)	170	170	170	170	170	170
A mixture of phosphorus-containing antiwear agents	0.33	0.33	0.33	0.33	0.33	0.33
Total amount of Phosphorus from dibutyl phosphite (ppm)	356 ppm	356 ppm	356 ppm	356 ppm	356 ppm	356 ppm
Total amount of Phosphorus in lubricant (ppm)	689	689	689	689	689	689
Mixture of amine-containing friction modifiers (wt %)	1.17	1.17	1.17	1.17	1.17	1.17
Linear dispersant polymeth acrylate copolymer (HLW)	0.78	0.30	0	0	0	0
Star polymeth acrylate copolymer	0	0	0.31	0.31	0.31	0.31
Linear dispersant polymeth acrylate copolymer	0.62	0.62	0.62	0.62	0.62	0,62
Other additives (wt %)	4.24	4.24	4.24	4.24	4.24	4.24
Base Oil	Balance to 100 wt % of 3 mm ² /s Ultra S-3 oil					

Footnote:

The linear dispersant poly(meth)acrylate is derived from a monomer composition comprising 2-ethylhexyl (meth)acrylate (30 wt %), C₁₂₋₁₅ alkyl (meth)acrylate (68.2 wt %), and dimethylaminopropyl (meth)acrylate (1.8 wt %).

The star polymers of INV7 to INV10 have a weight average molecular weight of about 540,000; 740,000; 920,000; and 1,200,000 respectively. The star polymers are prepared from a monomer mix methacrylate described below. The star polymers are prepared by RAFT polymerization process.

INV	C12-15	C1-C9	Difunctional Monomer
7	81	19	E
8	81	19	E
9	81	19	E
10	81	19	E

E = Ethylene glycol dimethacrylate.

INV	C12-C15	C1-C9	Acrylate Monomer*	Difunctional Monomer
11	80	19	1.0	
12	70	30	0	E

Footnote:

* is 2 Ethylhexylacrylate

The linear dispersant polymethacrylate copolymer (HLW) is a second dispersant viscosity modifier. The HLW of INV5 has a weight average molecular weight of 15,000; and is derived from a monomer mix of 68.2 wt % C₁₂₋₁₅ alkyl methacrylate, 30 wt % of 2-ethylhexylmethacrylate; and 1.8 wt % of dimethylaminopropyl (meth)acrylate.

The mixture of antiwear agents comprises phosphoric acid, dibutyl phosphite, and a dihydrocarbyl C16-18 hydrogen phosphite (wherein the hydrocarbyl groups are a mixture of alkyl and alkenyl groups).

The mixture of friction modifiers includes between 3 and 6 friction modifiers. The other additives treated at 4.24 wt % include a mixture of phenolic and aminic antioxidants, a carboxylic acid ester, borate esters, corrosion inhibitors, pour point depressants, antifoam agents, seal swell agents, and diluent oil.

- 5 [00235] INV5 to INV10 are evaluated for viscometric properties and summarized below:

Lubricant	KV40 (mm ² /s)	KV100 (mm ² /s)	BV-40 (mm ² /s)
INV5	17.55	4.12	4010
INV6	17.31	4.08	3720
INV7	18.26	4.28	3940
INV8	18.22	4.28	4200
INV9	18.27	4.32	4230
INV10	18.42	4.37	4450

- 10 [00236] 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:

(i) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form a ring);

15 (ii) 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 (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulphony);

20 (iii) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain

other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulphur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten
5 carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[00237] 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. The products formed thereby,
10 including the products formed upon employing lubricant 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 lubricant composition prepared by admixing the components
15 described above.

[00238] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to
20 be understood as modified by the word "about." Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical
25 component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or
30 amounts for any of the other elements.

[00239] While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will

become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

4030

What is claimed is:

1. A lubricating composition comprising:
 - 5 (a) an oil of lubricating viscosity having a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 104 to 130;
 - (b) 1.2 to 5.0 wt % of at least one borated dispersant, wherein at least one borated dispersant is further functionalised with a sulphur or phosphorus moiety;
 - (c) a calcium-containing detergent, wherein the detergent is present in an
10 amount to deliver at least 110 ppm to 700 ppm of calcium;
 - (d) a at least two phosphorus-containing compounds, wherein the phosphorus-containing compounds are present in an amount to deliver 360 to 950 ppm of phosphorus to the lubricating composition, wherein at least 150 ppm of the phosphorus is delivered by a C₄₋₆ hydrocarbyl phosphite; and
 - 15 (e) 0.1 wt % to 5 wt % of a linear polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of 5,000 to 25,000.
2. The composition of claim 1, wherein the calcium-containing detergent is
20 present in an amount to deliver 130 ppm to 600 ppm, or 160 ppm to 400 ppm of calcium.
3. The composition of any preceding claim, wherein the C₄₋₆ hydrocarbyl phosphite is a C₄ alkyl phosphite.
4. The composition of any preceding claim, wherein the borated dispersant
25 is a borated polyisobutylene succinimide dispersant, wherein the polyisobutylene of the borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.
5. The composition of any preceding claim further comprising a second borated dispersant wherein the borated dispersant is a borated polyisobutylene
30 succinimide dispersant, wherein the polyisobutylene of the borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.

6. The composition of any preceding claim further comprising a non-borated dispersant.
7. The composition of claim 6, wherein the non-borated dispersant is a polyisobutylene succinimide wherein the polyisobutylene of the borated polyisobutylene succinimide has a number average molecular weight of 750 to 2200, or 750 to 1350, or 750 to 1150.
8. The composition of any preceding claim, wherein the borated dispersant has a N:CO ratio of 0.9:1 to 1.6:1, or 0.95:1 to 1.5:1, or 1.0:1 to 1:4.
9. The composition of any preceding claim 1 to 8, wherein the composition further comprises 0.1 wt% to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of greater than 25,000 to 400,000 (or to 350,000).
10. The composition of any preceding claim 1 to 8, wherein the linear polymer viscosity modifier having dispersant functionality comprises:
- 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of 10,000 to 20,000; and
- 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality, wherein the linear polymer has a weight average molecular weight of greater than 20,000 to 250,000.
11. The composition of any preceding claim 1 to 8, wherein the linear polymer viscosity modifier having dispersant functionality comprises
- 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a linear (meth)acrylic polymer having dispersant functionality wherein the linear polymer has a weight average molecular weight of 5,000 to 25,000 or 10,000 to 20,000, and the composition further comprises
- 0.1 wt % to 4 wt % (or 0.2 wt % to 3 wt %) of a (meth)acrylic polymer having star architecture.

12. The composition of claim 11, wherein the (meth)acrylic polymer having star architecture has three or more arms that comprise a poly(meth)acrylate polymer is derived from a monomer composition comprising:

5 (a) 50 wt % to 100 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 12 to 15 carbon atoms;

(b) 0 wt % to 40 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 1 to 9 carbon atoms;

(c) 0 wt % to 10 wt % of a dispersant monomer,

10 (d) 0 wt % to 5 wt %, or 0 wt % to 2 wt %, or 0 wt % of a vinyl aromatic monomer (typically styrene); and

(e) 0 wt % to 20 wt %, or 0 wt % to 10 wt %, or 0 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 16 to 18 carbon atoms.

13. The composition of claim 11, wherein the (meth)acrylic polymer having star architecture has three or more arms that comprise a poly(meth)acrylate polymer is derived from a monomer composition comprising:

(a) 60 wt % to 95 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 12 to 15 carbon atoms;

20 (b) 5 wt % to 30 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 1 to 9 carbon atoms;

(c) 0 wt % to 10 wt % of a dispersant monomer,

(d) 0 wt % to 5 wt %, or 0 wt % to 2 wt %, or 0 wt % of a vinyl aromatic monomer (typically styrene); and

25 (e) 0 wt % to 20 wt %, or 0 wt % to 10 wt %, or 0 wt % of an alkyl (meth)acrylate, wherein the alkyl group of the (meth)acrylate has 16 to 18 carbon atoms.

14. The composition of any preceding claim 1 to 8, wherein the linear polymer viscosity modifier having dispersant functionality comprises:

30 the linear polymer viscosity modifier having dispersant functionality is a sole dispersant viscosity modifier present at 0.5 wt % to 4 wt % of a linear (meth)acrylic polymer viscosity modifier having dispersant functionality,

wherein the linear polymer has a weight average molecular weight of 5,000 to 25,000, or 10,000 to 20,000, and

wherein oil the of lubricating viscosity has a kinematic viscosity at 100°C of 2.8 to 3.1 cSt (mm²/s) and a viscosity index of 104 to 130.

5 15. The composition of any preceding claim, wherein the composition further comprises a C₈₋₂₀ hydrocarbyl phosphite, or a C₁₂₋₁₈ hydrocarbyl phosphite, or C₁₆₋₁₈ hydrocarbyl phosphite.

16. The composition of any preceding claim, wherein the calcium-containing detergent is a calcium sulphonate, or calcium phenate.

10 17. The composition of any preceding claim, wherein the calcium-containing detergent is a calcium sulphonate.

18. The composition of any preceding claim 1 to 14, or claims 16 to 17, wherein the oil of lubricating viscosity has a kinematic viscosity at 100°C of 2.8 to 3.6 cSt (mm²/s) and a viscosity index of 110 to less than 120.

15 19. A method of lubricating an automatic transmission comprising supplying to the automatic transmission a composition of any preceding claim 1 to 18.

20