(12) UK Patent Application (19) GB (11) 2 444 135 (13) A

(43) Date of A Publication **28.05.2008**

(21) Application No: **0713197.2**

(22) Date of Filing: **06.07.2007**

(30) Priority Data:
(31) **11457579** (32) **14.07.2006** (33) **US**

(71) Applicant(s):
Afton Chemical Corporation
(Incorporated in USA - Delaware)
500 Spring Street, Richmond,
Virginia 23219, United States of America

(72) Inventor(s):
John T Loper
William Y Lam
Mark Thomas Devlin

(74) Agent and/or Address for Service:
J A Kemp & Co.
14 South Square, Gray's Inn, LONDON,
WC1R 5JJ, United Kingdom

(51) INT CL:
C10M 141/00 (2006.01) ***C10M 141/06*** (2006.01)
C10N 20/02 (2006.01) *C10N 30/02* (2006.01)
C10N 40/25 (2006.01)

(56) Documents Cited:
EP 1785476 A1 **EP 1724330 A1**
EP 1518921 A1 **EP 1518919 A1**
WO 2003/064568 A3 **CA 002487767 A1**
US 5891786 A **US 5282991 A**
US 20060264340 A1 **US 20050137096 A1**
US 20050101494 A1 **US 20050043191 A1**

(58) Field of Search:
INT CL **C10M, C10N**
Other: **ONLINE - EPODOC, WPI**

(54) Abstract Title**: Boundary friction reducing lubricating composition**

(57) A lubricating composition comprises a base oil, a friction modifier and a dispersant, wherein the lubricating composition has less than about 325 ppm of boron. The dispersant may comprise a basic nitrogen or it may be a polyisobutylene-based dispersant. The friction modifier may be a non-nitrogen-containing compound, a nitrogen-containing compound or an ash-containing compound. The nitrogen-containing compound may be a long chain alkylene amine or diethanolamine. The ash-containing compound may be a molybdenum compound, a titanium compound or a tungsten compound. The composition can reduce boundary friction and improve fuel economy in automotive engines.

This print incorporates corrections made under Section 117(1) of the Patents Act 1977.

BOUNDARY FRICTION REDUCING LUBRICATING COMPOSITION

DESCRIPTION OF THE DISCLOSURE

Field of the Disclosure

[0001] The present disclosure relates to a lubricating composition comprising a base oil, a friction modifier, and a dispersant, wherein the lubricating composition comprises less than about 325 ppm of boron.

Background of the Disclosure

[0002] In recent years, there has been growing concern to produce energy-efficient lubricated components. Moreover, modern engine oil specifications require lubricants to demonstrate fuel efficiency in standardized engine tests. The thickness and frictional characteristics of lubricant films are known to affect the fuel economy properties of oils.

[0003] When rubbing surfaces in a machine (engine, gear system or transmission) come in contact a frictional force exists that retards the motion of the surfaces. This frictional force, called boundary friction, reduces the efficiency of the machine.

[0004] It is known that non-nitrogen-containing and molybdenum-containing friction modifiers reduce boundary friction. *See* SAE 2000-01-1972. Moreover, it is known that friction is lower with the combination of molybdenum-containing friction modifiers and ethylene-propylene polymeric dispersants than when the same friction modifiers are combined with other dispersants, such as Mannich or succinimides. *See* U.S. Patent No. 6,528,461.

[0005] What is needed is a lubricant composition that is inexpensive and can provide at least one of reduced boundary friction and increased fuel economy.

SUMMARY

[0006] In accordance with the disclosure, there is disclosed a lubricating composition comprising a base oil, a dispersant, and a friction modifier, wherein the composition comprises less than about 325 ppm of boron.

[0007] In an aspect, there is also disclosed a method of formulating a lubricating composition having improved fuel efficiency comprising providing a base oil, a dispersant, and a friction modifier, wherein the composition comprises less than about 325 ppm of boron.

[0008] In a further aspect, there is disclosed a method of reducing boundary friction on a surface comprising providing to the surface a lubricating composition comprising a base oil, a dispersant, and a friction modifier, wherein the composition comprises less than about 325 ppm of boron.

[0009] Additional objects and advantages of the invention will be set forth in part in the description which follows, or may be learned by practice of the disclosure. The objects and advantages of the disclosure will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[0010] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DESCRIPTION OF THE EMBODIMENTS

[0011] The present disclosure relates to a lubricating composition comprising a base oil, a friction modifier, and a dispersant, wherein the lubricating composition comprises less than about 325 ppm of boron.

[0012] The dispersant for use in the disclosed lubricating composition can be selected from any of the ashless dispersants known to those skilled in the art.

Suitable ashless dispersants may include ashless dispersants such as succinimide dispersants, Mannich base dispersants, and polymeric polyamine dispersants. In an aspect, the dispersant comprises a basic nitrogen. In another aspect, the dispersant is a non-boron-containing dispersant. Hydrocarbyl-substituted succinic acylating agents can be used to make hydrocarbyl-substituted succinimides. The hydrocarbyl-substituted succinic acylating agents include, but are not limited to, hydrocarbyl-substituted succinic acids, hydrocarbyl-substituted succinic anhydrides, the hydrocarbyl-substituted succinic acid halides (for example, the acid fluorides and acid chlorides), and the esters of the hydrocarbyl-substituted succinic acids and lower alcohols (e.g., those containing up to 7 carbon atoms), that is, hydrocarbyl-substituted compounds which can function as carboxylic acylating agents.

[0013] Hydrocarbyl substituted acylating agents can be made by reacting a polyolefin or chlorinated polyolefin of appropriate molecular weight with maleic anhydride. Similar carboxylic reactants can be used to make the acylating agents. Such reactants can include, but are not limited to, maleic acid, fumaric acid, malic acid, tartaric acid, itaconic acid, itaconic anhydride, citraconic acid, citraconic anhydride, mesaconic acid, ethylmaleic anhydride, dimethylmaleic anhydride, ethylmaleic acid, dimethylmaleic acid, hexylmaleic acid, and the like, including the corresponding acid halides and lower aliphatic esters.

[0014] The molecular weight of the olefin can vary depending upon the intended use of the substituted succinic anhydrides. Typically, the substituted succinic anhydrides can have a hydrocarbyl group of from about 8-500 carbon atoms. However, substituted succinic anhydrides used to make lubricating oil dispersants can typically have a hydrocarbyl group of about 40-500 carbon atoms. With high molecular weight substituted succinic anhydrides, it is more accurate to refer to number average molecular weight (Mn) since the olefins used to make these substituted succinic anhydrides can include a mixture of different molecular weight components resulting from the polymerization of low molecular weight olefin monomers such as ethylene, propylene and isobutylene.

[0015] The mole ratio of maleic anhydride to olefin can vary widely. It can vary, for example, from about 5:1 to about 1:5, or for example, from about 1:1 to about 3:1. With olefins such as polyisobutylene having a number average molecular weight of about 500 to about 7000, or as a further example, about 800 to about 3000 or higher and the ethylene-alpha-olefin copolymers, the maleic anhydride can be used in stoichiometric excess, e.g. 1.1 to 3 moles maleic anhydride per mole of olefin. The unreacted maleic anhydride can be vaporized from the resultant reaction mixture.

[0016] Polyalkenyl succinic anhydrides can be converted to polyalkyl succinic anhydrides by using conventional reducing conditions such as catalytic hydrogenation. For catalytic hydrogenation, a suitable catalyst is palladium on carbon. Likewise, polyalkenyl succinimides can be converted to polyalkyl succinimides using similar reducing conditions.

[0017] The polyalkyl or polyalkenyl substituent on the succinic anhydrides employed herein can be generally derived from polyolefins which are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene and butylene. The mono-olefin employed can have about 2 to about 24 carbon atoms, or as a further example, about 3 to about 12 carbon atoms. Other suitable mono-olefins include propylene, butylene, particularly isobutylene, 1-octene and 1-decene. Polyolefins prepared from such mono-olefins include polypropylene, polybutene, polyisobutene, and the polyalphaolefins produced from 1-octene and 1-decene. In an aspect, the dispersant is a polyisobutylene-based dispersant.

[0018] In some aspects, the ashless dispersant can include one or more alkenyl succinimides of an amine having at least one primary amino group capable of forming an imide group. The alkenyl succinimides can be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with an amine containing at least one primary amino group. The alkenyl succinic anhydride can be made readily by heating a mixture of polyolefin and maleic anhydride to about 180°-220°C. The polyolefin can be a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like, having a number average molecular weight in the range of about 300 to about 3000 as determined by gel permeation chromatography (GPC).

[0019] Amines which can be employed in forming the ashless dispersant include any that have at least one primary amino group which can react to form an imide group and at least one additional primary or secondary amino group and/or at least one hydroxyl group. A few representative examples are: N-methyl-propanediamine, N-dodecylpropanediamine, N-aminopropyl-piperazine, ethanolamine, N-ethanol-ethylenediamine, and the like.

[0020] Suitable amines can include alkylene polyamines, such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, and tetra-(1,2-propylene)pentamine. A further example includes the ethylene polyamines which can be depicted by the formula $H_2N(CH_2CH_2\text{-}NH)_nH$, wherein n can be an integer from about one to about ten. These include: ethylene diamine, diethylene triamine (DETA), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), pentaethylene hexamine (PEHA), and the like, including mixtures thereof in which case n is the average value of the mixture. Such ethylene polyamines have a primary amine group at each end so they can form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures can contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The commercial mixtures can have approximate overall compositions falling in the range corresponding to diethylene triamine to tetraethylene pentamine. The molar ratio of polyalkenyl succinic anhydride to polyalkylene polyamines can be from about 1:1 to about 3.0:1.

[0021] In some aspects, the dispersant can include the products of the reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, such as polyisobutene, of suitable molecular weight, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or more such substances.

[0022] Polyamines that are also suitable in preparing the dispersants described herein include N-arylphenylenediamines, such as N-phenylphenylenediamines, for example, N-phenyl-1,4-phenylenediamine, N-phenyl-1,3-phenylendiamine, and N-phenyl-1,2-phenylenediamine; aminothiazoles such as aminothiazole, aminobenzothiazole, aminobenzothiadiazole and aminoalkylthiazole; aminocarbazoles; aminoindoles; aminopyrroles; amino-indazolinones; aminomercaptotriazoles; aminoperimidines; aminoalkyl imidazoles, such as 1-(2-aminoethyl)imidazol- e, 1-(3-aminopropyl)imidazole; and aminoalkyl morpholines, such as 4-(3-aminopropyl)morpholine. These polyamines are described in more detail in U.S. Pat. Nos. 4,863,623 and 5,075,383, the disclosures of which are hereby incorporated by reference herein.

[0023] Additional polyamines useful in forming the hydrocarbyl-substituted succinimides include polyamines having at least one primary or secondary amino group and at least one tertiary amino group in the molecule as taught in U.S. Pat. Nos. 5,634,951 and 5,725,612, the disclosures of which are hereby incorporated by reference herein. Non-limiting examples of suitable polyamines include N,N,N",N"-tetraalkyldialkylenetriamines (two terminal tertiary amino groups and one central secondary amino group), N,N,N',N"-tetraalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal primary amino group), N,N,N',N",N'"-pentaalkyltrialkylenetetramines (one terminal tertiary amino group, two internal tertiary amino groups and one terminal secondary amino group), tris(dialkylaminoalkyl)aminoalkylmethanes (three terminal tertiary amino groups and one terminal primary amino group), and like compounds, wherein the alkyl groups are the same or different and typically contain no more than about 12 carbon atoms each, and which can contain from about 1 to about 4 carbon atoms each. As a further example, these alkyl groups can be methyl and/or ethyl groups. Polyamine reactants of this type can include dimethylaminopropylamine (DMAPA) and N-methyl piperazine.

[0024] Hydroxyamines suitable for herein include compounds, oligomers or polymers containing at least one primary or secondary amine capable of reacting with the hydrocarbyl-substituted succinic acid or anhydride. Examples of hydroxyamines suitable for use herein include aminoethylethanolamine (AEEA), aminopropyldiethanolamine (APDEA), ethanolamine, diethanolamine (DEA), partially propoxylated hexamethylene diamine (for example HMDA-2PO or HMDA-3PO), 3-

amino-1,2-propanediol, tris(hydroxymethyl)aminomethane, and 2-amino-1,3-propanediol.

[0025] The mole ratio of amine to hydrocarbyl-substituted succinic acid or anhydride can range from about 1:1 to about 3.0:1. Another example of a mole ratio of amine to hydrocarbyl-substituted succinic acid or anhydride may range from about 1.5:1 to about 2.0:1.

[0026] The foregoing dispersant can also be a post-treated dispersant made, for example, by treating the dispersant with maleic anhydride and boric acid as described, for example, in U.S. Pat. No. 5,789,353, or by treating the dispersant with nonylphenol, formaldehyde and glycolic acid as described, for example, in U.S. Pat. No. 5,137,980, the disclosures of which are hereby incorporated y reference in their entirety.

[0027] The Mannich base dispersants can be a reaction product of an alkyl phenol, typically having a long chain alkyl substituent on the ring, with one or more aliphatic aldehydes containing from about 1 to about 7 carbon atoms (for example, formaldehyde and derivatives thereof), and polyamines (especially polyalkylene polyamines). For example, a Mannich base ashless dispersants can be formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to about 2.5 moles of formaldehyde and from about 0.5 to about 2 moles of polyalkylene polyamine.

[0028] Hydrocarbon sources for preparation of the Mannich polyamine dispersants can be those derived from substantially saturated petroleum fractions and olefin polymers, such as polymers of mono-olefins having from 2 to about 6 carbon atoms. The hydrocarbon source generally contains, for example, at least about 40 carbon atoms, and as a further example, at least about 50 carbon atoms to provide substantial oil solubility to the dispersant. The olefin polymers having a GPC number average molecular weight range from about 600 to 5,000 can be suitable. However, polymers of higher molecular weight can also be used. Suitable hydrocarbon sources can be isobutylene polymers and polymers made from a mixture of isobutene and a raffinate stream.

[0029] Suitable Mannich base dispersants can be Mannich base ashless dispersants formed by condensing about one molar proportion of long chain hydrocarbon-substituted phenol with from about 1 to about 2.5 moles of formaldehyde and from about 0.5 to about 2 moles of polyalkylene polyamine.

[0030] Polymeric polyamine dispersants suitable as the ashless dispersants are polymers containing basic amine groups and oil solubilizing groups (for example, pendant alkyl groups having at least about 8 carbon atoms). Such materials are illustrated by interpolymers formed from various monomers such as decyl methacrylate, vinyl decyl ether or relatively high molecular weight olefins, with aminoalkyl acrylates and aminoalkyl acrylamides. Examples of polymeric polyamine dispersants are set forth in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,493,520; 3,519,565; 3,666,730; 3,687,849; and 3,702,300, the disclosures of which are hereby incorporated by reference in their entirety. Polymeric polyamines can include hydrocarbyl polyamines wherein the hydrocarbyl group is composed of the polymerization product of isobutene and a raffinate I stream as described above. PIB-amine and PIB-polyamines can also be used.

[0031] Methods for the production of ashless dispersants as described above are known to those skilled in the art and are reported in the patent literature. For example, the synthesis of various ashless dispersants of the foregoing types is described in such patents as U.S. Pat. Nos. 2,459,112; 2,962,442, 2,984,550;

3,036,003; 3,163,603; 3,166,516; 3,172,892; 3,184,474; 3,202,678; 3,215,707; 3,216,936; 3,219,666; 3,236,770; 3,254,025; 3,271,310; 3,272,746; 3,275,554; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,331,776; 3,340,281; 3,341,542; 3,346,493; 3,351,552; 3,355,270; 3,368,972; 3,381,022; 3,399,141; 3,413,347; 3,415,750; 3,433,744; 3,438,757; 3,442,808; 3,444,170; 3,448,047; 3,448,048; 3,448,049; 3,451,933; 3,454,497; 3,454,555; 3,454,607; 3,459,661; 3,461,172; 3,467,668; 3,493,520; 3,501,405; 3,522,179; 3,539,633; 3,541,012; 3,542,680; 3,543,678; 3,558,743; 3,565,804; 3,567,637; 3,574,101; 3,576,743; 3,586,629; 3,591,598; 3,600,372; 3,630,904; 3,632,510; 3,632,511; 3,634,515; 3,649,229; 3,697,428; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,441; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,804,763; 3,836,471; 3,862,981; 3,872,019; 3,904,595; 3,936,480; 3,948,800; 3,950,341; 3,957,746; 3,957,854; 3,957,855; 3,980,569; 3,985,802; 3,991,098; 4,006,089; 4,011,380; 4,025,451; 4,058,468; 4,071,548; 4,083,699; 4,090,854; 4,173,540; 4,234,435; 4,354,950; 4,485,023; 5,137,980, and Re 26,433, herein incorporated by reference.

[0032] An example of a suitable ashless dispersant is a borated dispersant. Borated dispersants can be formed by boronating ("borating") an ashless dispersant having basic nitrogen and/or at least one hydroxyl group in the molecule, such as a succinimide dispersant, succinamide dispersant, succinic ester dispersant, succinic ester-amide dispersant, Mannich base dispersant, or hydrocarbyl amine or polyamine dispersant. Methods that can be used for borating the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069;

3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387, the disclosures of which are hereby incorporated by reference in their entirety.

[0033] The borated dispersant can include a high molecular weight dispersant treated with boron such that the borated dispersant includes up to about 2 wt % of boron, for example from about 0.8 wt % or less of boron, as a further example from about 0.1 to about 0.7 wt % of boron, as an even further example, from about 0.25 to about 0.7 wt % of boron, and as a further example from about 0.35 to about 0.7 wt % of boron. The dispersant can be dissolved in oil of suitable viscosity for ease of handling. It should be understood that the weight percentages given here are for neat dispersant, without any diluent oil added.

[0034] A dispersant can be further reacted with an organic acid, an anhydride, and/or an aldehyde/phenol mixture. Such a process can enhance compatibility with elastomer seals, for example. The borated dispersant can further include a mixture of borated dispersants. As a further example, the borated dispersant can include a nitrogen-containing dispersant and/or may be free of phosphorus.

[0035] A dispersant can be present in the lubricating composition in an amount of about 0.1 wt % to about 10 wt %, for example from about 2 wt % to about 7 wt %, and as a further example from about 3 wt % to about 5 wt % of the lubricating composition.

[0036] The friction modifier for use in the disclosed lubricating composition can be selected from among many suitable compounds and materials useful for imparting this function in lubricant compositions. The friction modifier can be used as a single type of compound or a mixture of different types of compounds. Non-limiting examples of the friction modifier include a nitrogen-containing compound, an ash-containing compound, and a non-nitrogen-containing compound. In an aspect, the disclosed lubricating compositions can comprise a non-nitrogen-containing compound and a molybdenum-containing compound.

[0037] The nitrogen-containing compound can be any compound that comprises a basic nitrogen. In an aspect, the nitrogen-containing compound can be a long chain alkylene amine. The "long chain alkylene" moieties in the long chain alkylene amine friction modifying compounds preferably have in the range of about 10 to about 30 carbon atoms. More preferably they have in the range of about 14 to about 20 carbon atoms. Long chain alkylene amine friction modifying compounds include, for example, N-aliphatic hydrocarbyl-substituted trimethylenediamines in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms. A non-limiting example of such friction modifier compounds is N-oleyl-trimethylene diamine. Other suitable compounds include N-tallow-trimethylene diamine and N-coco-trimethylene diamine.

[0038] One group of friction modifiers includes the N-aliphatic hydrocarbyl-substituted diethanol amines in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms.

[0039] 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:

[0040] (1) 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 an alicyclic radical);

[0041] (2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxy);

[0042] (3) 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 sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, for example no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

[0043] As discussed above, the friction modifier can comprise a mixture of different compounds, such as a combination of at least one N-aliphatic hydrocarbyl-substituted diethanol amine and at least one N-aliphatic hydrocarbyl-substituted trimethylene diamine in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms. Further details concerning this friction modifier combination are set forth in U.S. Pat. Nos. 5,372,735 and 5,441,656, the disclosures of which are hereby incorporated by reference.

[0044] The friction modifier can be an ash-containing compound. In an aspect, the ash-containing compound can be a molybdenum-containing compound. The molybdenum-containing compound for use in the lubricating compositions disclosed herein can be sulfur- and/or phosphorus-free. A sulfur- and phosphorus-free molybdenum-containing compound can be prepared by reacting a sulfur and phosphorus-free molybdenum source with an organic compound containing amino and/or alcohol groups. Examples of sulfur- and phosphorus-free molybdenum sources include molybdenum trioxide, ammonium molybdate, sodium molybdate and potassium molybdate. The amino groups can be monoamines, diamines, or polyamines. The alcohol groups can be mono-substituted alcohols, diols or bis-alcohols, or polyalcohols. As an example, the reaction of diamines with fatty oils produces a product containing both amino and alcohol groups that can react with the sulfur- and phosphorus-free molybdenum source.

[0045] Examples of sulfur- and phosphorus-free molybdenum-containing compounds appearing in patents and patent applications which are fully incorporated herein by reference include the following: Compounds prepared by reacting certain basic nitrogen compounds with a molybdenum source as defined in U.S. Pat. Nos. 4,259,195 and 4,261,843. Compounds prepared by reacting a hydrocarbyl substituted hydroxy alkylated amine with a molybdenum source as defined in U.S. Pat. No. 4,164,473. Compounds prepared by reacting a phenol aldehyde condensation product, a mono-alkylated alkylene diamine, and a molybdenum source as defined in U.S. Pat. No. 4,266,945. Compounds prepared by reacting a fatty oil, diethanolamine, and a molybdenum source as defined in U.S. Pat. No. 4,889,647. Compounds prepared by reacting a fatty oil or acid with 2-(2-aminoethyl)aminoethanol, and a molybdenum source as defined in U.S. Pat. No. 5,137,647. Compounds prepared by reacting a secondary amine with a molybdenum source as defined in U.S. Pat. No. 4,692,256. Compounds prepared by reacting a diol, diamino, or amino-alcohol compound with a molybdenum source as defined in U.S. Pat. No. 5,412,130. Compounds prepared by reacting a fatty oil, mono-alkylated alkylene diamine, and a molybdenum source as defined in European Patent Application EP 1 136 496 A1. Compounds prepared by reacting a fatty acid, mono-alkylated alkylene diamine, glycerides, and a molybdenum source as defined in European Patent Application EP 1 136 497 A1. Compounds prepared by reacting a fatty oil, diethanolamine, and a molybdenum source as defined in U.S. Pat. No. 4,889,647.

[0046] In an aspect, a sulfur-containing, molybdenum-containing compound can also be used in the lubricating compositions disclosed herein. The sulfur-containing, molybdenum-containing compound can be prepared by a variety of methods. One method involves reacting a sulfur- and/or phosphorus-free molybdenum source with an amino group and one or more sulfur sources. Sulfur sources can include for example, but are not limited to, carbon disulfide, hydrogen sulfide, sodium sulfide and elemental sulfur. Alternatively, the sulfur-containing, molybdenum-containing compound can be prepared by reacting a sulfur-containing molybdenum source with an amino group or thiuram group and optionally a second sulfur source. As an example, the reaction of molybdenum trioxide with a secondary amine and carbon disulfide produces molybdenum dithiocarbanates. Alternatively, the reaction of $(NH_4)_2Mo_3S_{13}*n(H_2O)$ where n ranges from about 0 to 2, with a tetralkylthiuram disulfide, produces a trinuclear sulfur-containing molybdenum dithiocarbamate.

[0047] Non-limiting examples of sulfur-containing, molybdenum-containing compounds appearing in patents and patent applications include the following: Compounds prepared by reacting molybdenum trioxide with a secondary amine and carbon disulfide as defined in U.S. Pat. Nos. 3,509,051 and 3,356,702. Compounds prepared by reacting a sulfur-free molybdenum source with a secondary amine, carbon disulfide, and an additional sulfur source as defined in U.S. Pat. No. 4,098,705. Compounds prepared by reacting a molybdenum halide with a secondary amine and carbon disulfide as defined in U.S. Pat. No. 4,178,258. Compounds prepared by reacting a molybdenum source with a basic nitrogen compound and a sulfur source as defined in U.S. Pat. Nos. 4,263,152, 4,265,773, 4,272,387, 4,285,822, 4,369,119, 4,395,343. Compounds prepared by reacting ammonium tetrathiomolybdate with a basic nitrogen compound as defined in U.S. Pat. No. 4,283,295. Compounds prepared by reacting an olefin, sulfur, an amine and a molybdenum source as defined in U.S. Pat. No. 4,362,633. Compounds prepared by reacting ammonium tetrathiomolybdate with a basic nitrogen compound and an organic sulfur source as defined in U.S. Pat. No. 4,402,840. Compounds prepared by reacting a phenolic compound, an amine and a molybdenum source with a sulfur source as defined in U.S. Pat. No. 4,466,901. Compounds prepared by reacting a triglyceride, a basic nitrogen compound, a molybdenum source, and a sulfur source as defined in U.S. Pat. No. 4,765,918. Compounds prepared by reacting alkali metal alkylthioxanthate salts with molybdenum halides as defined in U.S. Pat. No. 4,966,719. Compounds prepared by reacting a tetralkylthiuram disulfide with molybdenum hexacarbonyl as defined in U.S. Pat. No. 4,978,464. Compounds prepared by reacting an alkyl dixanthogen with molybdenum hexacarbonyl as defined in U.S. Pat. No. 4,990,271. Compounds prepared by reacting alkali metal alkylxanthate salts with dimolybdenum tetra-acetate as defined in U.S. Pat. No. 4,995,996. Compounds prepared by reacting $(NH_4)_2Mo_3S_{13}\,{}^{*}{}_2H_2O$ with an alkali metal dialkyldithiocarbamate or tetralkyl thiuram disulfide as define in U.S. Pat. No. 6,232,276. Compounds prepared by reacting an ester or acid with a diamine, a molybdenum source and carbon disulfide as defined in U.S. Pat. No. 6,103,674.

Compounds prepared by reacting an alkali metal dialkyldithiocarbamate with 3-chloropropionic acid, followed by molybdenum trioxide, as defined in U.S. Pat. No. 6,117,826.

[0048] Non-limiting examples of molybdenum-containing compounds include molybdenum carboxylates, molybdenum amides, molybdenum thiophosphates, molybdenum thiocarbamates, molybdenum dithiocarbamates, and so forth.

[0049] Additional examples of ash-containing compounds include, but are not limited to, titanium-containing compounds and tungsten-containing compounds.

[0050] Another suitable group of friction modifiers include non-nitrogen-containing compounds, such as polyolesters, for example, glycerol monooleate (GMO), glycerol monolaurate (GML), and the like.

[0051] The friction modifying compound can be present in the lubricating composition in any desired or effective amount. In an aspect, the lubricating composition can comprise from about 0.05% to about 3% by weight, for example from about 0.2% to about 1.5%, and as a further example from about 0.3% to about 1% by weight relative to the total weight of the lubricating composition. However, one of ordinary skill in the art would understand that any amount can be used.

[0052] The lubricating composition disclosed herein can comprise a base oil. Base oils suitable for use in formulating the disclosed compositions can be selected from any of the synthetic or mineral oils or mixtures thereof. Mineral oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as other mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also suitable. Further, oils derived from a gas-to-liquid process are also suitable.

[0053] The base oil can be present in a major amount, wherein "major amount" is understood to mean greater than or equal to 50%, for example from about 80 to about 98 percent by weight of the lubricant composition.

[0054] The base oil typically has a viscosity of, for example, from about 2 to about 15 cSt and, as a further example, from about 2 to about 10 cSt at 100°C.

[0055] Non-limiting examples of synthetic oils include hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, etc.); polyalphaolefins such as poly(1-hexenes), poly-(1-octenes), poly(1-decenes), etc. and mixtures thereof; alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, di-nonylbenzenes, di-(2-ethylhexyl)benzenes, etc.); polyphenyls (e.g., biphenyls, terphenyl, alkylated polyphenyls, etc.); alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof and the like.

[0056] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic oils that can be used. Such oils are exemplified by the oils prepared through polymerization of ethylene oxide or propylene oxide, the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of about 1000, diphenyl ether of polyethylene glycol having a molecular weight of about 500-1000, diethyl ether of polypropylene glycol having a molecular weight of about 1000-1500, etc.) or mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C_{3-8} fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

[0057] Another class of synthetic oils that can be used includes the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol, etc.) Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid and the like.

[0058] Esters useful as synthetic oils also include those made from C_{5-12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol, tripentaerythritol, etc.

[0059] Hence, the base oil used which can be used to make the compositions as described herein can be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. Such base oil groups are as follows:

[0060] Group I contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120; Group II contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than

120; Group III contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120; Group IV are polyalphaolefins (PAO); and Group V include all other basestocks not included in Group I, II, III or IV.

[0061] The test methods used in defining the above groups are ASTM D2007 for saturates; ASTM D2270 for viscosity index; and one of ASTM D2622, 4294, 4927 and 3120 for sulfur.

[0062] Group IV basestocks, i.e. polyalphaolefins (PAO) include hydrogenated oligomers of an alpha-olefin, the most important methods of oligomerisation being free radical processes, Ziegler catalysis, and cationic, Friedel-Crafts catalysis.

[0063] The polyalphaolefins typically have viscosities in the range of 2 to 100 cSt at 100°C., for example 4 to 8 cSt at 100°C. They can, for example, be oligomers of branched or straight chain alpha-olefins having from about 2 to about 30 carbon atoms, non-limiting examples include polypropenes, polyisobutenes, poly-1-butenes, poly-1-hexenes, poly-1-octenes and poly-1-decene. Included are homopolymers, interpolymers and mixtures.

[0064] Regarding the balance of the basestock referred to above, a "Group I basestock" also includes a Group I basestock with which basestock(s) from one or more other groups can be admixed, provided that the resulting admixture has characteristics falling within those specified above for Group I basestocks.

[0065] Exemplary basestocks include Group I basestocks and mixtures of Group II basestocks with Group I bright stock.

[0066] Basestocks suitable for use herein can be made using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerisation, esterification, and re-refining.

[0067] The base oil can be an oil derived from Fischer-Tropsch synthesized hydrocarbons. Fischer-Tropsch synthesized hydrocarbons can be made from synthesis gas containing H_2 and CO using a Fischer-Tropsch catalyst. Such hydrocarbons typically require further processing in order to be useful as the base oil. For example, the hydrocarbons can be hydroisomerized using processes disclosed in U.S. Pat. No. 6,103,099 or 6,180,575; hydrocracked and hydroisomerized using processes disclosed in U.S. Pat. No. 4,943,672 or 6,096,940; dewaxed using processes disclosed in U.S. Pat. No. 5,882,505; or hydroisomerized and dewaxed using processes disclosed in U.S. Pat. No. 6,013,171; 6,080,301; or 6,165,949.

[0068] Unrefined, refined and rerefined oils, either mineral or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used in the base oils. Unrefined oils are those obtained directly from a mineral or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from primary distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques are known to those skilled in the art such as solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, etc. Rerefined oils are obtained by processes similar to those used to obtain refined oils applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques directed to removal of spent additives, contaminants, and oil breakdown products.

[0069] In an aspect, the lubricating composition can comprise less than about 325 ppm of boron. In a further aspect, the lubricating composition can comprise less than about 300 ppm of boron, and for example less than 280 ppm of boron.

[0070] The disclosed lubricating composition can reduce boundary friction on a surface of a machine as compared to a surface that is not lubricated with the disclosed lubricating composition. In an aspect, the lubricating composition can be applied/provided to any surface of any machine, such as for example an engine, a gear, etc.

[0071] Optionally, other components can be present in the lubricant composition. Non-limiting examples of other components include antiwear agents, dispersants, diluents, defoamers, demulsifiers, anti-foam agents, corrosion inhibitors, extreme pressure agents, seal well agents, antioxidants, pour point depressants, rust inhibitors and friction modifiers.

EXAMPLES

[0072] Example 1

[0073] Four dispersants (A-D) and two friction modifiers were blended/mixed/combined with base oil in various combinations to form lubricant compositions. The boundary friction coefficient of the resultant lubricant composition was determined using a high frequency reciprocating rig (HFRR) as described in

SAE paper 961142 (Jan. 1996), the disclosure of which is hereby incorporated by reference. The results are shown in Table 1.

Table 1

Example	B in oil (ppm)	Disp. A (wt.% active)	Disp. B (wt.% active)	non-nitrogen-containing compound (wt.%)	molybdenum-containing compound (wt.%)	Boundary Friction Coeff. At 130°C	% Reduction Friction Coeff. v. Compare 1
Compare 1	347	3.1	0.0	0.0	0.0	0.139	---
Invention 1	0	0.0	3.1	0.0	0.0	0.121	13%
Compare 2	347	3.1	0.0	0.5	0.0	0.102	27%
Invention 2	0	0.0	3.1	0.5	0.0	0.075	46%
Invention 3	174	1.55	1.55	0.5	0.0	0.090	35%
Invention 4	87	0.77	2.33	0.5	0.0	0.078	44%
Compare 3	347	3.1	0.0	0.0	0.5	0.103	26%
Invention 5	0	0.0	3.1	0.0	0.5	0.088	36%
Compare 4	347	3.1	0.0	0.0	0.8	0.097	30%
Invention 6	0	0.0	3.1	0.0	0.8	0.054	61%
		Disp. C	**Disp. D**				
Compare 5	295	2.5	0.0	0.3	0.05	0.109	22%
Invention 7	0	0.0	2.5	0.3	0.05	0.088	37%
Invention 8	74	0.63	1.88	0.3	0.05	0.083	40%

Dispersant A - High vinylidene PIB based dispersant with TEPA as the amine and is boronated. Typical Analytical %N 1.1; TBN 16.6 mgKOH/g; %B 1.12

Dispersant B - Conventional PIB based dispersant with with TEPA as the amine. Typical Analytical %N 1.2; TBN 16.6 mgKOH/g

Dispersant C - High vinylidene PIB based dispersant with E-100 as the amine and is boronated. Typical Analytical %N 1.52; TBN 32.7 mgKOH/g, %B 1.18

Dispersant D - High vinylidene PIB based dispersant with E-100 as the amine. Typical Analytical %N 1.95; TBN 41.4 mgKOH/g

[0074] The Comparative Example 1 and the Invention 1 results illustrated that in the absence of a friction modifier the use of a boron-containing dispersant (Dispersant A) produced a higher boundary friction coefficient as compared to non-boron containing dispersant (Dispersant B). In particular, Comparative Example 1 had 347 ppm of boron in the lubricant composition.

[0075] The Comparative Example 2 illustrated that a non-nitrogen-containing compound reduced boundary friction by 27% as compared to Comparative Example 1, which did not contain a friction modifier. However, the combination of a non-nitrogen-containing compound and a non-boron-containing dispersant (Invention 2) reduced boundary friction by 46% as compared to Comparative Example 1. Moreover, mixtures of a boron-containing and a non-boron-containing compound with a non-nitrogen-containing compound (Inventions 3 and 4) produced lower boundary friction coefficients as compared to Comparative Example 2.

[0076] Comparative Examples 3 and 4 illustrated that a molybdenum-containing compound and a boron-containing dispersant reduced boundary friction by 26% and 30%, respectively, as compared to the boron-containing dispersant alone (Comparative Example 1). However, the combination of a molybdenum-containing compound and a non-boron-containing dispersant (Inventions 5 and 6) reduced boundary friction by 36% and 61%, respectively.

[0077] Comparative Example 5 illustrated that a combination of a boron-containing dispersant, a non-nitrogen-containing compound, and a molybdenum-containing compound reduced boundary friction by 22%, as compared to Comparative Example 1. However, Invention 7 illustrated that a combination of a non-boron-containing dispersant, a non-nitrogen-containing compound, and a molybdenum-containing compound reduced boundary friction by 37%, as compared to Comparative Example 1.

[0078] At numerous places throughout this specification, reference has been made to a number of U.S. patents, published foreign patent applications and published technical papers. All such cited documents are expressly incorporated in full into this disclosure as if fully set forth herein.

[0079] For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0080] It is noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the," include plural referents unless expressly and unequivocally limited to one referent. Thus, for example, reference to "an antioxidant " includes two or more different antioxidants. As used herein, the term "include" and its grammatical variants are intended to be non-limiting, such that recitation of items in a list is not to the exclusion of other like items that can be substituted or added to the listed items.

[0081] While particular embodiments have been described, alternatives, modifications, variations, improvements, and substantial equivalents that are or can be presently unforeseen can arise to applicants or others skilled in the art. Accordingly, the appended claims as filed and as they can be amended are intended to embrace all such alternatives, modifications variations, improvements, and substantial equivalents.

CLAIMS

1. A lubricating composition comprising a base oil, a friction modifier, and a dispersant, wherein the lubricating composition comprises less than 325 ppm of boron.

2. The composition of claim 1, wherein the dispersant comprises a basic nitrogen.

3. The composition of claim 1 or 2, wherein the dispersant is a non-boron-containing dispersant.

4. The composition of claim 1, 2 or 3, wherein the dispersant is a polyisobutylene-based dispersant.

5. The composition of any one of claims 1 to 4, wherein the friction modifier is at least one of a non-nitrogen-containing compound, a nitrogen-containing compound, and an ash-containing compound.

6. The composition of claim 5, wherein the nitrogen-containing compound is a long chain alkylene amine.

7. The composition of claim 6, wherein the long chain alkylene amine is chosen from N-oleyl-trimethylene diamine, N-tallow-trimethylene diamine, coco-trimethylene diamine, and mixtures thereof.

8. The composition of claim 5, wherein the nitrogen-containing compound is diethanolamine.

9. The composition of any one of claims 5 to 8, wherein the ash-containing compound is chosen from molybdenum-containing compounds, titanium-containing

compounds, and tungsten-containing compounds.

10. The composition of claim 9, wherein the molybdenum-containing compound comprises sulfur.

11. The composition of claim 9, wherein the molybdenum-containing compound is chosen from molybdenum carboxylates, molybdenum amides, molybdenum thiophosphates, molybdenum thiocarbamates, and mixtures thereof.

12. The composition of any one of claims 5 to 11, wherein the non-nitrogen-containing compounds is polyolester.

13. The composition of claim 12, wherein the polyolester is chosen from glycerol monooleate and glycerol monolaurate.

14. A method of formulating a lubricating composition having improved fuel efficiency, which method comprises combining a base oil, a dispersant, and a fraction modifier, wherein the composition comprises less than 325 ppm of boron.

15. A method of reducing boundary friction on a surface comprising providing to the surface a lubricating composition as defined in any one of claims 1 to 13.

16. A method of lubricating an engine, which method comprises the step of providing to the engine a lubricating composition as defined in any one of claims 1 to 13.

17. An automotive engine lubricated with a lubricating composition as defined in any one of claims 1 to 13.

18. Use of a composition as defined in any one of claims 1 to 13 as a lubricant.

19. A lubricating composition according to claim 1 and substantially as hereinbefore described.

20. A method according to claim 14 or 15 and substantially as hereinbefore described.

21. An automotive engine according to claim 17 and substantially as hereinbefore described.

22. Use according to claim 18 and substantially as hereinbefore described.

30

Application No: GB0713197.2 **Examiner:** Mr Martin Price
Claims searched: 1-22 **Date of search:** 2 November 2007

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,P	1-22	EP 1785476 A1 Afton Chemical - see e.g. claims 16 and 17 and paragraphs 0076, 0082, 0083
X,P	1-22	EP 1724330 A1 Infineum - see e.g. claims 1-7
X	1-22	EP 1518921 A1 Afton Chemical - see e.g. claims 1, 18 and 22
X	1-22	EP 1518919 A1 Afton Chemical - see e.g. the front page abstract and the claims
X	1-22	WO 03/064568 A3 Exxonmobil - see e.g. Table 3 on page 10
X,P	1-22	US 2006/0264340 A1 Ethyl Corp - see e.g. claims 1 and 7 and paragraph 0030
X	1-22	US 2005/0137096 A1 Exxonmobil - see e.g. claims 1, 3, 4 and 6
X	1-22	US 2005/0101494 A1 Ethyl Corp - see e.g. examples 5-8 and 10
X	1-22	US 2005/0043191 A1 Exxonmobil - see e.g. claim 1 and Tables 1 and 3 (Oil 1)
X	1-22	US 5891786 A Ethyl Corp - see e.g. claim 1
X	1-22	US 5282991 A Exxon - see e.g. claim 1

X	1-22	CA 2487767 A1 Infineum - see e.g. claim 12

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C10M; C10N

The following online and other databases have been used in the preparation of this search report

ONLINE - EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
C10M	0141/00	01/01/2006
C10M	0141/06	01/01/2006
C10N	0020/02	01/01/2006
C10N	0030/02	01/01/2006
C10N	0040/25	01/01/2006