Abstract:
The present invention relates to a synergistic combination of an antioxidant and an antiwear additive that results in improved antioxidancy performance in turbine, hydraulic, and other industrial lubricating compositions. The invention further relates to the processes to make the improved lubricating compositions and methods of their use in industrial fluids.
Lubricating Compositions for Turbine and Hydraulic Systems with Improved Antioxidancy

Field of the Invention

[0001] The present invention relates to a synergistic combination of an antioxidant and an antiwear additive that results in improved antioxidancy performance in turbine, hydraulic, and other industrial lubricating compositions. The invention further relates to the processes to make the improved lubricating compositions and methods of their use in industrial fluids.

Background of the Invention

[0002] Turbine and other industrial lubricants must be highly stable, both thermally and oxidatively, due to the extended drain intervals and demanding operating conditions seen in such applications. Traditionally, small molecule antioxidants (compounds with a molecular weight less than 1000 g/mol) such as diaromatic amines are used to improve oxidative stability of industrial lubricants, which may be measured by the Rotary Bomb Oxidation Test (RBOT), ASTM D2272. Other small molecule antioxidants used include dithiocarbamates, sulfurized olefins, and phenolic antioxidants. In some cases, there can be a synergistic improvement of antioxidancy when two or more antioxidants are combined.

[0003] There is a need for compositions that provide improved thermal and oxidative stability.

[0004] This invention relates to compositions where aromatic amine antioxidants are used in combination with dithiocarbamates, in specific amounts, to synergistically improve the oxidative stability, and thus RBOT performance of industrial specialties lubricants in unexpected and surprising ways.

Summary of the Invention

[0005] The invention provides for a composition that includes: (a) an oil of lubricating viscosity; (b) an aromatic amine antioxidant; and (c) a dithiocarbamate antiwear agent. In the compositions of the invention (b) is present from 0.35 to 0.75
percent by weight, component c) is present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components (b) and (c) is from 0.60 to 1.25 percent by weight, with regards to the overall composition. The invention further allows for the addition of various other additives to the described compositions, in order to result in a fully formulated fluid. These additional additives that may be used in the compositions of the invention include an antioxidant other than component (b), an antiwear agent other than component (c), a corrosion inhibitor, a rust inhibitor, a foam inhibitor, a dispersant, a demulsifier, a metal deactivator, a friction modifier, a detergent, an emulsifier, an extreme pressure agent, or any combination thereof.

[0006] The invention provides for the composition described above where component (a) comprises a Group I base oil, a Group II base oil, a Group III base oil, or any combination thereof and is present from about 95 to about 99.9 percent by weight of the overall composition; component (b) comprises an alkylated diphenylamine and is present from about 0.35 to about 1.25, about 0.375 to about 0.75, or about 0.50 to about 0.75 percent by weight in the overall composition; component (c) comprises a dithiocarbamate ester and is present from about 0.25 to about 0.75 percent by weight in the overall composition; and the total weight percent of the combination of components (b) and (c) is from 0.8 to 1.2 percent by weight, with regards to the overall composition; where the composition further comprises: (d) an antioxidant other than component (b) that is present from about 0.01 to about 5.0 percent by weight of the overall composition; (e) an antiwear additive other than component (c) that is present from about 0.01 to about 2.5 percent by weight of the overall composition; (f) a corrosion inhibitor or metal deactivator that is present from about 0.001 to about 2.0 percent by weight of the overall composition; (g) a rust inhibitor, wherein component (f) and component (g) are different additives, where component (g) is present from about 0.001 to about 2.0 percent by weight of the overall composition; and (h) an antifoam additive that is present from about 0.01 to about 3.0 percent by weight of the overall composition.

[0007] The invention further provides a process to prepare a lubricating oil composition comprising the steps of: (I) mixing together the components of the described compositions, in the described amounts.
The invention further provides a method of lubricating a turbine system comprising the steps of: (I) supplying to a turbine system any of the compositions described herein.

The invention further provides a method of lubricating a hydraulic system comprising the steps of: (I) supplying to a turbine system any of the compositions described herein.

This invention concerns the synergistic combination of an aromatic amine antioxidant and a dithiocarbamate antiwear agent. Synergies are identified when a combination of two or more components provide a result that neither component on its own could have provided. The impact of treat rates must of course be taken into account as well, as the proper basis of comparison when identifying a synergy is very important. In addition, it is generally accepted that the performance benefit an additive imparts to a composition in which it is used increases with the treat rate. For example when you add an antioxidant to a lubricating composition, one would expect adding twice as much antioxidant would increase the benefit the additive provides to the composition. A plot of performance against treat rate that levels off, or that shows a peak of improved performance and then drops off despite an increased treat rate for a particular combination of additives, where this improved performance is limited to particular treat rates and/or ratios, would by definition be a synergistic combination and a surprising result.

**Detailed Description of the Invention**

Various features and embodiments of the invention will be described below by way of non-limiting illustration.

The invention provides for a composition that includes: (a) an oil of lubricating viscosity; (b) an aromatic amine antioxidant; and (c) a dithiocarbamate antiwear agent, where the amounts of (b) and (c) are present in amounts that provide a synergistic improvement in performance.

In these compositions component (b) is present from 0.35 to 0.75 and may also be present from 0.375 to 0.7; 0.4 to 0.7; 0.4 to 0.6; 0.5 to 0.75, 0.5 to 0.7, 0.5 to 0.6 or even 0.5 percent by weight, component (c) is present from 0.25 to 0.75 and may also be present from 0.3 to 0.75, 0.3 to 0.7, 0.4 to 0.6 or even 0.5 percent by weight, and the total weight percent of the combination of components b) and c)
is from 0.60 to 1.25 and may also be from 0.625 to 1.25, 0.75 to 1.25, 0.8 to 1.2, 0.9 to 1.1 or even 1.0 percent by weight, with regards to the overall composition. In some embodiments the weight ratio of component b) to component c) is from 1:0.5 to 1:1.5, or from 1:0.5 to 1:0.67, or from 1:1 to 1:1.67, or from 1:1 to 1:1.5, or from 1:0.5 to 1:1. In some embodiments the weight ratio is 1:1. These weight ratios are in addition to ranges specified above for the combined treat rate of components b) and c), particularly where the combined treat rate of components b) and c) is from 0.60 to 1.25, 0.75 to 1.25, 0.75 to 1.0, 1.0 to 1.25, or even 1.0 percent by weight in the overall composition.

[0014] The invention also provides for methods of making and using the described compositions, in the lubrication of hydraulic systems and also in the lubrication of turbines.

The Oil of Lubricating Viscosity

[0015] One component of the compositions of the invention is an oil of lubricating viscosity, which can be present in a major amount, for a lubricant composition, or in a concentrate forming amount, for a concentrate. Suitable oils include natural and synthetic lubricating oils and mixtures thereof. In a fully formulated lubricant, the oil of lubricating viscosity is generally present in a major amount (i.e. an amount greater than 50 percent by weight). Typically, the oil of lubricating viscosity is present in an amount of 75 to 95 percent by weight, and often greater than 80 percent by weight of the overall composition. The base oil component generally makes up 100 parts by weight (pbw) of the overall composition with the pbw ranges for the other components being provided with this 100 pbw of base oil in mind. In other embodiments the pbw ranges of the various components, including the base oils, are provided such that the total of the pbw of all components is 100. The pbw ranges provided for the various components described below may be taken either way.

[0016] The lubricating oil component of the present invention is not overly limited, and may include a Group I, Group II or Group III base oil, or a combination thereof. These are classifications established by the API (American Petroleum Institute). Group III oils contain < 0.03 percent sulfur and > 90 percent saturates and have a viscosity index of > 120. Group II oils have a viscosity index of 80 to
120 and contain < 0.03 percent sulfur and > 90 percent saturates. The oil can also be
derived from the hydroisomerization of wax, such as slack wax or a Fischer-Tropsch
synthesized wax. Such "Gas-to-Liquid" oils are typically characterized as Group III
base oils.

[0017] The compositions of the present invention may also include Group IV
and Group V base oils, either alone or in combination with any of the other oils
discussed herein. Polyalphaolefins are categorized as Group IV. Group V
encompasses "all others". However, in some embodiments the lubricating oil
component of the invention contains no more than 20, 10, 5, or even 1 percent by
weight Group I base oil. These limits may also apply to Group IV or Group V base
oils. In other embodiments the lubricating oil present in the compositions of the
invention is at least 60, 70, 80, 90, or even 95 percent by weight Group II and/or
Group III base oil. In some embodiments the lubricating oil present in the
compositions of the invention is essentially only Group II and/or Group III base oil,
where small amounts of other types of base oils may be present but not in amounts
that significantly impact the properties or performance of the overall composition.

[0018] In some embodiments the lubricating oil component includes a Group I
base oil, a Group II base oil, a Group III base oil, a poly(alpha-olefin), a GTL oil, or
any combination thereof. In some embodiments the base oil comprises a Group II
base oil, a Group III base oil, a poly(alpha-olefin), a GTL oil, or any combination
thereof. In some embodiments the base oil comprises a Group II base oil. In some
of these embodiments the base oil component may be essentially or substantially
free of Group I base oils.

[0019] The oil of lubricating viscosity may be present in the range from 60 to
99.9, from 95 to 99.9, 98.0 to 99.7, from 96.9 to 99.5, or from 98.5 to 99.4 weight
percent of the lubricating oil composition. Each oil of lubricating viscosity
described above may be used alone or as mixtures of one or more thereof.

The Antioxidant Component

[0020] The invention provides for a composition that includes an aromatic
amine antioxidant. In some embodiments the antioxidant includes an alkylated
diphenylamine and may be present from about 0.35 to about 0.75, or from 0.4 to
about 0.7 percent by weight in the overall composition. The aromatic amine
antioxidant may also be present from 0.375 to 0.75, 0.5 to 0.75, 0.4 to 0.7, 0.35 to 0.65, 0.4 to 0.6, 0.45 to 0.55, 0.35 to 0.75, or from 0.375 to 0.7 or even 0.5 percent by weight in the overall composition.

[0021] Amines suitable for use in the invention may be represented by the formula:

\[
\begin{align*}
\text{(R}_1, & \text{)} \quad \text{NH} \\
\text{(R}_2, & \text{)}
\end{align*}
\]

wherein \( \text{R}_1 \) and \( \text{R}_2 \) are independently a hydrogen or an alkyl group containing about 5 to 20 carbon atoms; or a linear or branched alkyl group containing 1 to 24 carbon atoms and \( q \) and \( r \) are each independently 0, 1, 2, or 3, provided that the sum of \( q \) and \( r \) is at least one. In some embodiments \( \text{R}_1 \) and \( \text{R}_2 \) are independently hydrogen or alkyl groups containing 1 to 24, 4 to 20, 5 to 16, or 6 to 12 or even 10 carbon atoms. In any of the embodiments described above, each \( \text{R}_1 \) and \( \text{R}_2 \) may be a linear alkyl group, a branched alkyl group, or even an alkylaryl group.

[0022] In some embodiments the alkylated diphenylamines of the invention are bis-nonylated diphenylamine and bis-octylated diphenylamine.

The Antiwear Component

[0023] The invention provides for a composition that includes a dithiocarbamate antiwear agent. In some embodiments the antiwear agent includes an ashless thio carbamate, in some embodiments a thio carbamate ester. The thio carbamates and ester thereof may be monothiocarbamates, dithiocarbamate, or mixtures thereof. In some embodiments the antiwear agent is a dithiocarbamate ester and is present from about 0.25 or 0.3 to about 0.7 percent by weight in the overall composition. The antiwear agent may be present from about 0.25, 0.3, 0.4 or even 0.5 up to 0.75, 0.7, 0.6 or even 0.55 percent by weight in the overall composition. In some embodiments the antiwear agent is present from 0.25 to 0.75, 0.3 to 0.7, 0.35 to 0.65, 0.4 to 0.6, 0.45 to 0.55 or even 0.5 percent by weight in the overall composition.
In some embodiments the dithiocarbamate antiwear agent is represented by the formula:

\[
R^3 - N - S - \left(\begin{array}{c} \text{X} \\ \text{R}^4 \end{array}\right) - C - S(=\text{R}^5) - \text{Y} - \text{R}^6
\]

(II)

wherein \(R^3\) and \(R^4\) are independently alkyl of 1 to about 7 carbons, aryl, aralkyl or together form an alicyclic or heteroalicyclic radical in which the ring is completed through the nitrogen; \(X\) is O or S; \(a\) is 1 or 2; \(R^5\) and \(R^6\) are independently H, alkyl or aryl; and \(Z\) is (i) -CN, (ii) -S(=0)-R\(^7\), (iii) -S(=0)(=0)-R\(^7\), (iv) -S(=0)(=0)-0-R\(^7\) wherein \(R^7\) is hydrogen, alkyl, aralkyl, (v) -C(=0)-Y wherein Y is -H, -OH, or -R\(^8\), -O-R\(^8\) (where \(R^8\) is alkyl, aryl, aralkyl), -O-R\(^9\)-OH (where \(R^9\) is alkylene of 1 to about 7 carbon atoms), -NR\(^{10}\)R\(^{11}\) (where \(R^{10}\) and \(R^{11}\) are independently hydrogen, alkyl, cycloaliphatic, heteroalicyclic or together form an alicyclic or heteroalicyclic radical in which the ring is completed through the nitrogen), or (vi) -S-C(=S)-Y ; with the proviso that when \(a\) is 1, Y is not -O-R\(^5\).

In some embodiments the thiocarbamate antiwear agent a dithiocarbamate represented by formula (II) above where \(X\) is S, \(R^5\) and \(R^6\) are independently H or alkyl, \(a\) is 2 and \(Z\) is -C(=0)-Y wherein Y is -OH, -R\(^8\), -O-R\(^8\), -0-R\(^9\)-OH, where \(R^9\) is an alkylene of 1 to about 7 carbon atoms or -NR\(^{10}\)R\(^{11}\) where \(R^{10}\) and \(R^{11}\) are as defined above. In still other embodiments the compound is defined by the above formula where \(X\) is S, \(R^5\) and \(R^6\) are H or methyl, and Y is -OH, -OR\(^8\) wherein \(R^8\) is methyl or ethyl, -O-R\(^9\)-OH, where \(R^9\) is an alkylene of 1 to about 4 carbon atoms, or NR\(^{10}\)R\(^{11}\) wherein \(R^{10}\) and \(R^{11}\) are H.

These materials are described in detail in U.S. patent 4,758,362, incorporated herein by reference.

In some embodiments the dithiocarbamate antiwear agent comprises (i) a compound represented by formula (II) where \(R^3\) and \(R^4\) are butyl groups, \(X\) is S, \(a\) is 2, \(R^5\) and \(R^6\) are hydrogen and \(Z\) is -C(=0)-0-CH\(_3\); (ii) a compound represented by formula (II) where \(a\) is 0, 1 or 2, and \(Z\) is -C(=O)-NR\(^{10}\)R\(^{11}\) where \(R^{10}\) and \(R^{11}\) have the same definitions provided above; (iii) a compound represented by formula (II)
where \( R^3 \) and \( R^4 \) are butyl groups, \( X \) is \( S \), \( a \) is 1, \( R^5 \) and \( R^6 \) are \( H \), and \( Z \) is \(-S-C(=S)-N-R^3R^4\) where \( R^3 \) and \( R^4 \) are again butyl groups; or any combinations thereof.

Additional Additives.

[0028] The compositions of the invention may also contain one or more additional additives. In some embodiments the additional additives may include an antioxidant other than component (b); an antiwear agent other than component (c); a corrosion inhibitor, a rust inhibitor, a foam inhibitor, a dispersant, a demulsifier, a metal deactivator, a friction modifier, a detergent, an emulsifier, an extreme pressure agent, a pour point depressant, a viscosity modifier, or any combination thereof.

[0029] In some of these embodiments, component (a) comprises a Group I base oil, a Group II base oil, a Group III base oil, or any combination thereof and is present from about 95 to about 99.9 percent by weight of the overall composition; component (b) comprises an alkylated diphenylamine and is present from about 0.4 to about 0.7 percent by weight in the overall composition; component (c) comprises a dithiocarbamate ester and is present from about 0.3 to about 0.7 percent by weight in the overall composition; the total weight percent of the combination of components (b) and (c) is from 0.8 to 1.2 percent by weight, with regards to the overall composition; the composition further comprises (d) an antioxidant other than component (b) that is present from about 0.01 to about 5.0 percent by weight of the overall composition; the composition further comprises (e) an antiwear additive other than component (c) that is present from about 0.01 to about 2.5 percent by weight of the overall composition; the composition further comprises (f) a corrosion inhibitor or metal deactivator that is present from about 0.001 to about 2.0 percent by weight of the overall composition; the composition further comprises (g) a rust inhibitor, wherein component (f) and component (g) are different additives, where component (g) is present from about 0.001 to about 2.0 percent by weight of the overall composition; and the composition further comprises (h) an antifoam additive that is present from about 0.01 to about 3.0 percent by weight of the overall composition. In some embodiments the composition may include a viscosity modifier and/or pour point depressant within any of the ranges provided above.

[0030] In any of these embodiments, component (a) may be present from 95 to 99.9, 98 to 99.7, or 98.5 to 99.5 percent by weight, component (b) may be present...
from 0.5 to 0.75, 0.4 to 0.7, 0.4 to 0.6, or even 0.5 percent by weight, and
cOMPONENT (C) may be present from 0.25 to 0.75, 0.3 to 0.7, 0.4 to 0.6, or even 0.5
percent by weight, where the combined treat rate of components (B) and (C) may be
from 0.75 to 1.25, 0.8 to 1.2, 0.9 to 1.1, or even 1.0 percent by weight where all
percent by weight values are in regards to the overall composition. In additional all
of the weight ratios described above may be applied here as well.

[0031] In addition component (D) may be present from 0.01 to 5.0, 0.01 to 1.5,
0.01 to 0.9 or even 0.09 percent by weight, component (E) may be present from
0.01 to 2.5, 0.01 to 1.5, 0.01 to 0.5 or even 0.05 percent by weight, component (F)
may be present from 0.001 to 2.0, 0.001 to 1.0, 0.001 to 0.002, or even 0.002 percent
by weight, component (G) may be present from 0.001 to 2.0, 0.001 to 1.0, 0.001 to
0.004, or even 0.004 percent by weight, and component (H) may be present from
0.01 to 3.0, 0.01 to 1.5, 0.01 to 0.2, or even 0.02 percent by weight where all
percent by weight values are in regards to the overall composition.

[0032] In some embodiments component (D) may include a sulfurized olefin, for
example a substituted hydrocarbyl mono-sulfide, while component (E) may include
an amine phosphate, component (F) may include a triazole, a tolyltriazole, or
combinations thereof, component (G) may include a polyether, a fatty carboxylic
acid or ester thereof, an ester of a nitrogen-containing carboxylic acid, an
ammonium sulfonate, an imidazoline, or any combinations thereof, and component
H) may include an acrylate copolymer. More specific examples of component (F)
include hydrocarbyl substituted benzotriazole, 5-methylbenzotriazole, or a
combination thereof.

[0033] In some embodiments component (D), the additional antioxidant, includes
a substituted hydrocarbyl mono-sulfide represented by the formula:

\[
\begin{array}{c}
R^7 \\
R^6 \quad S \\
R^8 \\
\end{array}
\begin{array}{c}
C \\
R^9 \\
\end{array}
\begin{array}{c}
C \\
OH \\
R_{10} \\
\end{array}
\]

wherein \(R^6\) is a saturated or unsaturated branched or linear alkyl group with about 8
to about 20 carbon atoms; \(R^7, R^8, R^9\) and \(R_{10}\) are independently hydrogen or alkyl
containing about 1 to about 3 carbon atoms. In some embodiments the substituted
hydrocarbyl monosulfides include n-dodecyl-2-hydroxyethyl sulfide, l-(tert-dodecylthio)-2-propanol, or combinations thereof. In some embodiments the substituted hydrocarbyl monosulfide is l-(tert-dodecylthio)-2-propanol.

[0034] The additional antioxidant component may also include sterically hindered phenols represented by the formula:

\[
\begin{align*}
&\text{R}^{11} \\
&\text{R}^{12} \\
&\text{q} \\
\end{align*}
\]

wherein \(\text{R}^{11}\) and \(\text{R}^{12}\) are independently branched or linear alkyl groups containing about 1 to about 24, preferably about 4 to about 18, and most preferably from about 4 to about 12 carbon atoms.

[0035] \(\text{R}^{11}\) and \(\text{R}^{12}\) may be either a straight or branched chain, branched is preferred. Preferably the phenol is butyl substituted containing two t-butyl groups. When the t-butyl groups occupy the 2,6-positions, the phenol is sterically hindered, \(q\) is hydrogen or hydrocarbyl. Examples of suitable hydrocarbyl groups include but are not limited to 2-ethylhexyl or n-butyl ester, dodecyl or mixtures thereof.

[0036] Other optional sterically hindered phenols suitable for the invention include but are not limited to those represented by the formulae:

\[
\begin{align*}
&\text{R}^{13} \\
&\text{R}^{14} \\
&\text{Y} \\
&\text{R}^{15} \\
&\text{R}^{16} \\
&\text{HO} \\
&\text{OH} \\
\end{align*}
\]
Preferably the phenol is butyl substituted.

\[ R^{19} \text{ and } R^{20} \text{ are independently hydrogen, an arylalkyl group or a linear or branched alkyl group. } R^{19} \text{ and } R^{20} \text{ are preferably in the para position. The arylalkyl or alkyl groups contain about 1 to about 15, preferably about 1 to about 10, and most preferably about 1 to about 5 carbon atoms. The bridging group } Y \text{ includes but is not limited to } -CH_2- \text{ (methylene bridge) or } -CH_2OCH_2- \text{ (ether bridge).} \]

Examples of methylene-bridged sterically hindered phenols include but are not limited to 4,4'-methylenebis(6-tert-butyl o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tertbutylphenol) or mixtures thereof.

In one embodiment the antioxidant is a hindered ester-substituted phenol represented by the formula:

\[ \text{wherein } R^{21}, R^{22} \text{ and } R^{23} \text{ are straight or branched alkyl group containing about 2 to about 22, preferably about 2 to about 18, more preferably about 4 to about 8 carbon atoms. Specific examples include but are not limited to alkyl groups such as 2-ethylhexyl or n-butyl ester, dodecyl or mixtures thereof.} \]
The compositions of the invention may also include dispersant additives. Suitable dispersants include: (i) polyetheramines; (ii) borated succinimide dispersants; (iii) non-borated succinimide dispersants; (iv) Mannich reaction products of a dialkylamine, an aldehyde and a hydrocarbyl substituted phenol; or any combination thereof. In some embodiments the dispersant component is present from 0.05 to 0.5 pbw of the overall composition.

Polyetheramines of the invention include compounds having two or more consecutive ether groups and at least one primary, secondary or tertiary amino group where the amine nitrogen has some basicity. The polyetheramines of this invention include poly(oxyalkylene) amines having a sufficient number of repeating oxyalkylene units to render the poly(oxyalkylene)amine soluble in a base oil while allowing acceptable performance in ASTM D1401 (Standard Test Method for Water Separability of Petroleum Oils and Synthetic Fluids) test. Generally, poly(oxyalkylene)amines having at least about 5 oxyalkylene units are suitable for use in the present invention. Poly(oxyalkylene)amines can include: hydrocarbylpoly(oxyalkylene)amines, hydrocarbylpoly(oxyalkylene)polyamines, and derivatives of polyhydric alcohols having at least two poly(oxyalkylene)amine and/or poly(oxyalkylene)polyamine chains on the molecule of the derivative. In one embodiment, the poly(oxyalkylene)amine for use in the invention is represented by the formula R-0-(AO)m-3RN-R2R3 wherein R is a hydrocarbyl group of 1 to 50 carbon atoms, or about 8 to about 30 carbon atoms; A is an alkylene group having 2 to 18 carbon atoms or 2 to 6 carbon atoms; m is a number from 1 to 50; R1 is an alkylene group having 2 to 18 carbon atoms or 2 to 6 carbon atoms; and R2 and R3 are independently hydrogen, a hydrocarbyl group or -(R4N(R5)3)nR6 wherein R4 is an alkylene group having 2 to 6 carbon atoms, R5 and R6 are independently hydrogen or a hydrocarbyl group, and n is a number from 1 to 7.

In another embodiment, the poly(oxyalkylene)amine of the present invention can be represented by the formula: RO[CH2CH(CH2CH3)0]mCH2CH2CH2NH2 wherein R is an aliphatic group or alkyl-substituted phenyl group of 8 to 30 carbon atoms; and m is a number from 12 to 30. In yet another embodiment, the poly(oxyalkylene)amine of the present invention can be represented by the formula: CH3CH(CH3)[CH2CH(CH3)2CH(CH3)CH2CH20 -
[CH₂CH(CH₂CH₃)ₐ]ₘCH₂CH₂CH₂NH₂ wherein m is a number from about 16 to about 28. Poly(oxyalkylene)amines of the present invention can have a molecular weight in the range from about 300 to about 5,000.

[0043] The polyetheramines of the present invention can be prepared by initially condensing an alcohol or alkylphenol with an alkylene oxide, mixture of alkylene oxides or with several alkylene oxides in sequential fashion in a 1:1-50 mole ratio of hydric compound to alkylene oxide to form a polyether intermediate. U.S. Patent Nos. 5,112,364 and 5,264,006 provide reaction conditions for preparing a polyether intermediate.

[0044] The alcohols can be monohydric or polyhydric, linear or branched, saturated or unsaturated and having 1 to 50 carbon atoms, or from 8 to 30 carbon atoms, or from 10 to 16 carbon atoms. Branched alcohols of the present invention can include Guerbet alcohols, as described in U.S. Patent No. 5,264,006, which generally contain between 12 and 40 carbon atoms and can be represented by the formula R-CH(CH₂CH₂R)CH₂OH where R is a hydrocarbyl group. In one embodiment, the alkyl group of the alkylphenols can be 1 to 50 carbon atoms, or 2 to 24 carbon atoms, or 10 to 20 carbon atoms.

[0045] In one embodiment, the alkylene oxides include 1,2-epoxyalkanes having 2 to 18 carbon atoms, or 2 to 6 carbon atoms. In yet another embodiment, the alkylene oxides can be ethylene oxide, propylene oxide and butylene oxide. Especially useful is propylene oxide, butylene oxide, or a mixture thereof. The number of alkylene oxide derived units in the polyether intermediate can be 1-50, or 12-30, or 16-28.

[0046] The polyether intermediates can be converted to polyetheramines by several methods. The polyether intermediate can be converted to a polyetheramine by a reductive amination with ammonia, a primary amine or a polyamine as described in U.S. Patent Nos. 5,112,364 and 5,752,991. In one embodiment, the polyether intermediate can be converted to a polyetheramine via an addition reaction of the polyether to acrylonitrile to form a nitrile which is then hydrogenated to form the polyetheramine. U.S. Patent No. 5,264,006 provides reaction conditions for the cyanoethylation of the polyether with acrylonitrile and the subsequent hydrogenation to form the polyetheramine. In yet another embodiment, the
polyether intermediate or poly(oxyalkylene) alcohol is converted to the corresponding poly(oxyalkylene) chloride via a suitable chlorinating agent followed by displacement of chlorine with ammonia, a primary or secondary amine, or a polyamine as described in U.S. Patent No. 4,247,301.

[0047] In some embodiments the polyetheramine of the present invention is derived from the reaction of a mixture of alcohols containing from 10 to 18 carbon atoms, an alkoxylation and an amine.

[0048] Another type of dispersant, which can be used in the invention, is a succinimide. Succinimide dispersants are well known in the field of lubricants and include primarily what are sometimes referred to as "ashless" dispersants because they do not contain ash-forming metals and they do not normally contribute any ash forming metals when added to a lubricant. Succinimide dispersants are the reaction product of a hydrocarbyl substituted succinic acylating agent and an amine containing at least one hydrogen attached to a nitrogen atom. The term "succinic acylating agent" refers to a hydrocarbon-substituted succinic acid or succinic acid-producing compound (which term also encompasses the acid itself). Such materials typically include hydrocarbyl-substituted succinic acids, anhydrides, esters (including half esters) and halides.

[0049] Succinic based dispersants have a wide variety of chemical structures including typically structures such as:

![Chemical Structure](image)

(VIII)

[0050] In the above structure, each $R^{24}$ is independently a hydrocarbyl group, which may be bound to multiple succinimide groups, typically a polyolefin-derived group having a number average molecular weight (Mn) of 500 or 700 to 10,000. Typically the hydrocarbyl group is an alkyl group, frequently a polyisobutylene group derived from polyisobutylene with a Mn of 500 or 700 to 5000, or 1500 or 2000 to 5000. Alternatively expressed, the $R^{24}$ groups can contain 40 to 500 carbon...
atoms or at least 50 to 300 carbon atoms, e.g., aliphatic carbon atoms. The \( R \) are alkylene groups, commonly ethylene \((C_2H_4)\) groups. Such molecules are commonly derived from reaction of an alkenyl acylating agent with a polyamine, and a wide variety of linkages between the two moieties is possible beside the simple imide structure shown above, including a variety of amides and quaternary ammonium salts. Succinimide dispersants are more fully described in U.S. Patents 4,234,435, 3,172,892, and 6,165,235.

[0051] The polyalkenes from which the substituent groups are derived are typically homopolymers and inter polymers of polymerizable olefin monomers of 2 to 16 carbon atoms; usually 2 to 6 carbon atoms.

[0052] The olefin monomers from which the polyalkenes are derived are polymerizable olefin monomers characterized by the presence of one or more ethylenically unsaturated groups (i.e., \( \geq C=C \)); that is, they are mono-olefinic monomers such as ethylene, propylene, 1-butene, isobutene, and 1-octene or polyolefinic monomers (usually diolefinic monomers) such as 1,3-butadiene, and isoprene. These olefin monomers are usually polymerizable terminal olefins; that is, olefins characterized by the presence in their structure of the group \( \geq C=CH_2 \). Relatively small amounts of non-hydrocarbon substituents can be included in the polyolefin, provided that such substituents do not substantially interfere with formation of the substituted succinic acid acylating agents. Each \( R^1 \) group may contain one or more reactive groups, i.e. succinic groups.

[0053] The amines which are reacted with the succinic acylating agents to form the carboxylic dispersant composition can be monoamines or polyamines. In either case they will be characterized by the formula \( R^4R^5NH \) wherein \( R^4 \) and \( R^5 \) are each independently hydrogen, hydrocarbon, amino-substituted hydrocarbon, hydroxy-substituted hydrocarbon, alkoxy-substituted hydrocarbon, amino, carbamyl, thiocarbamyl, guanyl, or acylimidoyl groups provided that no more than one of \( R^4 \) and \( R^5 \) is hydrogen. In all cases, therefore, they will be characterized by the presence within their structure of at least one \( H-N< \) group. Therefore, they have at least one primary (i.e., \( H_2N^- \)) or secondary amino (i.e., \( H-N< \)) group. Examples of monoamines include ethylamine, diethylamine, n-butylamine, di-n-butylamine, allylamine, isobutylamine, cocoamine, stearylamine, laurylamine,
methyllaurylamine, oleylamine, N-methyl-octylamine, dodecylamine, and octadecylamine.

[0054] The polyamines from which the dispersant is derived include principally alkylene amines conforming, for the most part, to the formula

\[
\begin{align*}
&\text{Alkylene}_t \\
&\text{H}
\end{align*}
\]  

(IX)

wherein \( t \) is an integer typically less than 10, \( A \) is hydrogen or a hydrocarbyl group typically having up to 30 carbon atoms, and the alkylene group is typically an alkylene group having less than 8 carbon atoms. The alkylene amines include principally, ethylene amines, hexylene amines, heptylene amines, octylene amines, other polymethylene amines. They are exemplified specifically by: ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(-(trimethylene) triamine. Higher homologues such as are obtained by condensing two or more of the above-illustrated alkylene amines likewise are useful. Tetraethylene pentamine is particularly useful.

[0055] The ethylene amines, also referred to as polyethylene polyamines, are especially useful. They are described in some detail under the heading "Ethylene Amines" in Encyclopedia of Chemical Technology, Kirk and Othmer, Vol. 5, pp. 898-905, Interscience Publishers, New York (1950).

[0056] Hydroxyalkyl-substituted alkylene amines, i.e., alkylene amines having one or more hydroxyalkyl substituents on the nitrogen atoms, likewise are useful. Examples of such amines include N-(2-hydroxyethyl)ethylenediamine, N,N'-bis(2-hydroxyethyl)ethylenediamine, 1-(2-hydroxyethyl)piperazine, monohydroxypropyl) piperazine, di-hydroxypropyl-substituted tetraethylenepentamine, N-(3-hydroxypropyl)-tetra-methylenediamine, and 2-heptadecyl-l-(2-hydroxyethyl)-imidazoline.

[0057] Higher homologues, such as are obtained by condensation of the above-illustrated alkylene amines or hydroxy alkyl-substituted alkylene amines through amino radicals or through hydroxy radicals, are likewise useful. Condensed
polyamines are formed by a condensation reaction between at least one hydroxy compound with at least one polyamine reactant containing at least one primary or secondary amino group and are described in U.S. Patent 5,230,714 (Steckel).

[0058] The succinimide dispersant is referred to as such since it normally contains nitrogen largely in the form of imide functionality, although it may be in the form of amine salts, amides, imidazolines as well as mixtures thereof. To prepare the succinimide dispersant, one or more of the succinic acid-producing compounds and one or more of the amines are heated, typically with removal of water, optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent at an elevated temperature, generally in the range of 80°C up to the decomposition point of the mixture or the product; typically 100°C to 300°C.

[0059] The succinic acylating agent and the amine (or organic hydroxy compound, or mixture thereof) are typically reacted in amounts sufficient to provide at least one-half equivalent, per equivalent of acid-producing compound, of the amine (or hydroxy compound, as the case may be). Generally, the maximum amount of amine present will be about 2 moles of amine per equivalent of succinic acylating agent. For the purposes of this invention, an equivalent of the amine is that amount of the amine corresponding to the total weight of amine divided by the total number of nitrogen atoms present. The number of equivalents of succinic acid-producing compound will vary with the number of succinic groups present therein, and generally, there are two equivalents of acylating reagent for each succinic group in the acylating reagents. Additional details and examples of the procedures for preparing the succinimide detergents of the present invention are included in, for example, U.S. Pat. Nos. 3,172,892; 3,219,666; 3,272,746; 4,234,435; 6,440,905 and 6,165,235.

[0060] In some embodiments the compositions of the invention include a non-borated succinimide dispersant derived from polyisobutylene having a number average molecular weight from 500 to 3000 and polyethylenepolyamines.

[0061] In some embodiments the succinimide dispersants above may be borated. Borated dispersants are well-known materials and can be prepared by treating one or more of dispersants described above with a borating agent such as boric acid. Typical conditions include heating the dispersant with boric acid at 100 to 150
degrees C. The dispersants may also be treated by reaction with maleic anhydride as described in PCT application US99/23940 filed 13 Oct. 1999.

[0062] In some embodiments the compositions of the invention include a borated succinimide dispersant derived from polyisobutylene having a number average molecular weight from 500 to 3000 and polyethylenepolyamines.

[0063] In some of these embodiments the composition contains less than 0.1 pbw of fatty carboxylic acids.

[0064] The dispersant of the invention can be a Mannich dispersant. Mannich dispersants are the reaction product of a hydrocarbyl-substituted phenol, an aldehyde, and an amine or ammonia, but in this invention generally a dialkylamine. The hydrocarbyl substituent of the hydrocarbyl-substituted phenol can have 10 to 400 carbon atoms, in another instance 30 to 180 carbon atoms, and in a further instance 10 or 40 to 110 carbon atoms. This hydrocarbyl substituent can be derived from an olefin or a polyolefm. Useful olefins include alpha-olefms, such as 1-decene, which are commercially available.

[0065] The polyolefms which can form the hydrocarbyl substituent can be prepared by polymerizing olefin monomers by well known polymerization methods and are also commercially available. The olefin monomers include monoolefms, including monoolefms having 2 to 10 carbon atoms such as ethylene, propylene, 1-butene, isobutylene, and 1-decene. An especially useful monoolefm source is a C₄ refinery stream having a 35 to 75 weight percent butene content and a 30 to 60 weight percent isobutene content. Useful olefin monomers also include diolefms such as isoprene and 1,3-butadiene. Olefin monomers can also include mixtures of two or more monoolefms, of two or more diolefms, or of one or more monoolefms and one or more diolefms. Useful polyolefms include polyisobutylenees having a number average molecular weight of 140 to 5000, in another instance of 400 to 2500, and in a further instance of 140 or 500 to 1500. The polyisobutylene can have a vinylidene double bond content of 5 to 69 percent, in a second instance of 50 to 69 percent, and in a third instance of 50 to 95 percent. The polyolefm can be a homopolymer prepared from a single olefin monomer or a copolymer prepared from a mixture of two or more olefin monomers. Also possible as the hydrocarbyl
substituent source are mixtures of two or more homopolymers, two or more copolymers, or one or more homopolymers and one or more copolymers.

[0066] The hydrocarbyl-substituted phenol can be prepared by alkylating phenol with an olefin or polyolefin described above, such as a polyisobutylene or polypropylene, using well-known alkylation methods.

[0067] The aldehyde used to form the Mannich dispersant can have 1 to 10 carbon atoms, and is generally formaldehyde or a reactive equivalent thereof such as formalin or paraformaldehyde.

[0068] The amine used to form the Mannich dispersant can be a monoamine or a polyamine, including alkanolamines having one or more hydroxyl groups. Useful amines include ethanolamine, diethanolamine, methylamine, dimethylamine, ethylenediamine, dimethylaminopropylamine, diethylenetriamine and 2-(2-aminoethylamino) ethanol. The Mannich dispersant can be prepared by reacting a hydrocarbyl-substituted phenol, an aldehyde, and an amine as described in U.S. Patent No. 5,697,988. In one embodiment of this invention the Mannich reaction product is prepared from an alkylphenol derived from a polyisobutylene, formaldehyde, and an amine that is a primary monoamine, a secondary monoamine, or an alkylated amine, in particular, ethylenediamine or dimethylamine. In some embodiments the Mannich is prepared from a dialkylamine or a dialkenylamine.

[0069] The Mannich reaction product of the present invention can be prepared by reacting the alkyl-substituted hydroxyaromatic compound, aldehyde and polyamine by well known methods including the method described in U.S. Patent 5,876,468.

[0070] The Mannich reaction product can be prepared by well known methods generally involving reacting the hydrocarbyl substituted hydroxy aromatic compound, an aldehyde and an amine at temperatures between 50 to 200°C in the presence of a solvent or diluent while removing reaction water as described in U. S. Patent No. 5,876,468.

[0071] In some embodiments the compositions of the present invention contain a Mannich reaction product derived from the reaction of a dialkylamine, formaldehyde, and a polyisobutylene substituted phenol where the polyisobutylene has a number average molecular weight from 500 to 3000. The Mannich dispersant
may be present in the overall composition from 0.07 to 0.44 pbw, from 0.05, 0.07, or even 0.088 up to 0.5, 0.45, or even 0.44 pbw.

[0072] The compositions may include still other additives, including: a foam inhibitor, a demulsifier, a pour point depressant, or mixtures thereof. The optional additives may be present in the range from 0.0005 to 1.3, from 0.00075 to 0.5, from 0.001 to 0.4, or from 0.0015 to 0.3 percent by weight of the composition, where these ranges may be applied to the total of all of these additional additives, or to each one individually.

[0073] Antifoams, also known as foam inhibitors, are known in the art and include but are not limited to organic silicones and non-silicon foam inhibitors. Examples of organic silicones include dimethyl silicone and polysiloxanes. Examples of non-silicon foam inhibitors include but are not limited to copolymers of ethyl acrylate and 2-ethylhexylacrylate, copolymers of ethyl acrylate, 2-ethylhexylacrylate and vinyl acetate, polyethers, polyacrylates and mixtures thereof. In some embodiments the antifoam is a polyacrylate. Antifoams may be present in the composition from 0.001 to 0.012 or 0.004 pbw or even 0.001 to 0.003.

[0074] Demulsifiers are known in the art and include but are not limited to derivatives of propylene oxide, ethylene oxide, polyoxyalkylene alcohols, alkyl amines, amino alcohols, diamines or polyamines reacted sequentially with ethylene oxide or substituted ethylene oxides or mixtures thereof. Examples of demulsifiers include polyethylene glycols, polyethylene oxides, polypropylene oxides, (ethylene oxide-propylene oxide) polymers and mixtures thereof. In some embodiments the demulsifiers is a polyether. Demulsifiers may be present in the composition from 0.002 to 0.012 pbw.

[0075] Pour point depressants are known in the art and include but are not limited to esters of maleic anhydride-styrene copolymers, polymethacrylates; polyacrylates; polyacrylamides; condensation products of haloparaffin waxes and aromatic compounds; vinyl carboxylate polymers; and terpolymers of dialkyl fumarates, vinyl esters of fatty acids, ethylene-vinyl acetate copolymers, alkyl phenol formaldehyde condensation resins, alkyl vinyl ethers and mixtures thereof.

[0076] The compositions of the invention may also include a rust inhibitor. Suitable rust inhibitors include hydrocarbyl amine salts of alkylphosphoric acid,
hydrocarbyl amine salts of dialkyldithiophosphoric acid, hydrocarbyl amine salts of hydrocarbyl aryl sulphonic acid, fatty carboxylic acids or esters thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, or any combination thereof; or mixtures thereof.

[0077] Suitable hydrocarbyl amine salts of alkylphosphoric acid of the invention are represented by the following formula:

\[ \text{(X)} \]

wherein \( R^{26} \) and \( R^{27} \) are independently hydrogen, alkyl chains or hydrocarbyl, preferably at least one of \( R^{26} \) and \( R^{27} \) are hydrocarbyl. \( R^{26} \) and \( R^{27} \) contain about 4 to about 30, preferably about 8 to about 25, more preferably about 10 to about 20, and most preferably about 13 to about 19 carbon atoms. \( R^{28} \), \( R^{29} \) and \( R^{30} \) are independently hydrogen, alkyl branched or linear alkyl chains with about 1 to about 30, preferably about 4 to about 24, even more preferably about 6 to about 20, and most preferably about 10 to about 16 carbon atoms. \( R^{28} \), \( R^{29} \) and \( R^{30} \) are independently hydrogen, alkyl branched or linear alkyl chains, preferably at least one, and most preferably two of \( R^{28} \), \( R^{29} \) and \( R^{30} \) are hydrogen.

[0078] Examples of alkyl groups suitable for \( R^{28} \), \( R^{29} \) and \( R^{30} \) include but are not limited to butyl, sec butyl, isobutyl, tert-butyl, pentyl, n-hexyl, sec hexyl, n-octyl, 2-ethyl, hexyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, octadecenyl, nonadecyl, eicosyl or mixtures thereof.

[0079] In one embodiment the hydrocarbyl amine salt of an alkylphosphoric acid is the reaction product of a C14 to C18 alkylated phosphoric acid with Primene 81R (produced and sold by Rohm & Haas) which is a mixture of Cn to C14 tertiary alkyl primary amines.

[0080] Hydrocarbyl amine salts of dialkyldithiophosphoric acid of the invention used in the rust inhibitor package are represented by the formula:
wherein \( R^{31} \) and \( R^{32} \) are independently branched or linear alkyl groups. \( R^{31} \) and \( R^{32} \) contain about 3 to about 30, preferably about 4 to about 25, more preferably about 5 to about 20, and most preferably about 6 to about 19 carbon atoms. \( R^{28}, R^{29} \) and \( R^{30} \) are as described above.

[0081] Examples of hydrocarbyl amine salts of dialkyldithiophosphoric acid of the invention include but are not limited to the reaction product(s) of heptyl or octyl or nonyl dithiophosphoric acids with ethylene diamine, morpholine or Primene 81R or mixtures thereof.

[0082] Suitable hydrocarbyl amine salts of hydrocarbyl aryl sulphonic acids used in the rust inhibitor package of the invention are represented by the formula:

\[
(\text{R}^{33})_2 \text{Cy} \text{SO}_2^-
\]

wherein Cy is a benzene or naphthalene ring. \( R^{33} \) is a hydrocarbyl group with about 4 to about 30, preferably about 6 to about 25, more preferably about 8 to about 20 carbon atoms, \( z \) is independently 1, 2, 3, or 4 and most preferably \( z \) is 1 or 2. \( R^{28}, R^{29} \) and \( R^{30} \) are as described above.

[0083] Examples of hydrocarbyl amine salts of hydrocarbyl aryl sulphonic acid of the invention include but are not limited to the ethylene diamine salt of dinonyl naphthalene sulphonic acid.

[0084] Examples of suitable fatty carboxylic acids or esters thereof include glycerol monooleate and oleic acid. An example of a suitable ester of a nitrogen-containing carboxylic acid includes oleyl sarcosine.

[0085] The rust inhibitors may be present in the range from 0.02-0.2, from 0.03 to 0.15, from 0.04 to 0.12, or from 0.05 to 0.1 pbw of the lubricating oil composition. The rust inhibitors of the invention may be used alone or in mixtures thereof.
The lubricating compositions of the invention may also include a metal deactivator. Metal deactivators are used to neutralise the catalytic effect of metal for promoting oxidation in lubricating oil. Suitable metal deactivators include but are not limited to triazoles, tolyltriazoles, a thiadiazole, or combinations thereof, as well as derivatives thereof. Examples include derivatives of benzotriazoles, benzimidazole, 2-alkyldithiobenzimidazoles, 2-alkyldithiobenzothiazoles, 2-(N,N'-dialkyldithio-carbamoyl)benzothiazoles, 2,5-bis(alkyl-dithio)-1,3,4-thiadiazoles, 2,5-bis(N,N'-dialkyldithiocarbamoyl)-1,3,4-thiadiazoles, 2-alkyldithio-5-mercaptothiadiazoles or mixtures thereof.

In some embodiments the metal deactivator is a hydrocarbyl substituted benzotriazole compound. The benzotriazole compounds with hydrocarbyl substitutions include at least one of the following ring positions 1- or 2- or 4- or 5- or 6- or 7- benzotriazoles. The hydrocarbyl groups contain about 1 to about 30, preferably about 1 to about 15, more preferably about 1 to about 7 carbon atoms, and most preferably the metal deactivator is 5-methylbenzotriazole used alone or mixtures thereof.

The metal deactivators may be present in the range from 0.001 to 0.1, from 0.01 to 0.04 or from 0.015 to 0.03 pbw of the lubricating oil composition. Metal deactivators may also be present in the composition from 0.002 or 0.004 to 0.02 pbw. The metal deactivator may be used alone or mixtures thereof.

The compositions of the invention are useful as hydraulic, turbine and other industrial application lubricating compositions. The additives described may also be in the form of an additive concentrate that can then be diluted with base oil to produce a final lubricating composition. In such additive concentrates, the relative proportions of the various additives would remain the same. In other words the percent by weight values provided above may be applied as pbw values for an additive concentrate, except for the base oil component. The concentrate would contain small amount of base oil, or some other diluent, and in some embodiments no base oil or diluent at all. The concentrates would contain sufficient base oil and/or diluent to ensure they have good handling properties. The description of
process below regarding the preparation of various lubricating compositions may also be read in terms of additive concentrate applications.

[0090] The invention further provides a process for preparing a composition comprising the steps of: (I) mixing together: a) an oil of lubricating viscosity; b) an aromatic amine antioxidant; and c) a dithiocarbamate antiwear agent. The compositions may optionally include one or more additional additives. Component b) may be present from 0.35, 0.375 or even 0.5 to 0.75 percent by weight, component c) may be present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) may be from 0.60, 0.625 or even 0.75 to 1.25 percent by weight, with regards to the overall composition. In addition, all of the ranges and examples of the various components provided above may apply here to the described processes as well.

[0091] The invention also provides methods of lubricating a turbine system, a hydraulic system, of any combination thereof, where the process includes the steps: 1. supplying to the system a lubricating composition comprising: a) an oil of lubricating viscosity; b) an aromatic amine antioxidant; and c) a dithiocarbamate antiwear agent. The compositions may optionally include one or more additional additives. Component b) may be present from 0.35, 0.375 or even 0.5 to 0.75 percent by weight, component c) may be present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) may be from 0.60, 0.625 or even 0.75 to 1.25 percent by weight, with regards to the overall composition. In addition, all of the ranges and examples of the various components provided above may apply here to the described processes as well.

[0092] It is known that substituted thiadiazoles which contain an aromatic ring in their structure, for example as a substituent group, can in some cases have a negative impact on the oxidation properties of the compositions in which they are used. Thus poorer oxidation properties in compositions containing such materials is expected, independent of the benefits of the invention. Still, in some embodiments the invention limits the presence of such materials. In some embodiments substituted thiadiazoles which contain an aromatic ring as a substituent group are present at less than 0.25 percent by weight in the overall composition, at less than 0.20 or 0.15 percent by weight. In some embodiments the compositions of the
invention contains no more than 0.10 percent by weight substituted thiadiazoles which contain an aromatic ring as a substituent group. In still other embodiments the compositions of the invention are essentially, substantially, or even completely free of such materials.

[0093] These limitations need not be applied to substituted thiadiazoles which do not contain an aromatic ring in their structure.

[0094] In some embodiments alkylated phenols are present at less than 0.25 percent by weight in the overall composition, at less than 0.20 or 0.15 percent by weight. In some embodiments the compositions of the invention contain no more than 0.10 percent by weight alkylated phenols. In still other embodiments the compositions of the invention are essentially, substantially, or even completely free of such materials.

[0095] The order of addition of the additives described in the processes above are not overly limited. The optional additives may be mixed in at the same time as the other components or at a later time using any of the mixing procedures described above.

[0096] In some embodiments a portion of oil or similar diluent is present with the components and the components are mixed into the oil. In other embodiments a minimal amount of oil or diluent is present, other than that amount inherently present in the additive from their means of production and preparation and additional base oil is added after the component have been mixed. In any event the described processes results in lubricating compositions.

[0097] In some embodiments the lubricating oil compositions may be prepared from a concentrate comprising the steps of: a) mixing all of the components described above with minimal oil and/or diluent present, other than optionally some relatively small amount to allow for reasonable handling properties. The resulting concentrate may then be used in the preparation of a lubricating composition by mixing the concentrate with an effective amount of base oil or mixtures thereof resulting in a finished fluid. Optional additives may be added to the concentrate or to the resulting final fluid. These optional additives include any of those described above. In some embodiments these optional additives include a foam inhibitor, a demulsifier, a viscosity modifier, a pour point depressant, or mixtures thereof, and
may be added such that they are present in the overall compositions in the range about 0, 0.01, 0.1 or even 0.25 or up to about 13, 10, 8 or even 6 pbw.

The compositions of the present invention may be used as industrial fluids, hydraulic fluids, turbine oils and circulating oils and combinations thereof.

In some embodiments the compositions are used in steam and gas turbine systems. The use of the lubricating oil composition in such systems may improve the oxidative and/or thermal stability of the formulation. The invention further provides a method of lubricating a steam or gas turbine comprising the steps of supplying to said turbine any of the lubricating compositions described herein.

Examples

The invention will be further illustrated by the following examples, which set forth particularly advantageous embodiments. While the examples are provided to illustrate the invention, they are not intended to limit it.

Example Set 1

An example set of compositions is prepared and tested to evaluate their oxidative and thermal stability, as measured by the Rotary Bomb Oxidation Test (RBOT), which is based on ASTM D2272. In this test a samples oxidation life is measured. The samples are reacted with oxygen, water and a copper catalyst coil at 150 degrees C in a rotating bomb unit. The bomb is sealed and the pressure in the unit is measured over time. Decreasing pressure indicates the extent and rate of oxidative reactions taking place in the sample. The time it takes for the pressure in the unit to drop 172.4 kPascals (2.5 psi) from the maximum pressure is recorded for each sample. The longer the time it takes for the pressure to drop the specified amount, the more resistant the sample is to oxidation and the more stable the sample is.

A set of six samples is prepared for this testing. Each sample has the exact same formulation except for the amounts of the aromatic amine antioxidant (AO) and the dithiocarbamate antiwear agents (AW). Each sample contains the same amount of an identical additive package that contains mixtures of phosphoric acid esters and amine salts, a sulfurized olefin secondary antioxidant, an acrylate polymer antifoam agent, a triazole metal deactivator, a polyether copolymer corrosion inhibitor, and lubricating oil. All of these examples were prepared in the same
Group II base oil. The table below summarizes the formulation of the sample set and the RBOT results each sample provided:

**Table 1 - Summary of Formulations and Results for Example Set 1**

<table>
<thead>
<tr>
<th></th>
<th>Ex 1-1 Inventive</th>
<th>Ex 1-2 Inventive</th>
<th>Ex 1-3 Inventive</th>
<th>Ex 1-4 Inventive</th>
<th>Ex 1-5 Inventive</th>
<th>Ex 1-6 Comp</th>
</tr>
</thead>
<tbody>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.375%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.75%</td>
<td>0.5%</td>
<td>0.75%</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.5%</td>
<td>0.25%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.75%</td>
<td>0.75%</td>
</tr>
<tr>
<td>Total of (b) &amp; (c) wt%</td>
<td>0.875%</td>
<td>0.75%</td>
<td>1.0%</td>
<td>1.25%</td>
<td>1.25%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1.33</td>
<td>1:0.5</td>
<td>1:1</td>
<td>1:0.67</td>
<td>1:1.5</td>
<td>1:1</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>469</td>
<td>2185</td>
<td>2866</td>
<td>2200</td>
<td>2107</td>
<td>1806</td>
</tr>
</tbody>
</table>

1 - All percent values in the table are weight percent values relative to the overall composition.

[0102] The results show that the examples consistent with the invention provide surprising results. Specifically, Examples 2, 3, 4 and 5 out perform Example 1 and 6 by giving significantly better RBOT results than the other two examples. This is true despite Example 6 having a higher treat rate than any of the other examples. In other words, the data shows that the RBOT performance, and so the oxidative stability of the examples, is surprisingly improved when components (b) and (c) are combined within a certain range of weight percents, also controlling for the amount of each component present, for example by controlling the ratio. It is noted that controlling the ratio is not enough by itself, as example 6 shows. Rather, a minimum amount of each additive must be present, and in some embodiments some range of ratio must be maintained. In addition the total treat rate of the additives in question must be controlled in a specific range, not going to high or to low, otherwise performance significantly drops off.

[0103] The data also shows a significantly improved peak of performance when the amount of component (b) present is more than 0.375% and less than 0.75% by weight, and the amount of component (c) present is more than 0.25% and less than 1.25% by weight, and the total combined amount of components (b) and (c) is from 0.625% up to 1.25% by weight. The data also shows that the high performing examples have a ratio for (b) to (c) from 1:1.33 to 1:0.67. Example 3 shows this combination gives the best results, particularly at a 1:1 ratio, better than any of the other samples, including samples at higher and lower treat rates and weight ratios.

*Example Set 2*
A second example set of compositions is prepared and tested to evaluate their oxidative and thermal stability, again using the RBOT test described above. The formulations of these examples, particularly the additional additives present vary widely. The formulations of these examples and the results obtained are summarized in the tables below. It is noted that the relative amounts of the individual additives listed in each additive package may vary slightly from example to example, but all of the additives listed in a given additive package are present in each example indicated and in comparable amounts.

Table 2a - Summary of Formulations and Results for Example Set 2

<table>
<thead>
<tr>
<th></th>
<th>Ex 2-1 INV</th>
<th>Ex 2-2 INV</th>
<th>Ex 2-3 INV</th>
<th>Ex 2-4 INV</th>
<th>Ex 2-5 COMP</th>
<th>Ex 2-6 COMP</th>
<th>Ex 2-7 COMP</th>
<th>Ex 2-8 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>0.05</td>
<td>0.01</td>
<td>0.25</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package A</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package B</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>0.13</td>
<td>0.10</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total of (b) &amp; (c) Wt %</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>2313</td>
<td>2831</td>
<td>995</td>
<td>4353</td>
<td>694</td>
<td>3510</td>
<td>1139</td>
<td>2654</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Example 2-1 uses the same group II base oil used in Example Set 1, while Examples 2-2 to 2-8 use a mixture of a 650N Group II base oil and a Group II base oil from Petro-Canada.
3 - Corrosion Inhibitor I is a substituted thiazadiazole that contains a aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package A is a combination of conventional additives, and includes a sulfurized olefin secondary antioxidant, a polyether corrosion inhibitor, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts, and diluent oil.
6 - Additive Package B is a combination of conventional additives and includes a polyether corrosion inhibitor, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts, and diluent oil.
7 - Additive Package C is a combination of conventional additives, and includes mixtures of phosphoric acid esters and amine salts, a sulfurized olefin secondary antioxidant, an acrylate polymer antifoam agent, a triazole metal deactivator, a polyether copolymer corrosion inhibitor, and diluent oil.
8 - Additive Package D is a combination of conventional additives, and includes a polyether corrosion inhibitor, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts, and diluent oil.

Table 2b - Summary of Formulations and Results for Example Set 2

<table>
<thead>
<tr>
<th></th>
<th>Ex 2-9 INV</th>
<th>Ex 2-10 INV</th>
<th>Ex 2-11 COMP</th>
<th>Ex 2-12 COMP</th>
<th>Ex 2-13 COMP</th>
<th>Ex 2-14 COMP</th>
<th>Ex 2-15 COMP</th>
<th>Ex 2-16 INV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Additive Package B</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package C</td>
<td></td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package D</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
(a) Base Oil
(b) Aromatic Amine AO
(c) Dithiocarbamate AW
Rust Inhibitor
Corrosion Inhibitor I
Alkylated Phenol AO
Additive Package E
Additive Package G

<table>
<thead>
<tr>
<th>Additive</th>
<th>Ex 2-17 COMP</th>
<th>Ex 2-18 INV</th>
<th>Ex 2-19 COMP</th>
<th>Ex 2-20 COMP</th>
<th>Ex 2-21 COMP</th>
<th>Ex 2-22 COMP</th>
<th>Ex 2-23 COMP</th>
<th>Ex 2-24 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
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</tr>
<tr>
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<td>0.25</td>
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<td>0.40</td>
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</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
<td>0.05</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

Additive

<table>
<thead>
<tr>
<th>Additive</th>
<th>Ex 2-17 COMP</th>
<th>Ex 2-18 INV</th>
<th>Ex 2-19 COMP</th>
<th>Ex 2-20 COMP</th>
<th>Ex 2-21 COMP</th>
<th>Ex 2-22 COMP</th>
<th>Ex 2-23 COMP</th>
<th>Ex 2-24 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
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</tr>
<tr>
<td>0.21</td>
<td>0.21</td>
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<tr>
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<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>1:1</td>
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<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td></td>
</tr>
</tbody>
</table>

***Table 2c - Summary of Formulations and Results for Example Set 2***

<table>
<thead>
<tr>
<th>Additive</th>
<th>Ex 2-17 COMP</th>
<th>Ex 2-18 INV</th>
<th>Ex 2-19 COMP</th>
<th>Ex 2-20 COMP</th>
<th>Ex 2-21 COMP</th>
<th>Ex 2-22 COMP</th>
<th>Ex 2-23 COMP</th>
<th>Ex 2-24 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

**RBOT Results (min)**

<table>
<thead>
<tr>
<th></th>
<th>Ex 2-17 COMP</th>
<th>Ex 2-18 INV</th>
<th>Ex 2-19 COMP</th>
<th>Ex 2-20 COMP</th>
<th>Ex 2-21 COMP</th>
<th>Ex 2-22 COMP</th>
<th>Ex 2-23 COMP</th>
<th>Ex 2-24 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
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<td>balance</td>
</tr>
<tr>
<td>4057</td>
<td>4339</td>
<td>2384</td>
<td>1985</td>
<td>1498</td>
<td>2452</td>
<td>3689</td>
<td>3316</td>
<td></td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Examples 2-9 to 2-16 use the same base oil mixture used in Examples 2-2 to 2-8, described above.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package E is a combination of conventional additives, and includes a polyether corrosion inhibitor, an ester copolymer antiFoam agent, a substituted triazole corrosion inhibitor, mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts, a substituted thiadiazole that does not contain an aromatic ring in its structure, and diluent oil.
6 - Additive Package F is the same as Additive Package E except there are no substituted thiadiazole that does not contain an aromatic ring in its structure present in the additive package.
7 - Additive Package G is the same as Additive Package E except there are no substituted thiadiazole that does not contain an aromatic ring in its structure present in the additive package and the additive package further includes a phosphite antiwear agent.
8 - Additive Package H is the same as Additive Package G except it further contains a substituted thiadiazole that does not contain an aromatic ring in its structure.
9 - Additive Package I is the same as Additive Package F except it further contains a substituted thiadiazole that does not contain an aromatic ring in its structure.

Table 2d - Summary of Formulations and Results for Example Set 2

<table>
<thead>
<tr>
<th></th>
<th>Ex 2-25 COMP</th>
<th>Ex 2-26 COMP</th>
<th>Ex 2-27 INV</th>
<th>Ex 2-28 INV</th>
<th>Ex 2-29 INV</th>
<th>Ex 2-30 INV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion Inhibitor I</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package F</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package K</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (b) &amp; (c) Wt %</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>3139</td>
<td>1786</td>
<td>2960</td>
<td>3503</td>
<td>2037</td>
<td>3309</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Examples 2-25 to 2-30 use the same base oil mixture used in Examples 2-2 to 2-8, described above.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package F is the same as that described in footnote 9 of Table 2c above.
6 - Additive Package J is the same as Additive Package I except that the package does not contain a substituted thiadiazole, and the package further contains an alkenyl phosphate antiwear additive.
7 - Additive Package K is the same as Additive Package K except it further contains a substituted thiadiazole that does not contain an aromatic ring in its structure.

[0105] The results show that various embodiments of the invention provide good performance when used in combination with numerous additive packages. The data shows that good performance (which in some instances may be defined as having RBOT result of more than 2000 min) is difficult to maintain at lower values of component (b), but when the features of the present invention are present in the examples, consistent good performance is seen across various embodiments, including examples that contain different additive packages, that are formulated in different base oils, that have different overall treat rates (so long as the features of the invention are met), and so forth.

Example Set 3

[0106] A third example set of compositions is prepared and tested to evaluate their oxidative and thermal stability, again using the RBOT test described above. The formulations of these examples, particularly the additional additives present
vary widely. The formulations of these examples and the results obtained are summarized in the tables below. It is noted that the relative amounts of the individual additives listed in each additive package may vary slightly from example to example, but all of the additives listed in a given additive package are present in each example indicated and in comparable amounts.

### Table 3a - Summary of Formulations and Results for Example Set 3

<table>
<thead>
<tr>
<th></th>
<th>Ex 3-1 COMP</th>
<th>Ex 3-2 COMP</th>
<th>Ex 3-3 COMP</th>
<th>Ex 3-4 COMP</th>
<th>Ex 3-5 COMP</th>
<th>Ex 3-6 COMP</th>
<th>Ex 3-7 COMP</th>
<th>Ex 3-8 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil²</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>0.20</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td>0.50</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
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</tr>
<tr>
<td>Corrosion Inhibitor I³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package L⁵</td>
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<tr>
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</tr>
<tr>
<td>Total of (b) &amp; (c) Wt %</td>
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<td>1.00</td>
<td>0.45</td>
<td>0.50</td>
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</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
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<td>1:1</td>
<td>1:1</td>
<td>1:1:25</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>640</td>
<td>2376</td>
<td>1835</td>
<td>2427</td>
<td>2435</td>
<td>1592</td>
<td>1871</td>
<td>577</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Example 3-1 to 3-8 all use the same base oil, a mixture of a 530N Group II base oil and a Group II base oil from Petro-Canada.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package L is a combination of conventional additives including a polyether corrosion inhibitor, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts, fatty acid friction modifier, and diluent oil.
6 - Additive Package M is the same as Additive Package L except it does not include a fatty acid friction modifier, while it further includes a substituted thiadiazole that does not contain an aromatic ring in its structure and an amine-containing friction modifier.
7 - Additive Package N is the same as Additive Package L except it does not include the polyether corrosion inhibitor or fatty acid friction modifier, but it further includes another polyether additive.
8 - Additive Package O is the same as Additive Package M except that it does not include amine-containing friction modifier, while it does include fatty acid friction modifier.

### Table 3b - Summary of Formulations and Results for Example Set 3

<table>
<thead>
<tr>
<th></th>
<th>Ex 3-9 COMP</th>
<th>Ex 3-10 COMP</th>
<th>Ex 3-11 COMP</th>
<th>Ex 3-12 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil²</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion Inhibitor I³</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO⁴</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package L⁵</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package O⁸</td>
<td>0.30</td>
<td>0.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total of (b) &amp; (c) Wt %</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>1511</td>
<td>741</td>
<td>1023</td>
<td>958</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Example 3-1 to 3-8 all use the same base oil, a mixture of a 530N Group II base oil and a Group II base oil from Petro-Canada.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package L is the same as that described in footnote 5 of Table 3a above.
6 - Additive Package O is the same as that described in footnote 8 of Table 3a above.

[0107] The results again show that various embodiments of the invention provide good performance when used in combination with numerous additive packages. The data shows that good performance (which in some instances may be defined as having RBOT result of more than 2000 min) is difficult to maintain at lower values of component (b), but when the features of the present invention are present in the examples, consistent good performance is seen across various embodiments, including examples that contain different additive packages, that are formulated in different base oils, that have difference overall treat rates (so long as the features of the invention are met), and so forth.

**Example Set 4**

[0108] A fourth example set of compositions is prepared and tested to evaluate their oxidative and thermal stability, again using the RBOT test described above. The formulations of these examples, particularly the additional additives present vary widely. The formulations of these examples and the results obtained are summarized in the tables below. It is noted that the relative amounts of the individual additives listed in each additive package may vary slightly from example to example, but all of the additives listed in a given additive package are present in each example indicated and in comparable amounts.

**Table 4a - Summary of Formulations and Results for Example Set 4**

<table>
<thead>
<tr>
<th></th>
<th>Ex 4-1 COMP</th>
<th>Ex 4-2 COMP</th>
<th>Ex 4-3 COMP</th>
<th>Ex 4-4 COMP</th>
<th>Ex 4-5 COMP</th>
<th>Ex 4-6 COMP</th>
<th>Ex 4-7 COMP</th>
<th>Ex 4-8 COMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Base Oil²</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.20</td>
<td>0.30</td>
<td>0.10</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.20</td>
<td>0.10</td>
<td>0.30</td>
<td>0.20</td>
<td>0.25</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Corrosion Inhibitor I²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkylated Phenol AO²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package B³</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package P⁶</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package Q⁷</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive Package R⁷</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
</tr>
<tr>
<td>Total of (b) &amp; (c) Wt %</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:0.33</td>
<td>1:3</td>
<td>1:1</td>
<td>1:1</td>
<td></td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>1490</td>
<td>1326</td>
<td>612</td>
<td>1168</td>
<td>635</td>
<td>592</td>
<td>803</td>
<td>1610</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Examples 4-1 to 4-8 all use the same base oil, a mixture of two Group II base oils, different from those used above.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant.
5 - Additive Package B is the same as that described in footnote 6 of Table 2a above.
6 - Additive Package P is the same as Additive Package B except it does not include the polyether corrosion inhibitor, while if further includes a different polyether additive.
7 - Additive Package Q is the same as Additive Package B if further includes an amine containing friction modifier.
8 - Additive Package R is the same as Additive Package P except it does not include the mixtures of phosphoric and/or dithiophosphoric acid esters and amine salts.

**Table 4b - Summary of Formulations and Results for Example Set 4**

<table>
<thead>
<tr>
<th>(a) Base Oil</th>
<th>Ex 4-9 COMP</th>
<th>Ex 4-10 COMP</th>
<th>Ex 4-11 COMP</th>
<th>Ex 4-12 COMP</th>
<th>Ex 4-13 COMP</th>
<th>Ex 4-14 COMP</th>
<th>Ex 4-15 INY</th>
<th>Ex 4-16 INY</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>(b) Aromatic Amine AO</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.375</td>
<td>0.375</td>
</tr>
<tr>
<td>(c) Dithiocarbamate AW</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Rust Inhibitor</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>Corrosion Inhibitor I</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Alkylated Phenol AO</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Additive Package R</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Additive Package S</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>Additive Package T</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>Additive Package U</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
</tr>
<tr>
<td>Additive Package W</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>Total of (b) &amp; (c) Wt %</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
<td>0.875</td>
<td>0.875</td>
</tr>
<tr>
<td>Weight Ratio of (b) &amp; (c)</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
<td>1:1</td>
</tr>
<tr>
<td>RBOT Results (min)</td>
<td>1493</td>
<td>1805</td>
<td>2914</td>
<td>1249</td>
<td>1195</td>
<td>3717</td>
<td>4875</td>
<td>6473</td>
</tr>
</tbody>
</table>

1 - All formulation values in the table are weight percent values relative to the overall composition.
2 - The base oil component makes up the balance of each composition. Examples 4-11 to 4-14 all use the same base oil, a mixture of two Group II base oils, different from those used above.
3 - Corrosion Inhibitor I is a substituted thiadiazole that contains an aromatic ring in its structure as a substituent group. It is the only corrosion inhibitor with such a group present in these examples.
4 - An alkylated phenol is present in some compositions as a secondary antioxidant. The alkylated phenol in the examples in this table has a different alkyl group than that used in the examples above.
5 - Additive Package R is the same as that described in footnote 8 of Table 4a above.
6 - Additive Package S is a combination of conventional additives including a polyether corrosion inhibitor, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, a salicylic acid based detergent, and diluent oil.
7 - Additive Package T is the same as Additive Package R, described in footnote 8 of Table 4a above, except that it further includes a polyether amine.
8 - Additive Package U is the same as Additive Package T, except that it further includes a salicylic acid based detergent.
Additive Package V is a combination of conventional additives including an antiwear additive containing a mixture of phosphoric acid ester and/or amine salts thereof, an ester copolymer antifoam agent, a substituted triazole corrosion inhibitor, a polyether additive, and an alkyl benzene.

Additive Package W is the same as Additive Package V except that it does not include the mixture of phosphoric acid ester and/or amine salts thereof.

Examples 4-15 and 4-16 use a different aromatic amine AO than the previous examples. Both materials are aromatic amine antioxidants, just different specific examples of such materials, and so show that the specific identity of the aromatic amine antioxidant used is not critical.

The results again show that various embodiments of the invention provide good performance when used in combination with numerous additive packages. The data shows that good performance (which in some instances may be defined as having RBOT result of more than 2000 min) is difficult to maintain at lower values of component (b), but when the features of the present invention are present in the examples, consistent good performance is seen across various embodiments, including examples that contain different additive packages, that are formulated in different base oils, that have difference overall treat rates (so long as the features of the invention are met), and so forth.

While the invention has been explained, 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.

In this specification the terms "hydrocarbyl substituent" or "hydrocarbyl group," as used herein are used in their ordinary sense, which is well-known to those skilled in the art. Specifically, they refer to a group primarily composed of carbon and hydrogen atoms that is attached to the remainder of the molecule through a carbon atom and does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the molecule having a predominantly hydrocarbon character. In general, no more than two, preferably 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. A more detailed definition of the terms "hydrocarbyl substituent" or "hydrocarbyl group," is described in US Patent 6, 583,092.

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, all percent and formulation values listed herein are on a weight basis. 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, 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 can be used together with ranges or amounts for any of the other elements. As used herein, the expression "consisting essentially of" permits the inclusion of substances that do not materially affect the basic and novel characteristics of the composition under consideration.
What is claimed is:

1. A composition comprising:
   a) an oil of lubricating viscosity;
   b) an aromatic amine antioxidant; and
   c) a dithiocarbamate antiwear agent;

   wherein component b) is present from 0.35 to 0.75 percent by weight, component c) is present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) is from 0.60 to 1.25 percent by weight, with regards to the overall composition;

   wherein the composition is an industrial lubricant.

2. The composition of claim 1 further comprising: an antioxidant other than component b); an antiwear agent other than component c); a corrosion inhibitor, a rust inhibitor, a foam inhibitor, a dispersant, a demulsifier, a metal deactivator, a friction modifier, a detergent, a demulsifier, an extreme pressure agent, a pour point depressant, a viscosity modifier, or any combination thereof.

3. The composition of any of the claims 1 to 2 wherein component a) comprises a Group I base oil, a Group II base oil, a Group III base oil, a poly(alpha-olefm), a GTL oil, or any combination thereof.

4. The composition of any of the claims 1 to 3 wherein component b) comprises an alkylated diphenylamine, a phenyl-naphthylamine, an alkylated phenyl-naphthylamine, or a combination thereof; and

   wherein component c) comprises an ashless dithiocarbamate.

5. The composition of any of the claims 1 to 4 wherein component b) is present from about 0.4 to about 0.7 percent by weight in the overall composition; and component c) is present from about 0.3 to 0.7 percent by weight in the overall composition; and wherein the total weight percent of the combination of
components b) and c) is from 0.8 to 1.2 percent by weight, with regards to the overall composition.

6. The composition of any of the claim 1 to 5 wherein component a) comprises a Group I base oil, a Group II base oil, a Group III base oil, or any combination thereof and is present from about 95 to about 99.9 percent by weight of the overall composition;

   wherein component b) comprises an alkylated diphenylamine and is present from about 0.4 to about 0.7 percent by weight in the overall composition;
   wherein component c) comprises a dithiocarbamate ester and is present from about 0.3 to about 0.7 percent by weight in the overall composition;
   wherein the total weight percent of the combination of components b) and c) is from 0.8 to 1.2 percent by weight, with regards to the overall composition;
   wherein the composition further comprises d) an antioxidant other than component b) that is present from about 0.01 to about 5.0 percent by weight of the overall composition;
   wherein the composition further comprises e) an antiwear additive other than component c) that is present from about 0.01 to about 2.5 percent by weight of the overall composition;
   wherein the composition further comprises f) a corrosion inhibitor or metal deactivator that is present from about 0.001 to about 2.0 percent by weight of the overall composition;
   wherein the composition further comprises g) a rust inhibitor, wherein component f) and component g) are different additives, where component g) is present from about 0.001 to about 2.0 percent by weight of the overall composition;
   wherein the composition further comprises h) an antifoam additive that is present from about 0.01 to about 3.0 percent by weight of the overall composition.

7. The composition of claim 6 wherein component d) comprises a sulfurized olefin;

   wherein component e) comprises an amine phosphate;
wherein component f) comprises a triazole, a tolyltriazole, or combinations thereof;

wherein component g) comprises a polyether, a fatty carboxylic acid or ester thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, or combinations thereof;

wherein component h) comprises an acrylate copolymer.

8. The composition of any of the claims 1 to 7 wherein component b), the aromatic amine antioxidant, comprises an alkylated diphenylamine represented by the formula:

\[
\begin{align*}
  &\text{NH} \\
  &\text{(R\textsuperscript{1})}_q - \text{H} - \text{(R\textsuperscript{2})}_r \\
  &\text{R\textsuperscript{1}} \text{ and } \text{R\textsuperscript{2}} \text{ are independently a hydrogen or an alkyl group containing about 5 to 20 carbon atoms; or a linear or branched alkyl group containing 1 to 24 carbon atoms and } q \text{ and } r \text{ are each independently 0, 1, 2, or 3, provided that the sum of } q \text{ and } r \text{ is at least one.}
\end{align*}
\]

9. The composition of any of the claims 1 to 8 wherein component c), the dithiocarbamate antiwear agent, comprises a dithiocarbamate ester represented by the formula:

\[
\begin{align*}
  &\text{R\textsuperscript{3}} - \text{N} - \text{S} - \text{C(Z)}_a \\
  &\text{R\textsuperscript{4}} \text{ and } \text{R\textsuperscript{5}} \text{ are independently H, alkyl, aralkyl or -C(=0)-Y wherein Y is -H, -OH, or -R\textsuperscript{8} where R\textsuperscript{8} is}
\end{align*}
\]

\[
\begin{align*}
  &\text{ wherein } \text{R\textsuperscript{3}} \text{ and } \text{R\textsuperscript{4}} \text{ are independently alkyl of 1 to about 7 carbons, aryl, aralkyl or together form an alicyclic or heteroalicyclic radical in which the ring is completed through the nitrogen; } X \text{ is O or S; a is 1 or 2; R\textsuperscript{5} and R\textsuperscript{6} are independently H, alkyl or aryl; and Z is -CN, -S(=0)-R\textsuperscript{7}, -S(=0)(=0)-R\textsuperscript{7}, or -S(=0)(=0)-0-R\textsuperscript{7}, wherein R\textsuperscript{7} is hydrogen, alkyl, aralkyl, or -C(=0)-Y wherein Y is -H, -OH, or -R\textsuperscript{8} where R\textsuperscript{8} is}
\end{align*}
\]

\[
\begin{align*}
  &\text{wherein } \text{component f comprises a triazole, a tolyltriazole, or combinations thereof;}
\end{align*}
\]

\[
\begin{align*}
  &\text{wherein component g comprises a polyether, a fatty carboxylic acid or ester thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazoline, or combinations thereof;}
\end{align*}
\]

\[
\begin{align*}
  &\text{wherein component h comprises an acrylate copolymer.}
\end{align*}
\]

\[
\begin{align*}
  &8. \text{ The composition of any of the claims 1 to 7 wherein component b), the aromatic amine antioxidant, comprises an alkylated diphenylamine represented by the formula:}
\end{align*}
\]

\[
\begin{align*}
  &\text{wherein } \text{R\textsuperscript{1}} \text{ and } \text{R\textsuperscript{2}} \text{ are independently a hydrogen or an alkyl group containing about 5 to 20 carbon atoms; or a linear or branched alkyl group containing 1 to 24 carbon atoms and } q \text{ and } r \text{ are each independently 0, 1, 2, or 3, provided that the sum of } q \text{ and } r \text{ is at least one.}
\end{align*}
\]

\[
\begin{align*}
  &9. \text{ The composition of any of the claims 1 to 8 wherein component c), the dithiocarbamate antiwear agent, comprises a dithiocarbamate ester represented by the formula:}
\end{align*}
\]

\[
\begin{align*}
  &\text{wherein } \text{R\textsuperscript{3}} \text{ and } \text{R\textsuperscript{4}} \text{ are independently alkyl of 1 to about 7 carbons, aryl, aralkyl or together form an alicyclic or heteroalicyclic radical in which the ring is completed through the nitrogen; } X \text{ is O or S; a is 1 or 2; R\textsuperscript{5} and R\textsuperscript{6} are independently H, alkyl or aryl; and Z is -CN, -S(=0)-R\textsuperscript{7}, -S(=0)(=0)-R\textsuperscript{7}, or -S(=0)(=0)-0-R\textsuperscript{7}, wherein R\textsuperscript{7} is hydrogen, alkyl, aralkyl, or -C(=0)-Y wherein Y is -H, -OH, or -R\textsuperscript{8} where R\textsuperscript{8} is}
\end{align*}
\]
alkyl, aryl, aralkyl, -O-R^8, -0-R^9-OH, where R^9 is alkylene of 1 to about 7 carbon atoms, or -NR^{10}R^{11} where R^{10} and R^{11} are independently hydrogen, alkyl, cycloaliphatic, heteroalicyclic or together form an alicyclic or heteroalicyclic radical in which the ring is completed through the nitrogen; with the proviso that when a is 1, Y is not -O-R^8.

10. The composition of any of the claims 6 to 9 wherein component d), the additional antioxidant, comprises a substituted hydrocarbyl mono-sulfide represented by the formula:

\[
\begin{align*}
\text{R}^6 & \quad \text{S} \quad \text{C} \quad \text{C} \quad \text{OH} \\
\text{R}^7 & \quad \text{R}^8 \\
\text{R}^{10} & \quad \text{R}^9
\end{align*}
\]

wherein R^6 is a saturated or unsaturated branched or linear alkyl group with about 8 to about 20 carbon atoms; R^7, R^8, R^9 and R^{10} are independently hydrogen or alkyl containing about 1 to about 3 carbon atoms.

11. A process to prepare an industrial lubricant composition comprising the steps of: (I) mixing together:

a) an oil of lubricating viscosity;

b) an aromatic amine antioxidant; and

c) a dithiocarbamate antiwear agent; and optionally one or more additional additives;

wherein component b) is present from 0.5 to 0.75 percent by weight, component c) is present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) is from 0.75 to 1.25 percent by weight, with regards to the overall composition.

12. The process of claim 11 wherein component a) comprises a Group I base oil, a Group II base oil, a Group III base oil, or any combination thereof and is present from about 95 to about 99.9 percent by weight of the overall composition;
wherein component b) comprises an alkylated diphenylamine and is present from about 0.4 to about 0.7 percent by weight in the overall composition;

wherein component c) comprises a dithiocarbamate ester and is present from about 0.3 to about 0.7 percent by weight in the overall composition;

wherein the total weight percent of the combination of components b) and c) is from 0.8 to 1.2 percent by weight, with regards to the overall composition;

wherein the composition further comprises d) an antioxidant other than component b) that is present from about 0.01 to about 5.0 percent by weight of the overall composition;

wherein the composition further comprises e) an antiwear additive other than component c) that is present from about 0.01 to about 2.5 percent by weight of the overall composition;

wherein the composition further comprises f) a corrosion inhibitor or metal deactivator that is present from about 0.001 to about 2.0 percent by weight of the overall composition;

wherein the composition further comprises g) a rust inhibitor, wherein component f) and component g) are different additives, where component g) is present from about 0.001 to about 2.0 percent by weight of the overall composition;

wherein the composition further comprises h) an antifoam additive that is present from about 0.01 to about 3.0 percent by weight of the overall composition.

13. The process of claim 12 wherein component d) comprises a sulfurized olefin;
wherein component e) comprises an amine phosphate;
wherein component f) comprises a triazole, a tolyltriazole, or combinations thereof;

wherein component g) comprises a polyether, a fatty carboxylic acid or ester thereof, an ester of a nitrogen-containing carboxylic acid, an ammonium sulfonate, an imidazolines, or combinations thereof;

wherein component h) comprises an acrylate copolymer.

14. A method of lubricating a turbine system comprising the steps:
   I. supplying to a turbine system a lubricating composition comprising:
a) an oil of lubricating viscosity;

b) an aromatic amine antioxidant; and

c) a dithiocarbamate antiwear agent;

wherein component b) is present from 0.5 to 0.75 percent by weight, component c) is present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) is from 0.75 to 1.25 percent by weight, with regards to the overall composition.

15. A method of lubricating a hydraulic system comprising the steps:

I. supplying to a turbine system a lubricating composition comprising:

a) an oil of lubricating viscosity;

b) an aromatic amine antioxidant; and

c) a dithiocarbamate antiwear agent;

wherein component b) is present from 0.5 to 0.75 percent by weight, component c) is present from 0.25 to 0.75 percent by weight, and the total weight percent of the combination of components b) and c) is from 0.75 to 1.25 percent by weight, with regards to the overall composition.
## A. CLASSIFICATION OF SUBJECT MATTER

**INV.** C10M141/08  C10M161/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CIOM

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP 2 248 876 Al (IDEMITSU KOSAN CO [JP]) 10 November 2010 (2010-11-10) paragraph [0038] - paragraph [0048]; examples 1, comp. ex. 3; table 1</td>
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<td>EP 0 994 175 A2 (ETHYL CORP [US]) 19 April 1 2000 (2000-04-19) paragraph [0039] - paragraph [0050]; claims 1-5, 9, 12, 14, 22, 25; tables 1, 2; figure 1</td>
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Date of the actual completion of the international search: 2 August 2012

Date of mailing of the international search report: 28/09/2012

Name and mailing address of the ISA:

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Fax. (+31-70) 340-3016

Authorized officer: Pohlmann, Klaus
### DOCUMENTS CONSIDERED TO BE RELEVANT

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