LONG LIFE LUBRICATING OIL WITH ENHANCED OXIDATION AND NITRATION RESISTANCE

Inventor: Stanley James Cartwright, Sarnia (CA)

Correspondence Address:
ExxonMobil Research and Engineering Company
P.O. Box 900
Annandale, NJ 08801-0900 (US)

Related U.S. Application Data

Provisional application No. 60/419,745, filed on Oct. 18, 2002.

Publication Classification

Int. Cl. 7 ........................................... C10M 159/20
U.S. Cl. ......................... 508/364; 508/363; 508/444;
................................. 508/443; 508/391; 508/460

Abstract

A long life lubricating oil, as evidenced by a reduction in oil thickening, oxidation and nitration, comprises a major amount of a base oil of lubricating viscosity and a minor amount of a mixture of neutral and overbased metallic detergents and at least one trinuclear molybdenum compound.
LONG LIFE LUBRICATING OIL WITH ENHANCED OXIDATION AND NITRATION RESISTANCE

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] Non-Provisional Application based on Provisional Application No. 60/419,745 filed Oct. 18, 2002.
[0002] This application claims the benefit of U.S. Provisional Application No. 60/419,745 filed Oct. 18, 2002.

FIELD OF INVENTION

[0003] The present invention relates to lubricating oils, especially gas engine oils, having extended life as evidenced by a reduction in viscosity increase, oxidation and nitration.

BACKGROUND OF INVENTION

[0004] Gas fired engines are typically used in the oil and gas industry to drive compressors that compress natural gas at well heads and along pipelines. These engines are large, having up to 16 cylinders and often generate between 500 to 3000 HP. The nature of their use requires them to be able to run continuously near full load conditions, shutting down only for maintenance such as for oil changes. Under these operating conditions severe demands are placed on the engine lubricant. Indeed, because the lubricant is subjected to a high temperature environment, the life of the lubricant often is limited by oil oxidation processes. Additionally, natural gas fired engines generate nitrogen oxides (NOx) that can limit lubricant life by oil nitration processes. Therefore, gas engine operators are constantly seeking gas engine oils that have improved resistance to oxidation and nitration.

[0005] In addition to controlling oxidation and nitration properties of a gas engine oil it also is necessary to control the ash content of the oil because the lubricant ashes acts as a solid lubricant protecting the valve/seat interface of the engine. For this reason gas engine oils are classified according to their ash content. The classifications are:

<table>
<thead>
<tr>
<th>Ash Designation</th>
<th>Ash Level, wt % (ASTM D874)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ashless</td>
<td>Ash &lt; 0.1%</td>
</tr>
<tr>
<td>Low Ash</td>
<td>0.1% &lt; Ash &lt; 0.5%</td>
</tr>
<tr>
<td>Medium Ash</td>
<td>0.5% &lt; Ash &lt; 1.5%</td>
</tr>
<tr>
<td>High Ash</td>
<td>Ash &gt; 1.5%</td>
</tr>
</tbody>
</table>

[0006] The ash level of the lubricant often is determined by its formulation components, with metal-containing detergents and metallic-containing antiwear additives contributing to the ash level of the lubricant. Gas engine manufacturers specify the appropriate lubricant ash level for correct operation of a given engine. Thus, manufacturers of 2-cycle engines often specify use of an ashless oil. Manufacturers of 4-cycle engine may specify low, medium or high ash depending upon the level required for engine cleanliness and durability.

[0007] As is known in the art, additives are used in lubricants to perform numerous functions. For example, some are antioxidants, some are friction modifiers; and some are extreme pressure agents. Indeed some additives perform more than one function. Also as is known in the art additives will lose their effectiveness if they are improperly combined. Therefore, extreme care must be exercised in combining various additives to assure both compatibility and effectiveness. For example, some friction modifiers affect metal surfaces differently than antiwear agents do. When both are present, friction-reducing and antiwear additives may compete for the surface of the metal parts which are subject to lubrication. This competition can produce a lubricant that is less effective than is suggested by the individual properties of the additive components.

[0008] Accordingly, the components of a gas engine lubricant need to be selected to meet the specified ash level and to provide, among other functions, a high level of oxidation and nitration resistance. Whether selected components and their amounts can be balanced to meet desired specification is not a priori predictable.

SUMMARY OF INVENTION

[0009] Simply stated the present invention relates to a lubricating oil, especially useful as a gas engine oil, comprising a major amount of a base oil of lubricating viscosity; effective amounts of a mixture of neutral and overbased metallic detergents; and, a minor amount of at least one trinuclear molybdenum compound.

[0010] The lubricant composition of the invention has extended life as evidenced by reductions in oxidation and nitration relative to commercial and reference oils and may also be compatible with other standard additives used in formulating commercial lubricating compositions.

DETAILED DESCRIPTION OF INVENTION

[0011] The lubricant compositions of the present invention include a major amount of a base oil of lubricating viscosity. Suitable base oils include natural and synthetic oils and mixtures thereof in API Categories I, II and III, and having a kinematic viscosity of about 9 to 13 cSt at 100°C.

[0012] The metallic detergent contained in the composition of the invention is a mixture of neutral and overbased metal sulfonates, phenates and alkylsalicylates. The metals may be alkali and alkaline earth metals and preferably are alkaline earth metals, especially calcium and barium. Examples of neutral metallic detergents are calcium sulfonates and calcium alkylsalicylates having a TBN of from 10 to 100. Examples of overbased metallic detergents are calcium phenates, sulphonates and alkylsalicylates having a TBN of 150 to 400. The amount of the neutral and overbased metallic detergent is chosen having regard to the desired TBN of the final product and especially having regard to the desired sulfated ash of the final product. Preferably the mixture of neutral and overbased metallic detergents is sufficient to provide the composition with a sulfated ash in the range of about 0.2 mass % to about 2.0 mass %.

[0013] The compositions of the present invention also include a minor amount of at least one trinuclear molybdenum compound. A preferred trinuclear molybdenum compound is represented by the formula $\text{Mo}_3\text{S}_n\text{L}_m\text{Q}_2$, where $L$ represents independently selected ligands, $n$ varies from 1 to 4, $k$ varies from 4 to 7 and $Q$ is selected from the group consisting of neutral electron donating compounds including...
water, amines, alcohols, phosphines and ethers and \( z \) ranges from 0 to 5. Such compounds and their method of preparation are disclosed in great detail in U.S. Pat. No. 6,232,276 B1 which is incorporated herein by reference. In the present invention, preferably is diethiocarbamate, \( n \) is 4, \( k \) is 7, \( Q \) is an electron-donating compound, and \( z \) is 0. The trinuclear molybdenum compound preferably constitutes from 0.1 vol % to about 2.0 vol % based on the total volume of the total lubricant composition.

[0014] Optionally, the composition may contain an anhless dihydrocarbonyl thio carbamoyl in combination with the trinuclear molybdenum compound.

[0015] Suitable dihydrocarbonylthiocarbamoyl compounds are represented by the formula

\[
\begin{align*}
&\text{R}_1^\text{S} \cdots \text{S} \cdots \text{S} \cdots \text{X} \\
&\text{C} \cdots \text{N} \cdots \text{R}_2^\text{X} \cdots \text{R}_3^\text{X} \\
&\text{X} \text{S}_\text{S}_\text{X} \text{S}_\text{S}_\text{X} \text{S}_\text{S}_\text{X} \\
&\text{R}_1^\text{S} \cdots \text{S} \cdots \text{S} \cdots \text{R}_2^\text{X} \cdots \text{R}_3^\text{X} \\
&\text{R}_1^\text{S} \cdots \text{S} \cdots \text{S} \cdots \text{R}_2^\text{X} \cdots \text{R}_3^\text{X}
\end{align*}
\]

where \( \text{R}_1, \text{R}_2, \text{R}_3 \), and \( \text{R}_4 \) are the same or different and each represents an alkyl group of 3 to 30 carbon atoms, \( \text{X} \) represents \( \text{S}, \text{S} \), \( \text{S}(\text{CH}_2)_2 \), \( \text{S} \cdots \text{CH}_2 \text{CH}(\text{CH}_3) \cdots \text{S} \) and \( \text{X} \) is an integer of 1 to 3.

[0017] Preferably the combined materials will constitute from about 0.1 vol % to about 2.0 vol % based on the volume of the total lubricant composition; however, the amount of dihydrocarbonyl thiocarbamoyl will not exceed about 1.90 vol %.

[0018] The fully formulated oil may contain additional, typical additives known to those skilled in the industry, used on an as-received basis.

[0019] Thus, the fully formulated oil may contain dispersants of the type generally represented by succinimides (e.g., polyisobutylene succinic acid/anhydride (PIBSA-polymamine having a PIB moiety molecular weight of about 700 to 2500). The dispersants may be borated or nonborated. The dispersant can be present in the amount of about 0.5 to 8 vol %, more preferably in the amount of about 1 to 6 vol %, most preferably in the amount of about 2 to 4 vol %.

[0020] Antioxidants may be of the phenol (e.g., o,o’diteritary alkyl phenol such as ditertbutyl phenol), or amine (e.g., dialkyl diphenyl amine such as dibutyl, octyl buty, or diocyl diphenyl amine) type, or mixtures thereof. More preferably, the antioxidants will be hindered phenols, or aryl amines which may or may not be sulfurized. Antioxidants can be present in the amount of about 0.05 to 2.0 vol %, more preferably in the amount of about 0.1 to 1.75 vol %, most preferably in the amount of about 0.5 to 1.5 vol %.

[0021] Metal deactivators may be of the aryl thiazines, triazoles, or alkyl substituted dimercaptobithiazoles (DMDT’s), or mixtures thereof. Metal deactivators can be present in the amount of about 0.01 to 0.2 vol %, more preferably in the amount of about 0.02 to 0.15 vol %, most preferably in the amount of about 0.05 to 0.1 vol %.

[0022] Antiwear additives such as metal dithiophosphates (e.g., zinc dialkyl dithiophosphate, ZDDP), metal dithiocarbamates, metal xanthates or tricreethylphosphates may be included. Antiwear additives can be present in the amount of about 0.05 to 1.5 vol %, more preferably in the amount of about 0.1 to 1.0 vol %, most preferably in the amount of about 0.2 to 0.5 vol %.

[0023] Pour point depressants such as poly(meth)acrylates, or alkyl-aromatic polymers may be included. Pour point depressants can be present in the amount of about 0.05 to 0.6 vol %, more preferably in the amount of about 0.1 to 0.4 vol %, most preferably in the amount of about 0.2 to 0.3 vol %.

[0024] Antifoamants such as silicone antifoaming agents can be present in the amount of about 0.001 to 0.2 vol %, more preferably in the amount of about 0.005 to 0.15 vol %, most preferably in the amount of about 0.01 to 0.1 vol %.

[0025] Viscosity Index Improvers (VI’s) may be any polymer which imparts multifunctional viscosity properties to the finished oil, including materials such as olefin copolymers, polymethylacrylates, styrene diene block copolymers, and star copolymers. The VI’s may also be multifunctional from the perspective of offering secondary lubricant performance features such as additional dispersancy. VI’s can be present in the amount of up to 15 vol %, more preferably in the amount of up to 13 vol %, most preferably in the amount of up to 10 vol %.

[0026] Lubricating oil additives are described generally in “Lubricants and Related Products” by Dieter Klamann, Verlag Chemie, Deerfield, Fla., 1984, and also in “Lubricant Additives” by C. V. Smallheer and R. Kennedy Smith, 1967, pages 1-11, the disclosures of which are incorporated herein by reference.

[0027] The present invention is further described in the following non-limiting examples and comparative examples.

EXPERIMENTAL

A. Lab Nitration Screen Test Results

[0028] A lab nitration screen test was used to assess the oil life performance of various oil compositions. The test results identify a number of parameters including oil viscosity increase, oxidation, and nitration. All measurements are reported on a relative basis (unless otherwise indicated) so that results greater than unity represent greater levels of degradation. Numerically lower relative results represent a measure of longer oil life. In each test, a Reference Oil is tested and results are reported as a ratio of the result for the test oil divided by the result for the Reference Oil. Thus, if a tested oil has an oxidation result of 1.0, then it has oxidation performance equal to that of the Reference Oil. If the tested oil has an oxidation result less than 1.0, then the tested oil demonstrates oxidation performance superior to that of the Reference Oil.

EXAMPLES AND COMPARATIVE EXAMPLES

[0029] In the Examples, the base oil in all cases was a heavy Group II basestock. Comparative Oil 1, Reference Oil 1 and Examples 1 and 2 contained the same viscosity index improver (VI). Comparative Oil 2 is a current commercial oil based solely on API Group II basestocks. Reference Oil 1 and Example Oils 1 and 2 each contained the same mixture
of neutral and overbased metallic detergents, ashless dispersant, ZDDP, pour point depressant, metal passivator and anti-foamant. Reference Oil 1, however, employed a phenolic antioxidant whereas the oils of Examples 1 and 2 employed a trinuclear molybdenum compound, Mo₂S₆(DTC)x, and a mixture of a trinuclear molybdenum compound, Mo₂S₆(DTC)y, and an ashless dihydrocarbyl thiocarbamoyl, (S-CNR)_z CH₂, respectively. Comparative Oil 1 used a commercially available gas engine oil additive package, Oloa 1255 sold by Chevron Chemical Company. Oloa 1255 is one of the most widely sold gas engine oil packages and therefore represents a "benchmark standard" against which other engine oil formulations may be measured.

The results show that the oils of the present invention, Examples 1 and 2, provided superior performance to both of the Comparative oils and the Reference Oil, in terms of reduced oxidation, nitration and viscosity increase. The invention examples provided superior oil life despite the absence of conventional aminic and phenolic antioxidants. The small negative normalized viscosity increase values for the invention examples simply reflect that there was no significant change in viscosity, unlike the Comparative and Reference oils.

### TABLE 1

<table>
<thead>
<tr>
<th>Component (vol %)</th>
<th>Comparative Oil 1</th>
<th>Reference Oil 1</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Comparative Oil 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group II basestock</td>
<td>87.90</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>—</td>
</tr>
<tr>
<td>NCEO commercial additive package</td>
<td>9.6</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>VI Phenolic antioxidant</td>
<td>1.00</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Moly trimer</td>
<td>—</td>
<td>—</td>
<td>1.00</td>
<td>1.00</td>
<td>—</td>
</tr>
<tr>
<td>Ashless dihydrocarbyl thiocarbamoyl</td>
<td>—</td>
<td>—</td>
<td>0.50</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Balance of additives</td>
<td>1.00</td>
<td>9.00</td>
<td>9.00</td>
<td>9.00</td>
<td>—</td>
</tr>
<tr>
<td>Commercial Oil Properties</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>100.00</td>
</tr>
<tr>
<td>KV, cSt @ 100° C.</td>
<td>13.25</td>
<td>13.14</td>
<td>13.20</td>
<td>13.13</td>
<td>13.51</td>
</tr>
<tr>
<td>Test Results</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nitration Screener Test</td>
<td>1.76</td>
<td>1.00</td>
<td>0.86</td>
<td>0.79</td>
<td>1.57</td>
</tr>
<tr>
<td>Nitration (relative)</td>
<td>1.55</td>
<td>1.00</td>
<td>1.15</td>
<td>0.91</td>
<td>1.48</td>
</tr>
<tr>
<td>Viscosity Increase (relative)</td>
<td>1.70</td>
<td>1.00</td>
<td>-0.16</td>
<td>-0.12</td>
<td>0.73</td>
</tr>
</tbody>
</table>

What is claimed is:

1. A lubricating composition comprising:
   - a major amount of an oil of lubricating viscosity;
   - a mixture of neutral and overbased metallic detergents;
   - and a minor amount of at least one trinuclear molybdenum compound.

2. The composition of claim 1 wherein the trinuclear molybdenum compound is represented by the formula Mo₂S₆L₁₂O₉, where L is an independently selected ligand, n is from 1 to 4, k is from 4 to 7, Q is a neutral electron donating moiety and z is from 0 to 5.

3. The composition of claim 2 wherein the neutral and overbased metallic detergents are selected from the group consisting of alkali and alkaline earth metal sulfonates, phenates, alkylsalicylates and mixtures thereof.

4. The composition of claim 3 wherein the amount of detergents is sufficient to provide the composition with a sullated ash content in the range of about 0.2 wt % to about 2 wt %.

5. The composition of claim 4 wherein the trinuclear molybdenum compound constitutes from about 0.1 vol % to about 2.0 vol % based on the volume of the total lubricant composition.

6. The composition of claim 5 including a minor amount of a dihydrocarbyl thiocarbamoyl compound.

7. The composition of claim 6 wherein the dihydrocarbyl thiocarbamoyl compound has the formula

![Chemical Structure]

Where R₁, R₂, R₃ and R₄ are the same or different alkyl groups of from 3 to 30 carbon atoms; X is S, S—S, S—CH₂—S—CH₂—CH₂—S, —CH₂(CH₂)n—S—; and y is an integer of 1 to 3.

8. A lubricating oil composition comprising:
   - a major amount of an oil of lubricating viscosity;
   - a mixture of neutral and overbased metallic detergents selected from the group consisting essentially of alkali earth metal sulfonates, phenates, alkylsalicylates and mixtures thereof in an amount sufficient to provide the composition with a sulfated ash content of from about 0.2 wt % to about 2.0 wt %;
   - a trinuclear molybdenum compound having the formula Mo₂S₆L₁₂O₉.
where \( L \) is an independently selected ligand, \( n \) is from 1 to 4, \( k \) is from 4 to 7, \( Q \) is a neutral electron donating moiety, and \( z \) is from 0 to 5;

from 0 to 2.0 vol \% of a dihydrocarbonyl thiocarbamoyl compound having the formula;

\[
\begin{align*}
R_1 & \equiv S \quad S \quad R_3 \\
\equiv C \equiv (X) \equiv C \equiv N \\
R_2 & \equiv R_4
\end{align*}
\]

where \( R_1, R_2, R_3 \) and \( R_4 \) are the same or different alkyl groups of from 3 to 30 carbon atoms; \( X \) is \( S, S \equiv S, S \equiv (CH_2)_2S, S \equiv CH_2CH_2(CH_3) \equiv S \), and \( y \) is an integer of 1 to 3;

the amount of trinuclear molybdenum compound and dihydrocarbonyl thiocarbamoyl compound being in the range of about 0.1 vol \% to about 2.0 vol \%.

9. A method for enhancing the life of a lubricating oil as evidenced by a reduction in viscosity increase, oxidation and nitration, the method comprising:

adding to the lubricating oil additives comprising:

a mixture of neutral and overbased metallic detergents selected from the group consisting essentially of alkali earth metal sulfonates, phenates, alkylsalicylates, and mixtures thereof in an amount sufficient to provide the composition with a sulfated ash content of from about 0.2 wt \% to about 2.0 wt \%;

at least 0.1 vol \% of a trinuclear molybdenum compound having the formula

\[
Mo_S_6L_3O_x
\]

Where \( L \) is an independently selected ligand, \( n \) is 1 to 4, \( k \) is 4 to 7, \( Q \) is a neutral electron donating moiety, and \( z \) is 0 to 5;

a dihydrocarbonylthiocarbamoyl compound;

the amount of trinuclear molybdenum compound and dihydrothiocarbamoyl compound being in the range of 0.1 vol \% about 2.0 vol \%.

10. The method of claim 9 wherein the dihydrothiocarbamoyl compound has the formula

\[
\begin{align*}
R_1 & \equiv S \quad S \quad R_3 \\
\equiv C \equiv (X) \equiv C \equiv N \\
R_2 & \equiv R_4
\end{align*}
\]

where \( R_1, R_2, R_3 \) and \( R_4 \) are the same or different alkyl groups of from 3 to 30 carbon atoms; \( X \) is \( S, S \equiv S, S \equiv (CH_2)_2S, S \equiv CH_2CH_2(CH_3) \equiv S \), and \( y \) is an integer of 1 to 3.