LUBRICATING OIL COMPOSITION AND USE THEREOF

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ABSTRACT
A lubricating oil composition having a sulfur content of from 0.3 to 0.5 wt. %, a phosphorus content of from 0.10 to 0.13 wt. % and a sulfated ash content of from 0.1 to 1.1 wt. %, based on the total weight of the lubricating oil composition is provided. The lubricating oil composition contains at least one Group II mineral base oil; at least one alkali and/or alkaline earth metal alkyl salicylate; an ashless dispersant; at least one zinc didithiophosphate; and at least one aminic ashless antioxidant and at least one phenolic ashless antioxidant.
LUBRICATING OIL COMPOSITION AND USE THEREOF

[0001] The present application claims the benefit of pending U.S. Provisional Patent Application Ser. No. 60/682,360 filed May 18, 2005, the entire disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to a lubricating oil composition and its use.

BACKGROUND OF THE INVENTION

[0003] Due to environmental considerations, exhaust after-treatment devices are often fitted to vehicles in order to reduce particulate matter and NOx emissions therefrom.

[0004] However, the sulfated ash, sulfur and phosphorus concentrations of lubricating oil compositions conventionally used in internal combustion engines may have adverse effects on such after-treatment devices.

[0005] Sulfated ash is the total weight percent of ash in a lubricating oil composition. The sulfated ash content in a lubricating oil composition is related to the total metal content therein. Sulfated ash may be conveniently measured according to ASTM D874.

[0006] In view of the adverse affects that the sulfated ash, sulfur and phosphorus concentrations of lubricating oil compositions may have on exhaust after-treatment devices, it is therefore prudent to develop lubricating oil compositions with reduced sulfated ash, sulfur and/or phosphorus concentrations therein.

[0007] For 2007, United States particulates and NOx emission standards will be reduced significantly compared with current levels. Further NOx restrictions are scheduled for European emission standards Euro 5 in 2008 and USA emission standard in 2010. In addition to NOx and particulate matter reductions, fuel sulfur levels are being reduced to decrease levels of SOx and sulfate containing particulate matter.

[0008] While meeting these lower levels of particulate matters, it is desirable that the lubricating oil composition meet other criteria of a good lubricating oil composition.

SUMMARY OF THE INVENTION

[0009] Accordingly, in one embodiment, a lubricating oil composition having a sulfur content of from 0.3 to 0.5 wt. %, a phosphorus content of from 0.10 to 0.13 wt. % and a sulfated ash content of from 0.1 to 1.1 wt. %, based on the total weight of the lubricating oil composition is provided, comprising:

[0010] a) at least one Group II mineral base oil;
[0011] b) at least one alkali and/or alkaline earth metal alkyl salicylate;
[0012] c) an ashless dispersant;
[0013] d) a zinc dithiophosphate; and
[0014] e) at least one amine ashless antioxidant and at least one phenolic ashless antioxidant.

[0015] In another embodiment, a method of lubricating an internal combustion engine using the lubricating oil composition is provided.

DETAILED DESCRIPTION OF THE INVENTION

[0016] It is therefore desirable to develop lubricating oil compositions having lower sulfated ash, sulfur and phosphorus concentrations than the formulations currently on the market while having good characteristic in one or more of performance property such as oxidative stability and/or detergency.

[0017] Whilst U.S. Pat. No. 6,569,818 is directed to lubricating oil composition having a low P content of 0.01 to 0.1 wt. %, and a sulphated ash of 0.1 to 1 wt. %, which is composed of a) a major amount of mineral base oil having a low S content of at most 0.1 wt. %; b) an ashless alkyl or alkyl-succinimide dispersant; c) a metal-containing detergent; d) Zn-DTP; and e) an oxidation inhibitor, there is further need to develop lubricating oil that has suitable performance property that meets the current and 2007 US regulation. The base oil used in the present invention contains at least one mineral of a Group II and/or Group II+ type. In the preferred embodiment, the amount of base oil present in the lubricating oil composition of the present invention is preferably present in an amount in the range of from 60 wt. %, more preferably from 65 wt. %, to 98 wt. %, more preferably to 75 wt. %, with respect to the total weight of the lubricating oil composition.

[0018] Typically group II base oils contain greater than or equal to 90% saturates (as determined by ASTM D 2007) and less than or equal to 0.03% sulfur (as determined by ASTM D 2622) and have a viscosity index greater than 80 and less than 120 (as determined by ASTM D 2270). Group II+ oils may also be used. These are oils that have a VI at the high end of the VI spectrum, e.g., about 120. The term “Group II mineral base oil” is meant to include such Group II and II+ base oils.

[0019] The Group II mineral base oil may be manufactured using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing including hydrocracking and hydrotreating, catalytic dewaxing, oligomerization, esterification, and re-refining. Examples of group II mineral base oil include “Star” base oils from Motiva Enterprise LLC, “RLOP” from Chevron Corporation, “Excel Paralubes” base oils from ConocoPhillips, group II base oils from Flint Hills Resources LP, “EHC” base oils from Exxon Mobil Corporation.

[0020] Major amount of the Group II base oil is present in the lubricating oil composition.

[0021] In the present invention, the phrase “optionally substituted branched or straight chain alkyl group” is used to describe alkyl groups optionally containing one or more “inert” heteroatom-containing functional groups.

[0022] By “inert” is meant that the functional groups do not interact to any substantial degree with the other components of the lubricating oil composition. Non-limiting examples of such inert groups are amines and halides, such as, for example, fluoride and chloride.

[0023] The lubricating oil composition may comprise a single zinc dithiophosphate or a combination of two or more
zinc dithiophosphates, the or each zinc dithiophosphate being selected from zinc dialkyl-, diaryl- or alkylaryl-dithiophosphates, provided that the total phosphorus content of the lubricating oil composition is preferably in the range of from 0.01 to 0.13 wt %.

[0024] Zinc dithiophosphate may be conveniently represented by general formula II:

R₂O \( \text{Zn-S-S-} \) R₃C \( \text{OR}^4 \)

wherein R² to R⁴ may be the same or different and are each a primary alkyl group containing from 1 to 20 carbon atoms preferably from 3 to 12 carbon atoms, a secondary alkyl group containing from 3 to 20 carbon atoms, preferably from 3 to 12 carbon atoms, an aryl group or an aryl group substituted with an alkyl group, said alkyl substituent containing from 1 to 20 carbon atoms preferably 3 to 18 carbon atoms.

[0025] Zinc dithiophosphate compounds in which R² to R³ are all different from each other or the same can be used alone or in admixture with zinc dithiophosphate compounds in which R² to R³ are all the same.

[0026] Preferably, the or each zinc dithiophosphate used in the present invention is a zinc dialkyl dithiophosphate.

[0027] Preferable zinc dithiophosphates which are commercially available include primary zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations “Lz 1097” and “Lz 1395”, those available ex. Chevron Onorite under the trade designations “OLOA 267” and “OLOA 269R”, and that available ex. Ethyl under the trade designations “HITEC 7197”; secondary zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations “Lz 677A”, “Lz 1095” and “Lz 1371”; that available ex. Chevron Onorite under the trade designation “OLOA 262” and that available ex. Ethyl under the trade designation “HITEC 7169”; and aryl type zinc dithiophosphates such as those available ex. Lubrizol Corporation under the trade designations “Lz 1370” and “Lz 1373” and that available ex. Chevron Onorite under the trade designation “OLOA 260”.

[0028] Preferable ashless dispersants that may be employed in the lubricating oil composition of the present invention, include alkenyl- or alkyl-succinimides or derivatives thereof. Said ashless dispersants may be borated. Ashless dispersants that may be employed in the lubricating oil composition of the present invention include those described in U.S. Pat. No. 6,569,818 which is hereby incorporated by reference. Ashless dispersants may also be a dual function additive such as, for example, those acting as a dispersant and a viscosity index improver.

[0029] Such ashless dispersants may be typically added in an amount in the range of from about 1 wt %, preferably from 2 wt %, more preferably from 4 wt %, to about 15 wt %, preferably to 10 wt %, based on the total weight of lubricating oil composition.

[0030] Typical detergents that may be used include one or more salicylate detergents. Alkali metal and/or alkaline earth metal-based detergents are particularly preferred.

[0031] In order to maintain the total sulfated ash content of the lubricating oil composition of the present invention in the range of from 0.1 to 1.1 wt %, said detergents are preferably used in amounts in the range of 0.05 to 5.0 wt %, more preferably from 1.0 to 5.0 wt % and most preferably in the range of from 2.0 to 4.0 wt %, based on the total weight of the lubricating oil composition.

[0032] Furthermore, it is preferred that said detergents, independently, have a TBN (total base number) value in the range of from 10 to 400 mg.KOH/g, more preferably in the range of from 30 to 350 mg.KOH/g and most preferably in the range of 50 to 300 mg.KOH/g, as measured by ASTM D2896.

[0033] The TBN value of the lubricating oil composition of the present invention is preferably in the range of from 6.0 to 14.0 mg.KOH/g, more preferably in the range of from 8.0 to 13.0 mg.KOH/g, most preferably in the range of from 8.0 to 12.0 mg.KOH/g, as measured by ASTM D2896.

[0034] Thus, in one of the preferred embodiment, the lubricating oil composition of the present invention may comprise one or more alkyl salicylate detergents, for example, alkali metal alkyl salicylates and/or alkaline earth metal alkyl salicylates such as, for example, calcium alkyl salicylates. In one preferred embodiment, an overbased calcium alkyl salicylate may be used.

[0035] Such salicylate detergents may be typically added in an amount in the range of from 1.0 wt %, preferably from 2.0 wt %, to 10.0 wt %, preferably to 5.0 wt %, based on the total weight of lubricating oil composition.

[0036] The lubricating oil composition of the present invention comprises one or more ashless phenolic and ashless aminic anti-oxidants. Antioxidants may be added in an amount in the range of from about 0.1 wt %, preferably from 0.5 wt %, to about 5.0 wt %, preferably to 3.0 wt %, based on the total weight of lubricating oil composition.

[0037] Ashless phenolic antioxidants are compounds containing a phenolic group and is effective as an antioxidant. Hindered phenolic antioxidants are preferred. Phenolic antioxidants that may be employed in the lubricating oil composition of the present invention include 2,6-di-t-butyl-p-cresol, 4,4'-methylenebis(2,6-di-t-butylphenol), 4,4'-methylenebis(6-t-butyl-o-cresol), 4,4'-thiodiisobis(2-methyl-6-t-butylphenol), 4,4'-isopropylidenecyclodextrin(2,6-di-t-butylphenol), 4,4'-bis(2,6-di-t-butylphenol), 2,2'-methylene(4-methyl-6-t-butylphenol), 4,4'-thiodiisobis(2-methyl-6-t-butylphenol), 2,2'-thiodiethylenediamino[3-(3,5-di-1-t-butyl-4-hydroxyphenyl)propionate, octyl 3-(3,5-di-1-t-butyl-4-hydroxyphenyl)propionate, and octadecyl 3-(3,5-di-1-t-butyl-4-hydroxyphenyl)propionate and those described in U.S. Pat. No. 5,300,243 and U.S. Pat. No. 5,629,440 which are hereby incorporated by reference. Preferable ashless phenolic antioxidants include phenolic compounds such as that available ex. Ciba Specialty Chemicals Co. under the trade designation “Inaglo X L-135”.

[0038] Ashless aminic antioxidants are compounds containing an amine group and is effective as an antioxidant. They are also referred to as amine-type antioxidants. Aminic
antioxidants that may be employed in the lubricating oil composition of the present invention include alkyldiphenylamine containing alkyl groups having 4 to 9 carbon atoms, p,p'-dicyclopentyldiphenylamine, phenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, alkylated alpha-naphthylamine, and alkylated phenyl-alpha-naphthylamine and those described in U.S. Pat. No. 5,300,243, U.S. Pat. No. 5,629,440, and U.S. Pat. No. 6,599,865 which are hereby incorporated by reference. Preferable amine antioxidants include aminic compounds such as diaryl amines, particularly diphenyl amines. Preferable amine antioxidants include, for example, diphenyl amine that are available ex. Ciba Specialty Chemicals Co. such as, for example, a diphenyl amine under the trade designation “Irganox 1-57”, and phenyl naphtyl amines.

[0039] In a preferred embodiment, the amine ashless antioxidant and the phenolic ashless antioxidant are present in a ratio of amine ashless antioxidant to phenolic ashless antioxidant in the range of about 1:1 to about 1:4, more preferably in the range of 1:1 to 1:3.

[0040] The lubricating oil compositions of the present invention may be conveniently prepared by admixing the one or more components of antibiotic a) to e).

[0041] The lubricating oil composition according to the present invention may contain further additives that are usually present in lubricating oil compositions, such as viscosity index improvers, friction modifiers, pour point depressants, anti-foam agents and demulsifiers. Examples of other additives that may be employed in the lubricating oil composition of the present invention include those described in U.S. Pat. No. 6,569,618 which is hereby incorporated by reference.

[0042] Pour point depressants generally are high molecular weight polymers such as alkylation polymers and polyampholytes. Suitable pour point depressants include those available ex. Rohmox under the trade designations “Viscoplex 1-572”. As anti-foam agents, silicone polymers and/or polyampholytes are generally used.

[0043] Viscosity Index Improvers generally are co-polymers such as olefin copolymer types (e.g., ethylene propylene copolymers), styrene-isoprene block copolymers and alkyl methacrylate/N-vinylpyrrolidone copolymers. Examples of suitable viscosity index improvers include those described in U.S. Pat. No. 6,331,510, U.S. Pat. No. 6,204,224 and U.S. Pat. No. 6,372,696, which are hereby incorporated by reference. Suitable viscosity index improvers include those available ex. Infineum USA LP under the trade designation “SV 165” and that available ex. Rohmox under the trade designations “Aculoid 985”, “Viscoplex 6-054”, “Viscoplex 6-054”, “Viscoplex 6-056” and “Viscoplex 1-372” and that available ex. The Lubrizol Corporation under the trade designation “LZ 770C” and “LZ 7077”.

[0044] Demulsifiers which are generally applied are polyalkylene glycol ethers.

[0045] The lubricating oil compositions provide good antioxidancy performance.

[0046] Furthermore, lubricating oil compositions may also provide one or more of the following properties: good detergent and give rise to beneficial engine cleanliness such as piston cleanliness and/or wear protection.

[0047] The lubricating oil composition according to the present invention may generally comprise in the range of from 0.11 wt % to 0.15 wt %, based on Zinc content, of zinc dithiophosphate, (if primary or secondary alkyl type), based on total weight of the lubricating oil composition.

[0048] The amount of phosphorus in the lubricating oil composition is generally in the range of from 0.1 wt %, preferably from above 0.1 wt %, more preferably from 0.11 wt %, to 0.13 wt %, preferably to 0.12 wt %, based on the total weight of the lubricating oil composition.

[0049] The lubricating oil composition has a sulfated ash content in the range of from 0.1 wt %, preferably from 0.4 wt %, more preferably from 0.7 wt %, most preferably from 0.9 wt %, to 1.2 wt %, preferably to 1.0 wt %, based on the total weight of the lubricating oil composition.

[0050] The lubricating oil composition of the present invention generally has a sulfur content in the range of from 0.3 wt %, preferably from 0.35 wt %, to 0.5 wt %, preferably to 0.4 wt %, based on the total weight of the lubricating oil composition.

[0051] It is further preferred that the base oil has a sulfur content of at most 0.05 wt %, preferably at most 0.03 wt %, calculated as elemental sulfur and measured according to ASTM D2622.

[0052] Preferably, the viscosity index of base oil is more than 80, more preferably more than 100 and most preferably more than 120, as measured according to ASTM D2270.

[0053] Preferably, the lubricating oil composition has a kinematic viscosity at 100° C. in the range of from 5 to 20 mm²/s, more preferably in the range of from 5 to 18 mm²/s, most preferably in the range of from 9 to 16.5 mm²/s.

[0054] Accordingly, the present invention furthermore provides for the use of a lubricating oil composition according to the present invention as a crankcase lubricant in diesel, gas-fueled and/or gasolene engine applications.

[0055] The present invention furthermore provides a method of lubricating an internal combustion engine, in particular a diesel engine, gasoline engine and a gas-fueled engine, with a lubricating oil composition as hereinbefore described. This includes engines equipped with exhaust gas recirculation (EGR).

[0056] In one preferred embodiment, lubricating oil compositions pass the API CI-4 requirements (ASTM D4485-03a; Standard Specification for Performance of Engine Oils) despite having the afore-mentioned sulfur content, phosphorus content, sulfated ash content and TBN values.

[0057] In a further embodiment, there is provided a method of lubricating an internal combustion engine, in particular a diesel engine, a gasoline engine and a gas-fueled engine, wherein said engine has EGR (exhaust gas recirculation), with a lubricating oil composition as hereinbefore described.

[0058] The present invention will now be illustrated by the following Examples, which should not be regarded as limiting the scope of the present invention in any way.
EXAMPLES

In the Examples, the various additives are designated as follows:

(a) Base Oil

Star 4, Star 5 and Star 8 base oil (Group II base oil) from Motiva Enterprise LLC was used for Example 2. TexHVI 5W base oil (a Group II+ base oil) from Motiva Enterprise LLC was used for Example 1.

(b) Detergent

As outlined in Table 1, the detergent additives used in Examples were a mixture of calcium alkyl salicylate (neutral base) and calcium alkyl salicylate (overbased).

(c) Dispersant

Infineum C9266 which is an ashless alkenyl succinimide dispersant

(d) Zinc Dithiophosphate Anti-wear Agent

A secondary C3-6 zinc dithiophosphate (ZnDTP) available ex. Lubrizol Corporation under the trade designation “Lz 1371” was used.

(e) Anti-oxidant

Phenolic antioxidant available ex. Ciba Specialty Chemicals Co. under the trade designation “Irganox L-135” and diphenyl amine available ex. Ciba Specialty Chemicals Co. under the trade designation “Irganox L-57” were used.

(f) Other Additives

(i) Pour Point Depressant

“Viscoplex 1-372” which is marketed ex. Rohmox as a pour point depressant was employed.

(ii) Viscosity Index Improver

“SW 165” which is available from Infineum USA LP (styrene-isoprene block copolymer) was employed.

The lubricating oil compositions that were prepared are indicated in Table 1.

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity grade (SAE)</td>
<td>10W-30</td>
<td>15W-40</td>
</tr>
<tr>
<td>Base oil*</td>
<td>69.9</td>
<td>71.4</td>
</tr>
<tr>
<td>Viscosity index improver (wt. %)</td>
<td>12.5</td>
<td>13.0</td>
</tr>
<tr>
<td>Pour Point Depressant (wt. %)</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Ca Alkyl Salicylate detergents (wt. %)</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnDTP (wt. %)</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Strenxiumide dispersant</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Phenolic antioxidant</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Aminic antioxidant</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Total Additive Package treat rate** (wt. %)</td>
<td>17.6</td>
<td>15.6</td>
</tr>
<tr>
<td>Total Sulfated ash (wt. %)(ASTM D874)</td>
<td>1.07</td>
<td>1.07</td>
</tr>
<tr>
<td>Total Sulfur (wt. %) (ASTM D2022)</td>
<td>0.322</td>
<td>0.338</td>
</tr>
<tr>
<td>Total Phosphorus (wt. %) (ICP-OES method)</td>
<td>0.117</td>
<td>0.117</td>
</tr>
</tbody>
</table>

*Balance of formulation.

**Package of additives containing detergents, dispersants, ZnDTP’s and supplementary antioxidants plus carrier oil

Test Method

Differential Scanning Calorimeter test was run on the formulations according to ASTM D6186. Results of the test is provided below in Table 2.

Results and Discussion

Example 1 and Example 2

An SAE 10W-30 lubricating oil composition (Example 1) and an SAE 15W-40 lubricating oil composition (Example 2) as described in Table 1 were prepared containing formulation containing a compounds a) to f).

The lubricating oil composition of Example 1 and Example 2 had a sulfated ash content, a phosphorus content and a sulfur content of as provided in Table 1 above.

The lubricating oil compositions were tested as described above and the results are shown in Table 2.

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation Induction Time (@ 210°C)</td>
<td>13 min.</td>
<td>14 min.</td>
</tr>
</tbody>
</table>

As can be seen from Table 2, the lubricating oil composition has good oxidation stability for an engine oil.

We Claim:

1. A lubricating oil composition having a sulfur content of from 0.3 to 0.5 wt %, a phosphorus content of from 0.10 to 0.13 wt % and a sulfated ash content of from 0.1 to 1.1 wt %, based on the total weight of the lubricating oil composition, comprising:
   a) at least one Group II mineral base oil;
   b) at least one alkali and/or alkaline earth metal alkyl salicylate;
   c) an ashless dispersant;
   d) a zinc dithiophosphate; and
   e) at least one aminic ashless antioxidant and at least one phenolic ashless antioxidant.

2. The lubricating oil composition of claim 1 wherein the at least one aminic ashless antioxidant and at least one phenolic ashless antioxidant are present in a ratio in the range of about 1:1 to about 1:4.

3. The lubricating oil composition of claim 1 wherein the alkali and/or alkaline earth metal alkyl salicylate is calcium alkyl salicylate.

4. The lubricating oil composition of claim 2 wherein component e) is present in an amount in the range of about 0.1 to about 5 weight percent based on the total weight of the lubricating oil composition.

5. The lubricating oil composition of claim 1 further comprises at least one of viscosity modifier and pour point depressant.

6. The lubricating oil composition of claim 1 wherein component d) is a zinc dialkyldithiophosphate.

7. The lubricating oil composition of claim 1 wherein a major amount of the Group II mineral base oil is present.
8. The lubricating oil composition of claim 1 wherein component d) is present in an amount in the range of from 0.11 to 0.15 wt %, based on zinc content, based on the lubricating oil composition.

9. The lubricating oil composition of claim 1 wherein component b) is present in an amount in the range of 0.05 to 5.0 wt %.

10. The lubricating oil composition of claim 1 wherein the sulfur content is from 0.3 wt % to 0.4 wt %.

11. The lubricating oil composition of claim 1 wherein the sulfur content is from 0.35 wt % to 0.5 wt %.

12. The lubricating oil composition of claim 6 wherein the viscosity index improver is a styrene-isoprene block copolymer.

13. The lubricating oil composition of claim 1 having a kinematic viscosity at 100°C in the range of from 5 to 20 mm²/s.

14. The lubricating oil composition of claim 7 wherein the Group II mineral base oil has a viscosity index of more than 80.

15. A lubricating oil composition having a kinematic viscosity at 100°C in the range of from 2 to 20 mm²/s, sulfur content of from 0.3 to 0.4 wt %, a phosphorus content of from 0.11 to 0.13 wt % and a sulfated ash content of from 0.9 to 1.1 wt %, based on the total weight of the lubricating oil composition, comprising:

a) a major amount of at least one Group II mineral base oil;
b) 2.0 to 5.0 wt % of at least one alkali and/or alkaline earth metal alkyl salicylate;
c) 5 to 15 wt % of at least one ashless dispersant;
d) 0.11 to 0.15 wt %, based on zinc content, of at least one zinc dithiophosphate; and
e) about 0.1 to about 5 weight percent of at least one aminic ashless antioxidant and at least one phenolic ashless antioxidant in a ratio of aminic ashless antioxidant to phenolic ashless antioxidant in the range of about 1:1 to about 1:4.

16. A method of lubricating an internal combustion engine comprising introducing into the internal combustion engine a lubricating oil composition of claim 1.

17. A method of lubricating an internal combustion engine comprising introducing into the internal combustion engine a lubricating oil composition of claim 15.