LUBRICANT COMPOSITION AND METHOD FOR USING THE LUBRICANT COMPOSITION

Inventors: Paul Francis Bastien, Katy, TX (US);
Cheng Chen, Houston, TX (US); Brian Lee Papke, Sugar Land, TX (US)

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ABSTRACT

A lubricant composition comprising a fully formulated commercial lubricating oil which comprises from 0.01 to 2.0 percent by weight of an oil soluble organo-molybdenum friction modifier and at least 0.1 percent by weight active sulfur of a surface active sulfur donor component is effective in preventing the removal of DLC coatings while at the same time allowing the beneficial friction-reducing effects from the molybdenum friction modifier to occur.
FIG. 3

HiTEC 312

FIG. 4

RC 2515
FIG. 5

RC 2540

FIG. 6

MoS2
FIG. 7

SYN-O-AD 8478

FIG. 8

RC 8103
LUBRICANT COMPOSITION AND METHOD FOR USING THE LUBRICANT COMPOSITION

FIELD OF INVENTION

[0001] The instant invention relates to a lubricant composition and method for using such lubricant compositions.

BACKGROUND OF THE INVENTION

[0002] Diamond-like coatings (DLC) are often used on metal surfaces to serve as a low friction sliding material and to reduce wear. DLC coatings are used in internal combustion engines which are lubricated by oils. DLC coatings impart lower friction compared with other wear-resistant hard coating materials such as TiN and CrN. To further reduce the frictional properties of DLC-coated lubricated engine components, and to also provide beneficial friction reducing properties for engine components which have not received a DLC coating, friction modifiers are added to lubricating oils.

[0003] One of the best classes of lubricant friction modifiers are organic molybdenum compounds such as molybdenum dithiocarbamate (MoDTC) and molybdenum dialkyldithiophosphates (MoDTP). However, while these friction modifiers are very effective in reducing boundary friction in steel to steel sliding contacts, they have been observed to remove the DLC coating in steel to DLC sliding contacts.

[0004] Thus, lubricants with MoDTC additives are incompatible with DLC treated parts where minimization of friction is desired. Such incompatibility is particularly pronounced in harsh applications, such as in DLC-coated crankcase engines, wherein in the use of high concentrations of MoDTC friction modifiers would be particularly useful.

[0005] Current approaches to such incompatibility include: (a) use of lubricants without MoDTC friction modifiers, and (b) the use of a non-hydrogenated DLC coating, which appears to be more resistant to the abrasive removal of the DLC coating by MoDTC friction modifiers. Neither solution is entirely acceptable, as they either limit or prohibit the use of the beneficial Mo friction modifiers, or require the use of non-hydrogenated DLC coatings which can accelerate wear on opposing steel surfaces due to their extreme hardness. In this regard, a softer hydrogenated DLC coating is preferred, and is the most common commercial coating type currently used in crankcase engine designs.

[0006] The invention provides a lubricant formulation and process using such formulation to compatibilize MoDTC additive containing lubricants with DLC materials.

SUMMARY OF THE INVENTION

[0007] The instant invention is a lubricant composition and a method for using such lubricant compositions.

[0008] In one embodiment, the instant invention provides a lubricant composition comprising: a lubricating oil which comprises from 0.01 to 2.0 percent by weight of an oil soluble organic molybdenum friction modifier and at least 0.1 percent by weight of a surface active sulfur donor component.

[0009] In an alternative embodiment, the instant invention further provides a method for improving the wear of surfaces having a diamond-like coating comprising: preparing a lubricant composition which comprises 0.01 to 2.0 percent by weight of an organic molybdenum friction modifier and at least 0.1 percent by weight of a surface active sulfur donor component, lubricating an interface between a first surface and a second surface with the lubricant wherein at least one of the first and second surfaces has a diamond-like coating thereon; wherein no greater than 10% of a thickness of the diamond-like coating is removed following three hours of relative movement between the first and second surfaces under a normal force of 200N, frequency of 20 Hz, temperature of 130°C.

[0010] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the lubricating oil is selected from the group consisting of synthetic oils, petroleum derived oils, plant derived oils, animal derived oils, and combinations thereof.

[0011] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the organic molybdenum friction modifier is selected from the group consisting of an oil-soluble organo-molybdenum compound (such as molybdenum dithiocarbamate or molybdenum dialkyldithiophosphate, and a surface-active organic sulfur compound (such as an aryl or alkyl sulfide, a dimercaptothiadiol or a metal dithiocarbamate) and combinations thereof. Surface-active organic sulfur compounds are most commonly classified as extreme-pressure (or EP) additives, but the present application is not limited to those compounds specifically identified as EP additives, as the essential properties are the surface-activity and the ability to act as a sulfur donor to the organo-molybdenum friction modifier.

[0012] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the surface active sulfur donor is selected from the group consisting of sulfurized vegetable fatty oils, sulfurized olefins, thiophosphates, sulfurized hydrocarbons, and combinations thereof.

[0013] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the surface active sulfur donor is an EP additive.

[0014] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the surface active sulfur donor is selected from dialkyldithiophosphate ester, sulfurized isobutylene, sulfurized vegetable fatty oils and olefins, dialkylpentasulphide, and combinations thereof.

[0015] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that no more than 10% of the thickness of the diamond-like coating is removed.

[0016] In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that no more than 1% of the thickness of the diamond-like coating is removed.
In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the diamond-like coating comprises from 0% to 35% hydrogen concentration.

In an alternative embodiment, the instant invention provides a lubricant composition and method for improving the wear of surfaces having a diamond-like coating, in accordance with any of the preceding embodiments, except that the lubricant composition further comprises one or more lubricant additive components selected from the group consisting of detergents, dispersants, antiwear, and anti-foam additives.

BRIEF DESCRIPTION OF THE DRAWINGS

For the purpose of illustrating the invention, there is shown in the drawings a form that is exemplary; it being understood, however, that this invention is not limited to the precise arrangements and instrumentalities shown.

FIG. 1 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 1;

FIG. 2 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 1;

FIG. 3 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Inventive Example 2;

FIG. 4 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Inventive Example 3;

FIG. 5 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Inventive Example 4;

FIG. 6 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 2;

FIG. 7 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 3;

FIG. 8 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 4;

FIG. 9 is a profilometry scan indicating the removal of a DLC coating using the lubricant composition of Comparative Example 5;

FIG. 10 illustrates the profilometry scans for Inventive Examples 5-6 and Comparative Examples 6-7; and

FIG. 11 illustrates the profilometry scans for Inventive Examples 7-8 and Comparative Example 8.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention provides a lubricant composition and a method for using such lubricant composition to reduce or eliminate the removal of DLC material in the presence of lubricating oils containing an organic molybdenum compound.

The lubricant composition according to the present invention comprises: a lubricating oil which comprises from 0.01 to 2.0 percent by weight of an organic molybdenum friction modifier and at least 0.1 percent by weight of a surface active sulfur donor component.

In an alternative embodiment of the invention, the organic molybdenum friction modifier is selected from the group consisting of molybdenum dithiocarbamates (MoDTC), molybdenum dialkylthiophosphates (MoDTP), and combinations thereof. In a particular embodiment, the organic molybdenum friction modifier is MoDTC.

In some embodiments, the lubricating oil is selected from the group consisting of synthetic oils, petroleum derived oils, plant derived oils, animal derived oils, and combinations thereof. In a particular embodiment, the lubricating oil is a synthetic oil. Exemplary synthetic oils useful in the invention include lubricants containing polyalphaolefin (PAO) or Group II lubricant basestocks. Exemplary petroleum derived oils useful in the invention include lubricants containing Group I or II basestocks. Exemplary plant derived oils useful in the invention include lubricants derived from coconut, rapeseed, soy or other plant-derived basestocks.

The organic molybdenum friction modifier is present in the lubricating oil in an amount from 0.01 to 2.0 percent by weight. All individual values and subranges from 0.01 to 2.0 weight percent are included herein and disclosed herein; for example, the amount of organic molybdenum in the lubricating oil can be from a lower limit of 0.01, 0.05, 0.1, 0.5, 1.0, 1.5, or 1.8 weight percent to an upper limit of 0.05, 0.1, 0.5, 1.0, 1.5, 1.8, or 2.0 weight percent. For example, the amount of organic molybdenum in the lubricating oil may be in the range of from 0.01 to 2.0 weight percent, or in the alternative, the amount of organic molybdenum in the lubricating oil may be in the range of from 0.05 to 1.5 weight percent, or in the alternative, the amount of organic molybdenum in the lubricating oil may be in the range of from 0.01 to 1.0 weight percent. When more than one surface organic molybdenum friction modifier are present in the inventive lubricant composition, the foregoing ranges indicate the total combined amounts of all organic molybdenum friction modifier.

Any organic molybdenum friction modifier, which can form MoS₂ in the presence of surface active sulfur, may be used in embodiments of the invention. In one embodiment, the organic molybdenum is selected from the group consisting of oil-soluble organo-molybdenum compounds, and combinations thereof. In a particular embodiment, the organic molybdenum friction modifier is selected from the group consisting of molybdenum dithiocarbamate, molybdenum dialkylthiophosphate, and combinations thereof.

In an embodiment of the inventive lubricant composition, the surface active sulfur donor is selected from the group consisting of surface active organic sulfur compounds, including, for example, sulfonized vegetable fatty oils, sulfonized olefins, thiophosphates, sulfonized hydrocarbons, aryl sulfides, alkyl sulfides, dimercaptodithiole, metal dithiocarbamates and combinations thereof. In a particular embodiment, the surface active sulfur donor is selected from the group consisting of dialkyl dithiophosphate ester, sulfonized isobutylene, sulfonized vegetable fatty oils and olefins, dialkylphensulphide, and combinations thereof.

In certain embodiments, the surface active sulfur donor is an extreme pressure (EP) additive. Exemplary commercially available EP additives which are surface active sulfur donors and which may be used in embodiments of the inventive lubricant composition include IRGAULUBE 355 (available from BASF Florham Park, N.J., USA), HITOC 312 (available from Afton Chemical Corporation, Richmond, Va.,
USA), and ADDITINRC 2515 and 2540 (both available from Rhein Chemie Rheinau GmbH, Mannheim, Germany).

[0039] An effective amount of a surface active sulfur donor is used in the inventive lubricant composition and method. As used herein, an “effective amount” is the amount which results in removal of less than or equal to 10% of the thickness of the DLC coating. Effective amounts of a surface active sulfur donor vary depending upon the specific sulfur donor. In general, effective amounts range from 0.04 wt % to 1.0 wt %. However, the upper limit can be extended beyond 1.0 wt % as shown below in Inventive Example 5 where 3.6 wt % surface active sulfur was found to be an effective amount. When more than one surface active sulfur donor is present in the inventive lubricant composition, the foregoing ranges indicate the total combined amounts of all surface active sulfur donors.

TEST METHODS

Amount of Surface Active Sulfur

[0040] The amount of surface active sulfur was measured in accordance with ASTM D1662.

Wear Testing and Removal of DLC Coating

[0041] Wear testing was conducted using an Optimol SRV-4 (available from Optimol Instruments Prüftechnik GmbH Munich, Germany (Optimol)), which is a modularly-structured friction and wear testing platform. A cylinder-on-flat geometry was used using test specimens purchased from Optimol. The hardened steel cylinder was 11x15 mm (diameter x length). A custom sample pan holder was manufactured to fit the 6.9x22 mm Optimol hardened steel disks. The sample pan holds approximately 2 mL of an exemplary oil, and allows fully flooded extended duration lubricant testing to be conducted in the SRV-4. The disk specimens were DLC-coated steel; the steel cylinder was not DLC-coated. The two test specimens (e.g. cylinder and disk) were installed in the test chamber and pressed together with a normal force of 200 Newtons (N). The top specimen oscillated on the bottom specimen. The frequency was 20 Hz, the stroke was 3.0 mm, the test temperature was 130°C, and the test duration was 180 minutes. The same DLC coating was used in testing all Inventive and Comparative Examples, specifically a diamond-like carbon coating available from Bekaert Corporation (Bekaert Diamond-Like Coatings, Karreweg 13, BE-9870 Zulte, Belgium). Wear was measured by profilometry using a Dektak 6M model, from Bruker Instruments and recorded either during and/or after the test.

EXAMPLES

[0042] The following examples illustrate the present invention but are not intended to limit the scope of the invention.

Inventive Examples 1-4 and Comparative Examples 2-5

[0043] Eight commercial EP additives representing a range of chemistries were obtained from various suppliers, as described in Table 1. The commercial EP additives used in each of the Inventive Examples 1-4 were surface active sulfur donors while those utilized in Comparative Examples 2-5 were not surface active sulfur donors. The lubricating oil used in each example lubricant composition was a Pennzol Platinum 5W30 formulation (API “SL” except that the friction modifier was omitted). Each of the Inventive Examples 1-4 and Comparative Examples 2-5 further included 1 weight percent of an organic molybdenum friction modifier, specifically, MoDTC additives made by Adeka Corporation (Japan, under the mark SAKURA-LUBE S515).

Comparative Example 1

[0044] The lubricant composition used in Comparative Example 1 contained a Pennzol Platinum 5W30 (API “SL” formulation) product top-treated with 1.0 wt % MoDTC friction modifier, specifically the SAKURA-LUBE S515.

[0045] FIGS. 1-9 show the profilometry scans of DLC coating surface across the wear track for each of the lubricant compositions of Inventive Examples 1-4 and Comparative Examples 1-5 after the SRV-4 friction test was complete. The Bekaert DLC coating was approximately 1.5 microns (1500 nm) thick. Comparative Example 1, which contained no EP additive, exhibited complete removal of the DLC film within the 3 hour test period. Wear testing utilizing the lubricant compositions of Comparative Examples 2-5, each of which contained a non-surface active sulfur donor EP additive, exhibited complete or partial removal of the DLC film. Use of the surface active sulfur donor EP additives in Inventive Examples 1-4 in wear testing resulted in no observable removal of the DLC coating.

TABLE 1

<table>
<thead>
<tr>
<th>Example</th>
<th>EP additive</th>
<th>Supplier</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventive Example 1</td>
<td>IRGALUBE 353</td>
<td>Ciba</td>
<td>Dialkyl dithiophosphate ester</td>
</tr>
<tr>
<td>Inventive Example 2</td>
<td>HiTEC 312</td>
<td>Afton Chemical Corporation</td>
<td>Sulfurized isobutylene</td>
</tr>
<tr>
<td>Inventive Example 3</td>
<td>ADDITINRC 2515</td>
<td>Rhein Chemie</td>
<td>Sulfurized vegetable fatty oils and olefins</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>MoS₂</td>
<td>Adeka Corporation</td>
<td>Molybdosilane dithioleide</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>SYN-O-AD 8478</td>
<td>ICL-IP Americas Inc.</td>
<td>Phosphate esters</td>
</tr>
<tr>
<td>Comparative Example 4</td>
<td>ADDITINRC 8103</td>
<td>Rhein Chemie</td>
<td>Trimethylolpropionic acid ester of special fatty acids</td>
</tr>
<tr>
<td>Inventive Example 4</td>
<td>ADDITINRC 2540</td>
<td>Rhein Chemie</td>
<td>Diallyl dipentamethylenepiphosphate</td>
</tr>
<tr>
<td>Comparative Example 5</td>
<td>SYN-O-AD 8499</td>
<td>ICL-IP Americas Inc.</td>
<td>Isopropylphenylphosphate</td>
</tr>
</tbody>
</table>
Inventive Examples 5-6 and Comparative Examples 6-7

[0046] Inventive Examples 5-6 were prepared as described in connection with Inventive Example 4 above except that the concentration of surface active sulfur was varied; 3.6 wt % of surface active sulfur (1 wt % ADDITIN RC 2540) in Inventive Example 5 (solid line in FIGS. 10) and 1.8 wt % of surface active sulfur (0.5 wt % ADDITIN RC 2540) in Inventive Example 6 (dashed line in FIG. 10).

[0047] Comparative Examples 6 and 7 were also prepared as was Inventive Example 4 except that lower level of surface active sulfur were used. Specifically, Comparative Example 6 (bold dotted line in FIG. 10) contained 0.9 wt % surface active sulfur (0.25 wt % ADDITIN RC 2540) and Comparative Example 7 (dotted line in FIG. 10) contained 0.36 wt % surface active sulfur (0.1 wt % ADDITIN RC 2540).

[0048] FIG. 10 illustrates the profilometry results following wear testing. As can be seen, a minimum amount of 0.5 wt % ADDITIN RC 2540 was an effective amount. In contrast, lower levels of ADDITIN RC 2540 were not effective, meaning that greater than 10% of the DLC coating thickness was removed. However, the entire DLC coating was not removed even at the lowest levels of ADDITIN RC 2540.

Inventive Examples 7-8 and Comparative Example 8

[0049] Inventive Examples 7-8 were prepared as described in connection with Inventive Example 7 above except that the concentration of surface active sulfur was varied; 0.4 wt % of surface active sulfur (1 wt % ADDITIN RC 2515) in Inventive Example 7 (solid line in FIGS. 11) and 0.2 wt % of surface active sulfur (0.5 wt % ADDITIN RC 2515) in Inventive Example 8 (dashed line in FIG. 11).

[0050] Comparative Example 8 was also prepared as was Inventive Example 3 except that lower levels of surface active sulfur were used. Specifically, Comparative Example 8 (dotted line in FIG. 11) contained 0.04 wt % surface active sulfur (0.1 wt % ADDITIN RC 2515).

[0051] FIG. 11 illustrates the profilometry results following wear testing. As can be seen, a minimum amount of 0.5 wt % ADDITIN RC 2515 was an effective amount. In contrast, lower levels of ADDITIN RC 2515, namely 0.1 wt %, were not effective. However, the entire DLC coating was not removed even at the lowest levels of ADDITIN RC 2515.

[0052] The present invention may be embodied in other forms without departing from the spirit and the essential attributes thereof; and, accordingly, reference should be made to the appended claims, rather than to the foregoing specification, as indicating the scope of the invention.

1. A method for improving the wear of surfaces having a diamond-like coating comprising:
preparing a lubricant composition which comprises 0.01 to 2.0 percent by weight of an organic molybdenum friction modifier and at least 0.1 percent by weight of a surface active sulfur donor component;
lubricating an interface between a first surface and a second surface with the lubricant composition wherein at least one of the first and second surfaces has a diamond-like coating thereon;
wherein no greater than 10% of a thickness of the diamond-like coating is removed following three hours of relative movement between the first and second surfaces under a normal force of 200N, frequency of 20 Hz, temperature of 130° C.

2. The method according to claim 1 wherein no more than 10% of the thickness of the diamond-like coating is removed.

3. The method according to claim 1 wherein no more than 1% of the thickness of the diamond-like coating is removed.

4. The method according to claim 1 wherein the diamond-like coating comprises from 0% to 35% hydrogen concentration.

5. The method according to claim 1 wherein the surface active sulfur donor component is selected from the group consisting of aryl sulfides, alkyl sulfides, dimercurithiodiazole, sulfurized isobutylene, dialkyldipentasulphide, and combinations thereof.

6. A lubricant composition comprising: a fully formulated commercial lubricating oil which comprises from 0.01 to 2.0 percent by weight of an oil soluble organo-molybdenum friction modifier and at least 0.1 percent by weight of a surface active sulfur donor component.

7. The lubricant composition according to claim 6 wherein the lubricating oil is selected from the group consisting of synthetic oils, petroleum derived oils, plant derived oils, animal derived oils, and combinations thereof.

8. The lubricant composition according to claim 6, wherein the organic molybdenum friction modifier is selected from the group consisting of molybdenum dithiocarbamate, molybdenum dialkyldithiophosphates, and combinations thereof.

9. The lubricant composition according to claim 6 wherein the surface active sulfur donor is selected from the group consisting of aryl sulfides, alkyl sulfides, dimercurithiodiazole, sulfurized isobutylene, dialkyldipentasulphide, and combinations thereof.

10. (canceled)