LUBRICATING COMPOSITION CONTAINING AN ESTER

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ABSTRACT
The invention relates to a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition containing (a) an oil of lubricating viscosity, and (b) a C4-30-diester of a dicarboxylic acid. The invention further provides for the use of the C4-30-diester of a dicarboxylic acid as a friction modifier, typically in a limited slip differential.
LUBRICATING COMPOSITION CONTAINING AN ESTER

FIELD OF INVENTION

[0001] The invention relates to a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition containing (a) an oil of lubricating viscosity, and (b) a C<sub>4-30</sub>-diester of a dicarboxylic acid. The invention further provides for the use of the C<sub>4-30</sub>-diester of a dicarboxylic acid as a friction modifier, typically in a limited slip differential.

BACKGROUND OF THE INVENTION

[0002] A limited slip differential in a vehicle typically employs a wet multi-plate clutch, i.e., clutch plates are immersed in a lubricant. The limited slip differential typically has bevel gear or spool gear planetary systems which distribute the drive torque evenly to the two driving wheels irrespective of their rotational speed. This makes it possible for the driven wheels to roll during cornering without slip between the wheel and road surface in spite of their different rotational speed. In order for the slip to be controlled lubricants containing compounds capable of improving friction performance, dispersants and sulfur- and/or phosphorus-containing extreme pressure agents may be used. Examples of lubricants of this type are disclosed in U.S. Pat. Nos. 4,308,154; 5,547,586; 4,180,466; 3,825,495; and European Patent Application 0 399 764 A1.

[0003] EP 0 767 236 A1 discloses a gear lubricant composition having a kinematic viscosity at 100°C in the range of 4 to 32 mm²/s. The composition contains more than 20% by volume a hydrogenated poly-α-olefin, and less than 80% by volume of mineral oil or synthetic ester oil or a combination thereof. The examples contain 10% by volume bis(tridecyl)-adipate. The gear is described as especially a transmission for use in large vehicles equipped with manual transmissions of the synchronizer type.

[0004] International Publication WO 98/04658 A1 discloses base stocks for synthetic gear oils for use in automatic heavy and medium duty axle gear lubricants and transmission fluid application. The lubricant disclosed therein contains 1% to 20% by weight of an ester. The ester includes diesters of C<sub>9-13</sub>-adipates, in particular di-isododecyl adipate.

[0005] U.S. Pat. No. 4,370,247 discloses a gear or axle lubricant containing 25 to 60 mass % of at least one di-C<sub>9-12</sub>-alkyl ester of a dicarboxylic acid. The whole lubricant disclosed therein is reported to decrease power loss due to friction, therefore conserving fuel consumption.

[0006] Canadian Publication CA 2 637 401 discloses the use as a lubricant a variety of diesters derived from a dicarboxylic acid having 2 to 36 carbon atoms and a branched alcohol having 4 to 40 carbon atoms. The lubricants can contain 0.1 to 100% by weight, or 5 to 99% by weight of the diesters.

SUMMARY OF THE INVENTION

[0007] The inventors of this invention have discovered that a lubricating composition and method as disclosed herein is capable of providing an acceptable level of at least one of (i) lubricant thermal stability, (ii) lubricant oxidative stability, (iii) high static coefficient of friction, (iv) fuel economy, (v) deposit control, (vi) seal compatibility, (vii) cleanliness and (viii) low tendency towards noise, vibration and harshness (NVH) often manifested as chatter (i.e. an abnormal noise typically referred to as a low-frequency “growl” and “groan”, particularly during higher-speed cornering manoeuvres). The inventors have also discovered that unexpectedly the lubricant composition and method disclosed herein may also be suitable for limited slip systems having one or more distinct plate materials. For example the plate materials may be steel, paper, ceramic, carbon fibers and systems employing a mixture of plate types such as steel on ceramic, carbon fibers in paper, or steel on paper. In one embodiment the plate material may be paper.

[0008] In one embodiment, the invention provides a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising (a) an oil of lubricating viscosity, and (b) a C<sub>4-30</sub>-diester of a dicarboxylic acid, or mixtures thereof, wherein the dicarboxylic acid has formula HOOCR—R<sub>1</sub>—C(O)OH, and R<sub>1</sub> may be an aliphatic group having 2 to 38, or 2 to 28 carbon atoms.

[0009] The number of carbon atoms present on an ester group of the C<sub>4-30</sub>-diester may contain 4 to 30 carbon atoms. As used herein, an “ester group” means the alcohol-derived portion of the ester, that is, R<sub>1</sub> in an ester RCOOR<sub>1</sub>, in the case of a carbonyl acid RCOOH, where R<sub>1</sub> may be a hydrocarbyl group of the indicated number of carbon atoms.

[0010] In one embodiment the dicarboxylic acid may have formula HOOCR—R<sub>1</sub>—C(O)OH, and R<sub>1</sub> may be an aliphatic group having 5 to 8 carbon atoms (typically R<sub>1</sub> may be an alkylene group). The dicarboxylic acid may be saturated or unsaturated.

[0011] In different embodiments the alcohol-derived portion of the ester groups of the C<sub>4-30</sub>-diester of the dicarboxylic acid disclosed herein may be C<sub>8-20</sub>-alkyl or C<sub>10-15</sub>-alkyl or C<sub>13</sub>-alkyl. The ester groups of the diester may be linear or branched, typically branched.

[0012] In one embodiment, the invention provides a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising (a) an oil of lubricating viscosity, and (b) a C<sub>4-30</sub>-diester of adipic acid.

[0013] In one embodiment, the invention provides a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising (a) an oil of lubricating viscosity, (b) a C<sub>4-30</sub>-diester of a dicarboxylic acid, wherein the dicarboxylic acid has formula HOOCR—R<sub>1</sub>—C(O)OH, and R<sub>1</sub> may be an aliphatic group having 2 to 38, or 2 to 28 carbon atoms (typically a C<sub>4-30</sub>-diester of adipic acid), and (c) a phosphorus containing compound.

[0014] In one embodiment, the invention provides a method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising (a) an oil of lubricating viscosity, and a friction modifier package consisting of, or, alternatively, comprising, a C<sub>4-30</sub>-diester of a dicarboxylic acid, wherein the dicarboxylic acid has formula HOOCR—R<sub>1</sub>—C(O)OH, and R<sub>1</sub> may be an aliphatic group having 2 to 38, or 2 to 28 carbon atoms (typically a C<sub>4-30</sub>-diester of adipic acid), and a phosphorus containing compound.

[0015] In one embodiment the lubricating composition comprises (a) an oil of lubricating viscosity, and a friction modifier package consisting of, or, alternatively, comprising, a C<sub>4-30</sub>-diester of adipic acid, and 0.05 wt % to 4.5 wt % of a phosphorus containing compound.
In one embodiment, the invention provides a method of lubricating a limited slip differential comprising (a) an oil of lubricating viscosity, wherein the oil of lubricating viscosity is an API Group III or API Group IV base oil, or mixtures thereof, (b) a C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid, wherein the dicarboxylic acid has formula HOOC-C<sub>R</sub>-C(O)OH, and R'<sub>4</sub> may be an aliphatic group having 2 to 38 carbon atoms (typically a C<sub>4</sub>-C<sub>30</sub>-diester of adipic acid), and (c) a phosphorus containing compound.

In one embodiment, the lubricating compositions disclosed herein may contain 0.01 wt % to less than 1 wt %, or 0.02 wt % to 0.9 wt %, or 0.05 wt % to 0.5 wt %, or 0.1 wt % to 0.3 wt % of the C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid, wherein the dicarboxylic acid has formula HOOC-C<sub>R</sub>-C(O)OH, and R' may be an aliphatic group having 2 to 38 carbon atoms (typically a C<sub>4</sub>-C<sub>30</sub>-diester of adipic acid).

The limited slip differential in one embodiment may have plate contact surfaces of steel on paper (or cellulose).

In one embodiment, the invention provides for the use of a lubricating composition comprising (a) a C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid wherein the dicarboxylic acid has formula HOOC-C<sub>R</sub>-C(O)OH, and R' may be an aliphatic group having 2 to 38 carbon atoms (typically a C<sub>4</sub>-C<sub>30</sub>-diester of adipic acid), and (b) an oil of lubricating viscosity in a limited slip differential to provide an acceptable level of at least one of (i) lubricant thermal stability, (ii) lubricant oxidative stability, (iii) friction, (iv) fuel economy, (v) deposit control, (vi) seal compatibility, and (vii) churning (abnormal noise). In one embodiment the use provides an acceptable level of friction.

In one embodiment the invention provides for the use of a lubricating composition comprising (a) an oil of lubricating viscosity, (b) a C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid wherein the dicarboxylic acid has formula HOOC-C<sub>R</sub>-C(O)OH, and R' may be an aliphatic group having 2 to 38 carbon atoms (typically a C<sub>4</sub>-C<sub>30</sub>-diester of adipic acid), and (c) a phosphorus containing compound in a limited slip differential to provide friction modification.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides a lubricating composition and method as disclosed herein above.

**C<sub>4</sub>-C<sub>30</sub>-Diester of a Dicarboxylic Acid**

The C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid disclosed herein may include C<sub>4</sub>-C<sub>30</sub>-esters of glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, brassyllic acid, dodecanedioic acid, thapsic acid, or mixtures thereof. In one embodiment the C<sub>4</sub>-C<sub>30</sub>-diester of a dicarboxylic acid disclosed herein may be a C<sub>4</sub>-C<sub>30</sub>-diester of adipic acid.

**Ester groups of the C<sub>4</sub>-C<sub>30</sub>-diester of the dicarboxylic acid disclosed herein may be C<sub>8</sub>-C<sub>20</sub> or C<sub>10</sub>-C<sub>15</sub> or C<sub>13</sub>. Examples of ester groups include butyl, 2-methylpentyl, 2-propylheptyl, 2-butyloctyl, 2-ethylhexyl, octyl, neoctyl, neoheptyl, nonyl, isoctyl, isononyl, neononyl (may also be called 3,5,5-trimethyl-1-hexyl), decyl, neodecyl, undecyl, 5-methylundecyl, dodecyl, 2-methyldodecyl, tridecyl, 5-methyltridecy, tetradecyl, pentadecyl, hexadecyl, 2-methylhexadecyl, heptadecyl, 5-isopropylheptadecyl, 3-isopropylheptadecyl, octadecyl, nonadecyl, eicosyl, cetleylosyl, stearylosyl, docosyl, eicosyltetracontyl, or mixtures thereof.**
alkyl amines include monoamines such as tert-butylamine, tert-hexylamine, 1-methyl-1-aminocyclohexane, tert-octylamine, tert-decylamine, tert-dodecylamine, tert-tetradecylamine, tert-hexadecylamine, tert-octadecylamine, tert-tetraicosylamine, and tert-octacosylamine.

[0035] The amine may be represented by the formula: 
\[ R^2(R^3)_nN-R^4\equiv C(=O)-X-(R^5)_m, \]
wherein \( R^2 \) is a hydrocarbyl group of 12 to 20 carbon atoms, or \( R^2 \) is an aminoalkyl group of up to 3 carbon atoms substituted on the nitrogen atom thereof by a hydrocarbyl group of 12 to 22 carbon atoms; \( R^4 \) is hydrogen or a hydrocarbyl group; \( a \) is 1 or 2, and \( b \) is 2-a. That is, there may be 1 or 2 
\[ -R^4\equiv C(=O)X(R^5), \]
groups on the amine nitrogen. If there are multiple amine nitrogen atoms in the molecule and if there are multiple 
\[ -R^4\equiv C(=O)X(R^5), \]
groups, such groups may be attached to the same or to different nitrogens.

[0036] \( R^2 \) may be a linking group which is attached to the amine nitrogen. If there are multiple \( R^2 \) groups, they may be the same or different from each other. They may be an alkylene group of 1 to 4 carbon atoms such as methylene, ethylene, vinylene, propylene (in the 1,2 configuration, that is, methylvinylene, or in the 1,3 configuration, that is, trimethylene), or butylene (in the 1,2 configuration or any other configurations such as 1,4, that is, tetramethylene). They may also comprise a chain of 2 to 8 carbon atoms interrupted by one or two nitrogen or oxygen atoms within the chain. Examples of these include:

- \( \text{CH}_2-\text{CH}-\text{CH-NHCCH}_3- \) 
- \( \text{CH}_2-\text{CH}-\text{CH-NHCCH}_2\text{CH}_2\text{NHCCH}_3- \) 
- \( \text{CH}_2\text{CH}_2\text{OCH}-\text{CH}_3- \) 
- \( \text{CH}_2\text{CH}_2\text{OCH}-\text{CH}_3- \)

[0037] \( X \) may represent either oxygen or nitrogen. In the case of oxygen, the resulting group will be a carboxylic acid or an ester. In the case of nitrogen, the resulting group will be an amide. One or two \( R^5 \) groups will be attached to the \( X \) to satisfy its valence: one such group for oxygen and two such groups for nitrogen. That is, \( c \) will be 1 or 2, as the case may be. If a mixture of materials is present such that some of the \( X \) are nitrogen and some are oxygen, then \( c \) may have a fractional value between 1 and 2, but it will be either 1 or 2 for any given molecule. The \( R^2 \) group or groups may independently be hydrogen, or a hydrocarbyl group of 1 to 20 carbon atoms, such as 12 to 20 carbon atoms (as described above) or a nitrogen-containing group represented by the formula 
\[ -R^2\equiv NHR^4, \]
where \( R^4 \) is as defined above and \( R^2 \) is a hydrocarbyl group of 12 to 20 carbon atoms. The \( R^2 \) groups not identical to any of the \( R^4 \) linking groups as used above, as is implicit from the statement that each \( R^2 \) is independently one of the groups listed. Specific examples of 
\[ \text{C}(=\text{O})(R^2), \]
include:
- \( \text{COOH}, \) 
- \( \text{CONH}_2, \) 
- \( \text{COOCH}_2, \) 
- \( \text{CONHCH}_3, \) 
- \( \text{CON(CH}_2)_2, \) 
- \( \text{CONH}-\text{coco}, \) 
- \( \text{CONH}-\text{tallow}, \) and 
- \( \text{CONH-CH}_2\text{CH}_2\text{NH}-\text{tallow}, \) where “coco” and “tallow” are the hydrocarbyl residues of coconum and tallowamime, as described above.

[0038] Certain of the amines of the present invention (that is, containing the carbonyl functionality) may be obtained by reaction of an amine with an equivalent amount of an unsaturated ester such as methyl acrylate. A generalized reaction scheme would be as follows:

\[
\begin{align*}
\text{NH} & + \text{COO-CH}_3 \\
\text{R}^3 & \quad \text{CH}_2
\end{align*}
\]
and the resulting ester may be converted to an amide or other functionality by known methods. The starting amine, designated here as \( R^2\equiv R^4\equiv \text{NH} \) may have suitable \( R \) groups provided that at least one of them is selected so as to meet the requirements of the present invention, e.g., containing a hydrocarbyl group of 12 to 22 carbon atoms. In certain embodiments the precursor amine itself \( R^2\equiv R^4\equiv \text{NH} \) may be a polyamine in the “Duomeen” series, available from Akzo, having a general structure such as:

\[
\begin{align*}
\text{N} & \quad \text{R}_2^3 \\
\text{R}_2^3 & \quad \text{N} \quad \text{NH}_2
\end{align*}
\]
[0039] The amine salt of a phosphorus acid ester may be a reaction product of a \( C_{12-20} \) alkyl phosphoric acid with a tertiary \( C_{11-22} \) alkyl primary amine.
[0040] In one embodiment the amine salt of a phosphoric acid ester includes an amine which is a \( C_{11} \) to \( C_{14} \) tertiary alkyl primary amine or mixtures thereof. In one embodiment the amine salt of a phosphorus compound includes an amine which is a \( C_{18} \) to \( C_{22} \) tertiary alkyl primary amine or mixtures thereof.
[0041] In one embodiment the amine salt of a phosphorus acid ester includes the reaction product of octadecenyl phosphoric acid with Primene \( 81R^TM \).
[0042] Mixtures of amines may also be used in the invention. In one embodiment a useful mixture of amines is “Primene\textsuperscript{TM} 81R” and “Primene\textsuperscript{TM} JMT,” Primene\textsuperscript{TM} 81R and Primene\textsuperscript{TM} JMT (both produced and sold by Rohm & Haas) are mixtures of \( C_{11} \) to \( C_{14} \) tertiary alkyl primary amines and \( C_{18} \) to \( C_{22} \) tertiary alkyl primary amines respectively.
[0043] In one embodiment the amine salt of a phosphorus acid ester is the reaction product of a \( C_{14} \) to \( C_{18} \) alkyl phosphoric acid with Primene \( 81R^TM \) (produced and sold by Rohm & Haas) which is a mixture of \( C_{11} \) to \( C_{14} \) tertiary alkyl primary amines.
[0044] The amine salt of a phosphate hydrocarbon ester may be prepared as is described in U.S. Pat. No. 6,468,946, wherein column 10, lines 15 to 63 describes phosphoric acid esters formed by reaction of phosphorus compounds, followed by reaction with an amine to form an amine salt of a phosphate hydrocarbon ester. Column 10, line 64, to column 12, line 23, describes preparative examples of reactions between phosphorus pentoxide with an alcohol (having 4 to 13 carbon atoms), followed by a reaction with an amine (typically Primene\textsuperscript{TM} 81-R) to form an amine salt of a phosphate hydrocarbon ester. In one somewhat oversimplified

schematic representation using $P_2O_5$ for illustrative purposes, the reaction of a phosphating agent with alcohol(s) may be represented as follows:

$$3 \text{ROH} + P_2O_5 \rightarrow (\text{RO})_3P(=\text{O})\text{H} + \text{P}(\text{=O})(\text{OH})_2$$

where ROH represent an alcohol (such as monols or polyols or hydroxy-containing carboxylic compounds or mixtures thereof). As is described herein, the residual phosphoric acid functionality may be reacted at least in part with an amine.

Examples of the amine salt of a phosphorus acid ester include the reaction product(s) of isopropyl, methylamyl (1,3-dimethylbutyl or mixtures thereof), 2-ethylhexyl, heptyl, octyl, nonyl or decyl di(hydroxiphosphoric acids with ethylene diamine, morpholine, or Primene 81R™, and mixtures thereof.

Examples of the amine salt of a phosphorus acid ester include the reaction product(s) of tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl or eicosyl di(hydrophosphoric acids with ethylenediamine, morpholine, or Primene 81R™, and mixtures thereof. In one embodiment the amine salt of a phosphorus acid ester includes the reaction product of octadecenyl di(hydrophosphoric acid with Primene 81R™.

In one embodiment the amine salt of a phosphorus compound may be an amine salt of (i) a hydroxy-substituted diester of phosphoric acid, (ii) a phosphorylated hydroxy-substituted di- or tri-ester of phosphoric acid, or (iii) or mixtures thereof. A more detailed description of this type of compound is described in International Publication WO 2008/094759.

In one embodiment the amine salt of a phosphoric acid is a compound described in U.S. Pat. No. 3,197,405. In one embodiment the amine salt of a phosphorus compound other than those disclosed above, may be prepared by any one of the above methods.

In one embodiment the amine salt of a phosphorus compound other than those disclosed above, is a reaction product prepared from a di(hydrophosphoric acid) reacting with an epoxide or a glycol. This reaction product is further reacted with a phosphorus acid, anhydride, or lower ester (where “lower” signifies 1 to 8, or 1 to 6, or 1 to 4, or 1 to 2 carbon atoms in the alcohol-derived portion of the ester). The epoxide includes an aliphatic epoxide or a styrene oxide. Examples of useful epoxides include ethylene oxide, propylene oxide, butene oxide, octene oxide, dodecene oxide, syrene oxide and the like. In one embodiment the epoxide is propylene oxide. The glycols include aliphatic glycols having 1 to 12, or 2 to 6, or 2 to 3 carbon atoms. The di(hydrophosphoric acid), glycols, epoxides, inorganic phosphorus reagents and methods of reacting the same are described in U.S. Pat. Nos. 3,197,405 and 3,544,465. The resulting acids are then salted with amines.

An example of suitable di(hydrophosphoric acid) based product is prepared by adding phosphorus pentoxide (about 64 grams) at 58°C over a period of 45 minutes to 514 grams of hydroxypropyl O,O-di-(1,3-dimethylbutyl)phosphorodithioate (prepared by reacting di(1,3-dimethylbutyl) phosphorodithioic acid with 1.3 moles of propylene oxide at 25°C). The mixture is heated at 75°C for 2.5 hours, mixed with a diatomaceous earth and filtered at 70°C. The filtrate contains 11.8% by weight phosphorus, 15.2% by weight sulphur, and an acid number of 87 (bromophenol blue).

Oils of Lubricating Viscosity

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

Oils of lubricating viscosity may also be defined as specified in April 2008 version of “Appendix E—API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils”, section 1.3 Subheading 1.3. “Base Stock Categories”. In one embodiment the oil of lubricating viscosity may be an API Group II, Group III or Group IV base oil. In one embodiment the oil of lubricating viscosity may be an API Group III (typically including hydrocracked/ or hydrosisomerized base oil), or API Group IV base oil or mixtures thereof.

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

The lubricating composition may be in the form of a concentrate and/or a fully formulated lubricant. If the lubricating composition of the invention (comprising the additives disclosed herein) is in the form of a concentrate which may be combined with additional oil to form, in whole or in part, a finished lubricant), the ratio of the of these additives to the oil of lubricating viscosity and/or to diluent oil include the ranges of 1:99 to 99:1 by weight, or 10:90 to 80:20 by weight.

Other Performance Additives

The composition of the invention optionally further includes at least one other performance additive. The other performance additives include dispersants, metal deactivators, detergents, viscosity modifiers, extreme pressure agents (typically boron- and/or sulphur- and/or phosphorus-containing), antiwear agents, antioxidants (such as hindered phenols, aminic antioxidants or molybdenum compounds), corrosion inhibitors, foam inhibitors, demulsifiers, pour point depressants, seal swelling agents, friction modifiers and mixtures thereof.

The total combined amount of the other performance additives (excluding the viscosity modifiers) present on an oil free basis may include ranges of 0 wt % to 25 wt %, or 0.01 wt % to 20 wt %, or 0.1 wt % to 15 wt % or 0.5 wt % to 10 wt %, or 1 to 5 wt % of the composition. Although one or more of the other performance additives may be present, it is common for the other performance additives to be present in different amounts relative to each other.
In one embodiment the lubricating composition is free of molybdenum-containing additives.

Viscosity Modifiers

When present the viscosity modifier may be present in an amount of 0.5 wt % to 70 wt %, 1 wt % to 60 wt %, or 5 wt % to 50 wt %, or 10 wt % to 50 wt % of the lubricating composition.

Viscosity modifiers include (a) polymethacrylates, (b) esterified copolymers of (i) a vinyl aromatic monomer and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, (c) esterified interpolymer of (i) an alpha-olefin; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, or (d) hydrogenated copolymers of styrene-butadiene, (e) ethylene-propylene copolymers, (f) polyisobutlenes, (g) hydrogenated styrene-isoprene polymers, (h) hydrogenated isoprene polymers, or (i) mixtures thereof.

In one embodiment the viscosity modifier includes (a) a polymethacrylate, (b) an esterified copolymer of (i) a vinyl aromatic monomer, and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, (c) an esterified interpolymer of (i) an alpha-olefin; and (ii) an unsaturated carboxylic acid, anhydride, or derivatives thereof, or (d) mixtures thereof.

Extreme Pressure Agents

Extreme pressure agents include compounds containing boron and/or sulphur and/or phosphorus.

The extreme pressure agent may be present in the lubricating composition at 0 wt % to 20 wt %, or 0.05 wt % to 10 wt %, or 0.1 wt % to 8 wt % of the lubricating composition.

In one embodiment the extreme pressure agent is a sulphur-containing compound. In one embodiment the sulphur-containing compound may be a sulphurised olefin, a polysulphide, or mixtures thereof.

Examples of the sulphurised olefin include a sulphurised olefin derived from propylene, isobutylene, pentene, an organic sulphide and/or polysulphide including benzylidisulphide; bis-(chlorobenzyl)disulphide; dibutyl tetrasulphide; di-tertiary butyl polysulphide; and sulphurised methyl ester of oleic acid, a sulphurised alkylpheno, a sulphurised dipentene, a sulphurised terpene, a sulphurised Diels-Alder adduct, an alkyl sulphenyl N,N-diaryl dithiocarbamates; or mixtures thereof. In one embodiment the sulphurised olefin includes a sulphurised olefin derived from propylene, isobutylene, pentene or mixtures thereof.

In one embodiment the extreme pressure agent sulphur-containing compound includes a dimercaptothiadiazone or derivative, or mixtures thereof. Examples of the dimercaptothiadiazone include compounds such as 2,5-dimercapto-1,3,4-thiadiazole or a hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole, or oligomers thereof. The oligomers of hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically form by forming a sulphur-sulphur bond between 2,5-dimercapto-1,3,4-thiadiazole units to form derivatives or oligomers of two or more of said thiadiazone units. Suitable 2,5-dimercapto-1,3,4-thiadiazole derived compounds include for example 2,5-bis(tert-nonyldithio)-1,3,4-thiadiazole or 2-tert-nonylthio-5-mercaptop-1,3,4-thiadiazole.

The number of carbon atoms on the hydrocarbyl substituents of the hydrocarbyl-substituted 2,5-dimercapto-1,3,4-thiadiazole typically include 1 to 30, or 2 to 20, or 3 to 16.

In one embodiment the dimercaptothiadiazone may be a thiadiazone-functionalised dispersant. A detailed description of the thiadiazone-functionalised dispersant is described in paragraphs [0028] to [0052] of International Publication WO 2008/014315.

The thiadiazone-functionalised dispersant may be prepared by a method including heating, reacting or complexing a thiadiazone compound with a dispersant substrate. The thiadiazone compound may be covalently bonded, salted, complexed or otherwise solubilised with a dispersant, or mixtures thereof.

The relative amounts of the dispersant substrate and the thiadiazone used to prepare the thiadiazone-functionalised dispersant may vary. In one embodiment the thiadiazone compound is present at 0.1 to 10 parts by weight relative to 100 parts by weight of the dispersant substrate. In different embodiments the thiadiazone compound is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or 0.2 to less than 5: to 100 parts by weight of the dispersant substrate. The relative amounts of the thiadiazone compound to the dispersant substrate may also be expressed as 0.1-10:100, or (0.1-9):100, (such as 0.5-5):100, or (0.1 to less than 5):100, or (0.2 to less than 5):100.

In one embodiment the dispersant substrate is present at 0.1 to 10 parts by weight relative to 1 part by weight of the thiadiazone compound. In different embodiments the dispersant substrate is present at greater than 0.1 to 9, or greater than 0.1 to less than 5, or about 0.2 to less than 5: to 1 part by weight of the thiadiazone compound. The relative amounts of the dispersant substrate to the thiadiazone compound may also be expressed as (0.1-10):1, or (0.1-9):1, (such as 0.5-5):1, or (0.1 to less than 5):1, or (0.2 to less than 5):1.

The thiadiazone-functionalised dispersant may be derived from a substrate that includes a succinimide dispersant (for example, N-substituted long chain alkoxyl succinimides, typically a polyisobutylene succinimide), 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 polyehter dispersant, a polyetheramine dispersant, a viscosity modifier containing dispersant functionality (for example polymeric viscosity index modifiers (VIMs) containing dispersant functionality), or mixtures thereof. In one embodiment the dispersant substrate includes a succinimide dispersant, an ester-containing dispersant or a Mannich dispersant.

In one embodiment the extreme pressure agent includes a boron-containing compound. The boron-containing compound includes a boronate ester (which in some embodiments may also be referred to as a borated epoxide), a borated alcohol, a borated dispersant, a borated phospholipid or mixtures thereof. In one embodiment the boron-containing compound may be a borate ester or a borated alcohol.

The boronate ester may be prepared by the reaction of a boron compound and at least one compound selected from epoxy compounds, halohydrin compounds, epiphosphorin compounds, alcohols and mixtures thereof. The alcohols include dihydric alcohols, trihydric alcohols or higher alco-
hols, with the proviso for one embodiment that hydroxyl groups are on adjacent carbon atoms, i.e., vicinal.

[0075] Boron compounds suitable for preparing the borate ester include the various forms selected from the group consisting of boric acid (including metaboric acid, HBO₂, orthoboric acid, H₃BO₃, and tetraboric acid, H₄B₁₀O₁₄), boric oxide, boron trioxide and alkyl borates. The borate ester may also be prepared from boron halides.

[0076] In one embodiment suitable borate ester compounds include tripropyl borate, tributyl borate, tripropyl borate, triethyl borate, trioxyl borate, and tridecyl borate. In one embodiment the borate ester compounds include tributyl borate, tri-2-ethylhexyl borate or mixtures thereof.

[0077] In one embodiment, the boron-containing compound is a borated dispersant, typically derived from an N-substituted long chain alkyl succinimide. In one embodiment the borated dispersant includes a polysisobutylene succinimide. Borated dispersants are described in more detail in U.S. Pat. No. 3,087,936; and U.S. Pat. No. 3,254,025.

[0078] In one embodiment the borated dispersant may be used in combination with a sulphur-containing compound or a borate ester.

[0079] In one embodiment the extreme pressure agent is other than a borated dispersant.

[0080] The number average molecular weight of the hydrocarbon from which the long chain alkyl group was derived includes ranges of 350 to 5000, or 500 to 3000, or 550 to 1500. The long chain alkyl group may have a number average molecular weight of 550, or 750, or 950 to 1000.

[0081] The N-substituted long chain alkyl succinimides are borated using a variety of agents including boric acid (for example, metaboric acid, HBO₂, orthoboric acid, H₃BO₃, and tetraboric acid, H₄B₁₀O₁₄), boric oxide, boron trioxide, and alkyl borates. In one embodiment the borating agent is boric acid which may be used alone or in combination with other borating agents.

[0082] The borated dispersant may be prepared by blending the boron compound and the N-substituted long chain alkyl succinimides and heating them at a suitable temperature, such as, 80°C to 250°C, or 90°C to 230°C, or 100°C to 210°C, until the desired reaction has occurred. The molar ratio of the boron compounds to the N-substituted long chain alkyl succinimides may be 1:1. Alternatively, the ratio of moles B:moles N (that is, atoms of B:atoms of N) in the borated dispersant may be 0.25:1 to 10:1 or 0.33:1 to 4:1 or 0.2:1 to 1:5:1, or 0.25:1 to 1:3:1 or 0.8:1 to 1.2:1 or about 0.5:1. An inert liquid may be used in performing the reaction. The liquid may include toluene, xylene, chlorobenzene, dimethylformamide or mixtures thereof.

[0083] In one embodiment the lubricating composition further includes a borated phospholipid. The borated phospholipid may be derived from boronation of a phospholipid (for example boronation may be carried out with boric acid). Phospholipids and lecithins are described in detail in Encyclopedia of Chemical Technology, Kirk and Othmer, 3rd Edition, in “Fats and Fatty Oils”, Volume 9, pages 795-831 and in “Lecithins”, Volume 14, pages 250-269.

[0084] The phospholipid may be any lipid containing a phosphoric acid, such as lecithin or cephalin, or derivatives thereof. Examples of phospholipids include phosphatidylcholine, phosphatidylserine, phosphatidylinositol, phosphatidyethanolamine, phosphotidic acid and mixtures thereof. The phospholipids may be glycerophospholipids, glycerol derivatives of the above list of phospholipids. Typically, the glycerophospholipids have one or two acyl, alkyl or alkyl ester groups on a glycerol residue. The alkyl or alkyl ester groups may contain 8 to 30, or 8 to 25, or 12 to 24 carbon atoms. Examples of suitable alkyl or alkyl ester groups include octyl, decyl, hexadecyl, octadecyl, docosanyl, octenyl, dodecenyl, hexadecenyl and octadecenyl. In one embodiment the phospholipid is lecithin, or derivatives thereof.

[0085] Phospholipids may be prepared synthetically or derived from natural sources. Synthetic phospholipids may be prepared by methods known to those in the art. Naturally derived phospholipids are often extracted by procedures known to those in the art. Phospholipids may be derived from animal or vegetable sources. A useful phospholipid is derived from sunflower seeds. The phospholipid typically contains 35% to 60% phosphatidylcholine, 20% to 35% phosphatidylinositol, 1% to 25% phosphatidic acid, and 10% to 25% phosphatidylethanolamine, wherein the percentages are by weight based on the total phospholipids. The fatty acid content may be 20 wt% to 50 wt% by weight palmitic acid, 2 wt% to 10 wt% stearic acid, 15 wt% to 25 wt% oleic acid, and 40 wt% to 55 wt% linoleic acid.


[0087] Friction modifiers (other than those described above) may include fatty amines, esters such as borated glycerol esters, fatty phosphites, fatty acid amides, fatty epoxides, borated fatty epoxides, alkoxylated fatty amines, borated alkoxyalkylated fatty amines, metal salts of fatty acids, or fatty imidazolines, condensation products of carboxylic acids and polyalkylene-polyamines.

[0088] In one embodiment the lubricating composition may contain phosphorus- or sulphur-containing antiwear agents other than compounds described as an extreme pressure agent of the amine salt of a phosphoric acid ester described above. Examples of the antiwear agent may include a non-ionic phosphorus compound (typically compounds having phosphorus atoms with an oxidation state of +3 or +5), a metal dialkyldithiophosphate (typically zinc dialkyldithiophosphates), a metal mono- or di-alkylphosphate (typically zinc phosphates), or mixtures thereof.

[0089] The non-ionic phosphorus compound includes a phosphate ester, a phosphate ester, or mixtures thereof. A more detailed description of the non-ionic phosphorus compound include column 9, line 48 to column 11, line 8 of U.S. Pat. No. 6,103,673.

[0090] In one embodiment the lubricating composition of the invention further includes a dispersant. The dispersant may be a succinimide dispersant (for example N-substituted long chain alkyl succinimides), a Mannich dispersant, an ester-containing dispersant, a condensation product of a fatty hydrocarbyl mono- and/or dialkylaminocarbonyl acylating agent with an amine or ammonia, an alkyl amino phenol dispersant, a hydrocarbyl-amine dispersant, a polyether dispersant or a polyetheramide dispersant.

[0091] In one embodiment the succinimide dispersant includes a polyisobutylene-substituted succinimide, wherein
the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000, or 950 to 1600.

[0092] Succinimide dispersants and their methods of preparation are more fully described in U.S. Pat. Nos. 4,234, 435 and 3,172,892.

[0093] Suitable ester-containing dispersants are typically high molecular weight esters. These materials are described in more detail in U.S. Pat. No. 3,381,022.

[0094] In one embodiment the dispersant includes a borated dispersant. Typically the borated dispersant includes a succinimide dispersant including a polyisobutylene succinimide, wherein the polyisobutylene from which the dispersant is derived may have a number average molecular weight of 400 to 5000. Borated dispersants are described in more detail above within the extreme pressure agent description.

[0095] Dispersant viscosity modifiers (often referred to as DVMs) include functionalised polyolefins, for example, ethylene-propylene copolymers that have been functionalised with the reaction product of maleic anhydride and an amine, a polymethacrylate functionalised with an amine, or esterified styrene-maleic anhydride copolymers reacted with an amine may also be used in the composition of the invention.

[0096] Crosslinking inhibitors include 1-amino-2-propanol, octamethylene octanoate, condensation products of dodecanol succinic acid or anhydride and/or a fatty acid such as oleic acid with a polyamine.

[0097] Metal deactivators include derivatives of benzotriazoles (typically tolyltriazole), 1,2,4-triazoles, benzimidazoles, 2-alkylthiobenzimidazoles or 2-alkylthiobenzothiazoles. The metal deactivators may also be described as corrosion inhibitors.

[0098] Foam inhibitors include copolymers of ethyl acrylate and 2-ethylhexyl acrylate and optionally vinyl acetate.

[0099] Demulsifiers include trialkyl phosphates, and various polymers and copolymers of ethylene glycol, ethylene oxide, propylene oxide, or mixtures thereof.

[0100] Four point depressants including esters of maleic anhydride-styrene, polythiocellulose, polyacrylates or polycrylic acids.

[0101] Seal swell agents including Exxon Necton®-37™ (FN 1380) and Exxon Mineral Seal Oil™ (FN 3200).

INDUSTRIAL APPLICATION

[0102] The limited slip differential typically incorporates a self-contained lubricant supply isolated from the lubricant disposed in the differential housing or carrier. The self-contained lubricant of the limited slip differential is generally different from the lubricant supplied to a manual transmission or an automatic transmission fluid. In both the manual and automatic transmission systems not comprising a limited slip differential one lubricant is sufficient to lubricate all of the transmission constituents.

[0103] An axle gear may have any one of a number of different types of differential. A differential typically has three major functions. The first function is to transmit engine power to the wheels. The second function is as the final gear reduction in the vehicle, slowing the rotational speed from the transmission to the wheels. The third function is to transmit the power to the wheels while allowing them to rotate at different speeds. A number of differentials are known and include an open differential, a clutch-type limited slip differential, a viscous coupling differential, a torque sensing differential (such as those sold under the trademark Torsen® by JTEKT Torsen North America Inc) and a locking differential. All of these differentials may be generically referred to as axle gears.

[0104] Axle gears typically require a lubricant. The lubricant composition is dependent on the type of axle gear, and the operating conditions of the axle gear. For example an open differential axle gear is believed to require antiwear and/or extreme pressure additives. In contrast, a limited slip differential typically requires a friction modifier because in addition to an open differential (known from many axle fluids), a spring pack and a clutch pack are typically present. The clutch pack may contain one or more reaction plates (often made from steel) and one or more friction plates. The friction plates are known, and may be made from a number of materials including paper (or cellulosic), carbon, graphite, steel and a composite.

[0105] The lubricating composition suitable for the limited slip differential may have a sulphur content in the range of 0.3 wt % to 5 wt %, or 0.5 wt % to 5 wt %, or 0.5 wt % to 3 wt % or 0.8 wt % to 2.5 wt %, or 1 wt % to 2 wt %.

[0106] In one embodiment the lubricating composition suitable for the limited slip differential may be a fully formulated fluid.

[0107] In one embodiment the lubricating composition suitable for the limited slip differential may be a top treat concentrate (that is, a concentrate suitable to be added to an existing lubricant formulation as a top treat).

[0108] When the lubricating composition is in the form of a top treat concentrate, the concentrate may be added at 0.2 wt % to 10 wt %, or 0.5 wt % to 7 wt % relative to the amount of lubricant in a limited slip differential.

[0109] 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, 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 described above.

[0110] Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word “about.” Unless otherwise indicated, each chemical or composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil, which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the upper and lower amount, range, and ratio limits set forth herein may be independently combined. Similarly, the ranges and amounts for each element of the invention may be used together with ranges or amounts for any of the other elements.

[0111] As used herein, the term “hydrocarbyl substituent” or “hydrocarbyl group” is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to
a group having a carbon atom directly attached to the remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include: hydrocarbon substituents, including aliphatic, alicyclic, and aromatic substituents; substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon nature of the substituent; and hetero substituents, that is, substituents which similarly have a predominantly hydrocarbon character but contain other than carbon in a ring or chain. A more detailed definition of the term “hydrocarbyl substituent” or “hydrocarbyl group” is described in paragraphs [0118] to [0119] of International Publication WO2008147704.

[0112] 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.

1-23. (canceled)

24. A method of lubricating a limited slip differential comprising supplying to the limited slip differential a lubricating composition comprising (a) an oil of lubricating viscosity, and (b) a C_{4,30}-diester of adipic acid, wherein the C_{4,30}-diester of adipic acid is present at 0.01 wt % to less than 1 wt % of the lubricating composition.

25. The method of claim 24, wherein the C_{4,30}-diester of adipic acid is present at 0.05 wt % to 0.5 wt % of the lubricating composition.

26. The method of claim 24, wherein the C_{4,30}-diester of adipic acid is present at 0.1 wt % to 0.3 wt % of the lubricating composition.

27. The method of claim 24, wherein the alcohol-derived portion of the diester is C_{8,20}.

28. The method of claim 24, wherein the alcohol-derived portion of the diester is C_{10,15}.

29. The method of claim 24, wherein the alcohol-derived portion of the diester is C_{13}.

30. The method of claim 24, wherein the ester groups of the diester are branched.

31. The method of claim 24, wherein the lubricating composition further comprises a phosphorus-containing compound, wherein the phosphorus-containing compound is an amine salt of a phosphoric acid ester.

32. The method of claim 24, wherein the lubricating composition comprises (a) an oil of lubricating viscosity, and a friction modifier package consisting of a C_{4,30}-diester of adipic acid, and a phosphorus-containing compound, wherein the phosphorus-containing compound is an amine salt of a phosphoric acid ester.

33. The method of claim 31, wherein the phosphorus compound is present at 0.01 wt % to 5 wt % of the lubricating composition.

34. The method of claim 24, wherein the lubricating composition comprises (a) an oil of lubricating viscosity, and a friction modifier package consisting of a C_{4,30}-diester of adipic acid, and 0.05 wt % to 4.5 wt % of a phosphorus-containing compound.

35. The method of claim 24 further comprising a sulphur-containing compound, wherein the sulphur-containing compound is a dimercaptothiadiazole or derivative, or mixtures thereof.

36. The method of claim 31, wherein the phosphorus-containing compound is an amine salt of a phosphoric acid ester, wherein the amine salt of a phosphoric acid ester is an amine salt of (i) a hydroxy-substituted di-ester of phosphoric acid, (ii) a phosphorylated hydroxy-substituted di- or tri-ester of phosphoric acid, or (iii) mixtures thereof.

37. The method of claim 24, wherein the lubricating composition further comprises a boron-containing compound, wherein the boron-containing compound is a borated dispersant, a borate ester or a borated phospholipid, typically a borated phospholipid.

38. The method of claim 24, wherein the limited slip differential has a plate material of steel on paper.