LIQUID ADDITIVES FOR THE STABILIZATION OF LUBRICANT COMPOSITIONS

Inventor: Jun DONG, Cheshire, CT (US)

Correspondence Address:
Jaimes Sher
199 Chemtura Corporation, Benson Road
Middlebury, CT 06749 (US)

Assignee: Chemtura Corporation,
Middlebury, CT (US)

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ABSTRACT
A lubricating oil composition comprising: (A) a base stock; and (B) a liquid additive package. The liquid additive package comprises: (i) an alkylated diphenylamine; (ii) at least 5 weight % of a phenyl naphthylamine, based on the weight of the additive package; and (iii) a sulfur-containing phenol.
LIQUID ADDITIVES FOR THE STABILIZATION OF LUBRICANT COMPOSITIONS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Application No. 61/080,547, filed on Jul. 14, 2008, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to lubricating oil compositions. More specifically, lubricating oil compositions comprising additive packages for reducing oxidative deterioration.

BACKGROUND OF THE INVENTION

[0003] Lubricants, such as those used in a variety of machinery, are susceptible to oxidative deterioration during storage, transportation, and usage, particularly when such lubricants are exposed to high temperatures and iron catalytic environments, which greatly promote the oxidation of the lubricant. This oxidation, if not controlled, contributes to the formation of corrosive acidic products, sludge, varnishes, resins, and other oil-insoluble products and may lead to a loss of designated physical and tribological properties of the lubricants. These oxidation products may lead to the formation of harmful deposits on critical engine parts, such as the pistons, piston liners, valves, and valve lifters.

[0004] It is therefore a common practice to include deposit-control compounds and/or additives, e.g., antioxidant additives, in lubricants to prevent, at least to some extent, oxidation, thereby extending the useful life of the lubricants. One of these antioxidant additives is alkylated diphenylamine (ADPA), which has been used extensively because of its performance and low cost. However, driven by escalating performance and environmental requirements in recent years, there has been a general trend in the industry toward machinery being built smaller yet operating at higher speeds and higher operating temperatures. As such, more output and higher fuel economy are achieved. However, under such operating conditions, the thermal and oxidative stress on the lubricants has become severe that conventional ADPA antioxidants insufficiently stabilize the lubricants.

[0005] Lubricant compositions containing various antioxidants are widely known in the art. As an example, U.S. Pat. No. 6,326,336 to Gatto, et al. (hereinafter “Gatto”) discloses a turbine lubricating oil comprising (A) an amine antioxidant selected from the group consisting of alkylated diphenylamines, phenylaliphatics and mixtures thereof; (B) sulfur-containing additives selected from the group consisting of sulfurized olefins, sulfurized fatty acids, ashless dithiocarbamates, tetraalkylthiuram disulfides and mixtures thereof; and (C) a base oil. According to Gatto, such a composition provides superior oxidation protection and acceptable sludge control in turbine oils formulated with Group II or higher base oils. An important criterion for selecting the concentration of sulfur-containing additive is the sulfur content of the additive package. According to Gatto, the sulfur-containing additive should deliver between 0.005 wt. % and 0.07 wt. % of sulfur to the finished turbine oil. However, Gatto utilizes only sulfurized olefins, sulfurized fatty acids, ashless dithiocarbamates, tetraalkylthiuram disulfides and mixtures thereof. Gatto states that there are a number of problems that may be associated with the use of hindered phenols. Gatto states that hindered phenols under high temperatures can dealkylate and produce free phenol and that water extractability of certain water soluble phenols is another potential problem. Thus, Gatto states, a phenol-free formulation may be desired.

[0006] U.S. Pat. No. 5,091,099 discloses to a phosphate-free lubricating oil composition comprising a) a mineral oil or a synthetic oil or a mixture thereof; and b) a mixture containing at least one aromatic amine of the formula (I),

\[
\begin{align*}
\text{HO} & \quad \text{A}, \\
\text{R} & \quad \text{R}', \\
\text{R} & \quad \text{R}'
\end{align*}
\]

and at least one phenol of the formula (II)

\[
\begin{align*}
\text{HO} & \quad \text{A}, \\
\text{R} & \quad \text{R}', \\
\text{R} & \quad \text{R}'
\end{align*}
\]

and the compounds are present in the mixture in a ratio of 2 to 6 parts by weight of the aromatic amine(s) of the formula (I) to 1 part by weight of the phenol(s) of the formula (II).

[0007] U.S. Pat. No. 5,523,007 discloses a lubricating oil composition comprising a diesel engine oil and, as antioxidant, a compound of formula I

\[
\begin{align*}
\text{HO} & \quad \text{X} \\
\text{R} & \quad \text{R}', \\
\text{R} & \quad \text{R}'
\end{align*}
\]

wherein X is

\[
\begin{align*}
\text{O} & \quad \text{OR}, \\
\text{CH}_2 & \quad \text{CH}_2, \\
\text{C} & \quad \text{OR}.
\end{align*}
\]

and R is a straight chain or branched alkyl radical of the formula C_{n}H_{2n+1}, wherein n is an integer from 8 to 22. Such a phenol may contain sulfur, but weight percentages and relationships to other components are not taught.

[0008] One potential antioxidant that can be utilized to achieve superior performance in antioxidant packages is phenyl napthylamine (PNA). However, PNA is typically sold as a solid at room temperature, and, as such, is not easily blended into the base oil.
[0009] Even in view of these known lubricant compositions, the need remains for a cost-effective antioxidant package that provides improved antioxidant stability and blends easily with base stocks.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] The present invention generally relates to lubricating oil compositions that may be utilized in high temperature environments. Typically, such high temperature environments promote oxidative deterioration of the lubricants. The lubricating oil compositions of the present invention are less susceptible to such oxidative deterioration, i.e., they are more stable, and, as such, provide improved physical and tribological properties at high temperatures.

[0011] In one embodiment of the invention, the composition comprises a liquid antioxidant package having at least about 1 weight percent (wt %), e.g., at least about 3 wt %, at least about 5 wt %, at least about 7 wt %, at least about 10 wt %, or at least about 15 wt %, of a phenyl naphthylamine (PNA), e.g., phenyl-alpha-naphthylamine, and a base stock. In terms of ranges, the PNA may be present in amounts ranging from about 1 wt % to about 50 wt %, e.g., from about 2 wt % to about 50 wt %, from about 3 wt % to about 40 wt %, from about 5 wt % to about 30 wt %, or from about 5 wt % to about 30 wt %. Such additive packages, when combined with a suitable base stock, reduces the amount of harmful deposits resulting from oxidation of the lubricating oil composition as compared to additive packages with less than 5 wt % PNA.

[0012] Preferably, the liquid additive package, e.g., liquid antioxidant additive package, comprises a diphenylamine, e.g., an alkyldiphenylamine (ADPA), and at least about 5 wt % PNA. Typically, the PNA is solid at room temperature and is difficult to dissolve in liquids, e.g., ADPA or base stocks. In a preferred embodiment of the invention, the PNA is combined with ADPA, e.g., under heat, e.g., at about 150° C., about 100° C., about 65° C., or about 50° C., and/or under nitrogen or a similar inert atmosphere until a homogenous mixture is achieved. The mixture is a stable liquid at room temperature. The ADPA and the PNA may be mixed for about 10 to about 20 minutes, e.g., about 12 to about 18 minutes, or about 14 to about 16 minutes. It should be noted that the time periods listed above are merely exemplary and that the time will vary as the quantities of each of the materials vary. In one embodiment, the resultant composition is dark redish in color and has a viscosity of less than about 50,000 cP, e.g., less than about 30,000 cP, or less than about 20,000 cP, as measured at 25° C. In terms of ranges, the viscosity of the composition ranges from about 100 to about 100,000 cP, e.g., from about 100 to about 50,000 cP, or from about 1,000 to about 25,000 cP, as measured at 25° C.

[0013] In one embodiment of the present invention, the lubricant oil composition, when combined with a polyalpha-olefin base stock at a weight ratio of about 99: 1, base stock to additive package, shows an oxidation induction time (OIT), as tested under the pressurized differential scanning calorimeter (PDSC) conditions shown in TABLE 1, of at least about 25 minutes, e.g., at least about 38 minutes, at least about 40 minutes, at least about 50 minutes or at least about 75 minutes. This is a significant improvement over a similar lubricant oil composition comprising the same poly-alpha-olefin base stock and pure ADPA, which, in similar testing, shows an oxidation time of 28.6 minutes. It should be noted that the test parameters under which the PDSC is operated may affect the OIT of the sample. For example, the a sample tested at 160° C. may have a longer OIT than a similar sample tested at 185° C.

| TABLE 1 |
|-----------------|--------------|
| Test Parameters | PDSC Test Conditions |
| Inertothermal Temperature | 185° C. |
| O2 Gas Pressure | 500 psi |
| O2 Gas Flow Rate Through Cell | 100 ml/min, continuous |
| Catalyst | 80 ppm of iron |
| Sample Holder | Open Aluminum Pan |
| Sample size | 1.0-2.0 mg |
| Induction Time | Euthalpy Change |

[0014] In another embodiment of the invention, the additive package comprises ADPA, PNA and a sulfur-containing phenol. Typically, the sulfur-containing phenol is solid at room temperature. However, sulfur-containing phenols that are liquids at room temperature may be utilized as well. In one embodiment, the combination of the ADPA, PNA and sulfur-containing phenol forms a clear liquid. In another embodiment, the combination of the ADPA, PNA and sulfur-containing phenol produces an additive package that significantly improves the oxidative stability and reduces the amount of Mid-High Temperature Thermo-Oxidation Engine Oil Simulation Test (TEOST MHT, ASTM D 7097) deposits (see below) over that of ADPA alone. Such an additive package, when blended (at a wt % of about 1 wt %) into an engine oil containing an API Group II base stock demonstrated an OIT of about 40 minutes and showed deposits of 37 milligrams (mg). In one embodiment of the invention, the lubricant oil composition has a TEOST MHT value of less than about 60 mg, e.g., less than about 50 mg, less than about 40 mg or less than about 20 mg. It should be noted that an additive package of pure ADPA yields a TEOST MHT value of about 55 mg, pure PNA yields a TEOST MHT value of about 80 mg, and pure sulfur-containing phenol yields a TEOST MHT value of about 63 mg. Hence, a TEOST MHT value of less than 55 mg, for the lubricant composition, is surprising and unexpected.

[0015] In one preferred embodiment of the invention, the ADPA is present in an amount of at least about 50 wt %, e.g., at least about 60 wt %, or at least about 70 wt %, based on the weight of the additive package. In terms of ranges, preferably, the ADPA is present in an amount ranging from about 50 to about 99 wt %, e.g., from about 60 to about 99 wt %, from about 70 to about 95 wt %, or from about 70 to about 90 wt %, based on the weight of the additive package.

[0016] In one embodiment of the invention, the PNA is present in an amount of at least about 1 wt % e.g., at least about 3 wt %, at least about 5 wt %, at least about 7 wt %, at least about 10 wt %, at least about 15 wt %, at least about 20 wt %, at least about 25 wt %, or at least about 50 wt %, based on the weight of the additive package. In terms of ranges, the PNA is present in an amount ranging from about 1 wt % to about 50 wt %, e.g., from about 2 wt % to about 50 wt %, from about 5 wt % to about 50 wt %, from about 3 wt % to about 40 wt %, from about 5 wt % to about 30 wt %, or from about 5 wt % to about 30 wt %, based on the weight of the additive package. Additive packages having the above-mentioned amounts of PNA demonstrate results that are surprising and unexpected when compared to the results of additive packages utilizing less than 50 wt %, e.g., less than 25 wt %, less than 20 wt %, less than 15 wt %, less than 10 wt %, less than 5 wt % or less than 1 wt %.
In another embodiment of the invention, the sulfur-containing phenol is present in an amount of at least about 1 wt% e.g., at least about 5 wt%, at least about 10 wt%, at least about 15 wt%, at least about 20 wt%, at least about 25 wt% or at least about 50 wt%, based on the weight of the additive package. In terms of ranges, the sulfur-containing phenol is present in an amount ranging from about 5 to about 50 wt%, e.g., from about 10 wt% to about 25 wt%, from about 10 wt% to about 20 wt% or from about 10 wt% to about 15 wt%, based on the weight of the additive package.

In one embodiment of the invention, the ADPA is present in an amount of at least 50 wt%, e.g., at least 60 wt%, or at least 70 wt%, the PNA is present in an amount of at least 1 wt%, e.g., at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt% or at least 25 wt%, and the sulfur-containing phenol is present in an amount of at least 1 wt%, e.g., at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 25 wt% or at least 50 wt%, and the sulfur-containing phenol is present in an amount of at least 1 wt%, e.g., at least 5 wt%, at least 10 wt%, at least 15 wt%, at least 20 wt%, at least 25 wt% or at least 50 wt%, all wt% being based on the weight of the additive package.

In a preferred embodiment of the invention, the ADPA is present in an amount of about 70 wt % ±10 wt %, e.g., ±5 wt %, ±3 wt % or ±1 wt%; the PNA is present in an amount of about 15 wt% ±14 wt%, e.g., ±10 wt %, ±5 wt %, ±3 wt % or ±1 wt%; and the sulfur-containing phenol is present in an amount of about 15 wt% ±10 wt %, e.g., ±5 wt %, ±3 wt % or ±1 wt%; all wt% being based on the weight of the additive package. Additional preferred embodiments utilize the wt % combinations of ADPA, PNA and sulfur-containing phenol listed in TABLE 2. Each of the weight percentages listed for these embodiments can vary by ±10 wt%, e.g., ±5 wt %, ±3 wt %, ±2 wt % or ±1 wt %.

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>Exemplary Combination</td>
</tr>
<tr>
<td>1</td>
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<tr>
<td>12</td>
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<td>13</td>
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</table>

In one embodiment of the invention, the weight ratio of ADPA to sulfur-containing phenol in the additive package is at least about 3:1, e.g., at least about 6:1 or at least about 10:1.

In another embodiment of the invention, the weight ratio of PNA to sulfur-containing phenol in the additive package ranges from about 1:10 to about 10:1, e.g., from about 1:8 to about 8:1, from about 1:5 to about 5:1 or from about 1:3 to about 3:1.

In another embodiment of the invention, the weight ratio of ADPA and PNA, combined to sulfur-containing phenol is at least about 2:1, e.g., at least about 3:1, at least about 4:1, at least about 5:1 or at least about 10:1.

In another embodiment of the invention, the weight ratio of ADPA to PNA in the additive package is at least about 2:1, e.g., at least about 3:1, at least about 4:1, at least about 5:1 or at least about 10:1. In terms of ranges, the weight ratio ranges from about 3:1 to about 20:1, e.g., from about 3:1 to about 15:1 or from about 3:1 to about 10:1.

In one embodiment, the base stock is present in an amount of at least about 50 wt%, e.g., at least about 75 wt%, at least about 95 wt% or at least about 99 wt%, based on the weight of the lubricating oil composition (including the additive package).

In one embodiment, the additive package is present in an amount of at least about 0.05 wt%, e.g., at least about 0.5 wt%, at least about 1 wt% or at least about 10 wt%, based on the weight of the lubricating oil composition.

In terms of ranges, the ratio of base stock to additive package ranges from about 50:50 to about 99:0.05, e.g., from about 75.25 to about 99.9:0.05, from about 90:10 to about 99:1 or from about 95:5 to about 99:1. In a preferred embodiment of the invention, the lubricating oil composition comprises about 99 wt% of the base stock combined with about 1 wt% of the additive package based on the total weight of the lubricating oil.

The additive packages of the present invention are especially useful as components in combination with many potential base stocks. The additive packages may be included in a variety of oils with lubricating viscosity, including natural and synthetic lubricating oils and mixtures thereof. As an example, the additive packages are included in crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines. The additive packages can also be used, for example, with gas engine lubricants, turbine lubricants, automatic transmission fluids, gear lubricants, compressor lubricants, metal-working lubricants, hydraulic fluids, and other lubricating oil and grease compositions. In one embodiment of the invention, the additive package is utilized in the preparation of lubricants that may have food contact e.g., incidental food contact. More specifically, the additive package may be utilized with an H1 food grade base stock.

In one embodiment, the additive packages are combined with a grease or a combination of greases. Greases are often used in applications having high pressures and slow speed. Such applications include, but are not limited to, continuous casting operations.

In one embodiment of the invention, the ADPA of the present invention comprises ADPAs of the Formula I:

![Formula I](image)

wherein R₁ and R₂ are independently selected from the group consisting of linear or branched C₃-C₆₆ alkyl, substituted or unsubstituted C₃-C₆₆ cycloalkyl.

In one embodiment of the invention, R₁ and R₂ may be the same substituent. In one embodiment of the invention, R₁ or R₂ are both not hydrogen.
Representative examples of alkyl groups for use herein for \( R_1 \) and \( R_2 \) include, for example, a straight or branched hydrocarbon chain radical containing from 1 to 20 carbon atoms, e.g., methyl, ethyl, n-propyl, 1-methylethyl (isopropyl), n-butyl, isobutyl, n-pentyl, etc., mixtures and isomers thereof, and the like.

Representative examples of cycloalkyl groups for use herein for \( R_1 \) and \( R_2 \) include, for example, substituted or unsubstituted rings containing from about 5 to about 20 carbon atoms, e.g., cyclopentyl, cyclohexyl, n-methyl-cyclohexyl, n-dimethyl-cyclohexyl, n-ethyl-cyclohexyl, cycloheptyl, cyclooctyl, etc., mixtures and thereof, and the like.

In another embodiment of the invention, the ADPA is further alkylated with more than two substituent groups. In another embodiment of the invention, the ADPA is alkylated with only one substituent group.

Preferred ADPAs that can be employed in the practice of the present invention include, for example, nonylated diphenylamine, octylated diphenylamine (e.g., di(octylphenyl)amine), styrenated diphenylamine, octylated styrenated diphenylamine, butylated octylated diphenylamine, diphenylamine, butyldiphenylamine, dibutylphenylamine, octyl-diphenylamines, dioctylphenylamine, nonylphenylamine, dinonylphenylamine, heptyldiphenylamine, diheptylphenylamine, methylstyryldiphenylamine, mixed butyl/octyl alkylated diphenylamines, mixed butyl/styryl alkylated diphenylamines, mixed nonyl/ethyl alkylated diphenylamines, mixed octyl/styryl alkylated diphenylamines, mixed styryl/styryl alkylated diphenylamines, tert-butyl diphenylamine, di-tert-butyl diphenylamine, mono-octyl diphenylamine, dodecyl diphenylamine, hexadecyl diphenylamine, eicosyl diphenylamine, tetraeicosyl diphenylamine, octacosyl diphenylamine, polyisobutyl diphenylamine and mixtures thereof.

Preferred commercially produced ADPAs that can be utilized in the present invention include, for example, Irganox® L60, Irganox® L57, and Irganox® L67 from Ciba Specialty Chemicals; Naugalube® AMS, Naugalube® 438, Naugalube® 438R, Naugalube® 438L, Naugalube® 500, Naugalube® 640, and Naugalube® 680 from Chemtura Corporation; Goodrite® 3123, Goodrite® 3190X36, Goodrite® 3127, Goodrite® 3128, Goodrite® 33185X1, Goodrite® 3190, Goodrite® 3190X29, Goodrite® 33190X40, and Goodrite® 3191, Goodrite® 3192 from BFGoodrich Specialty Chemicals; HiTEC® 569 antioxidant and HiTEC® 4793 antioxidant available from Ethyl Corporation; Vanlube® DND, Vanlube® NA, Vanlube® PNA, Vanlube® SL, Vanlube® SLHP, Vanlube® SS, Vanlube® 81, Vanlube® 848, and Vanlube® 849 and Vanlube® 961 from R. T. Vanderbilt Company, Inc. In one embodiment of the invention, the additive package comprises a mixture of two or more ADPAs selected from the structures and compounds identified above. Exemplary mixtures are mixed mono- and di-octyl diphenylamines (DPAs), mixed mono and di-styryl DPAs, mixed butyl/styryl alkylated DPAs, mixed octyl/styryl alkylated DPAs and mixed butyl/octyl alkylated DPAs.

In one embodiment of the present invention, the PNA comprises phenyl-\( \alpha \)-naphthylamine. In another embodiment of the invention, the PNA comprises phenyl-p-naphthylamine.

In one embodiment of the present invention, the PNA comprises one or more PNAs of formula II:

\[
\text{Formula II}
\]

In another embodiment of the present invention, the PNA comprises one or more PNAs of formula III:

\[
\text{Formula III}
\]

In another embodiment of the present invention, the PNA comprises a blend of PNAs of the previous two formulae.

In another embodiment of the invention, the PNA is substituted, e.g., alkylated, with one or more substituent groups. The potential substituent groups include, for example, the substituents mentioned above as candidates for \( R_1 \) and \( R_2 \). In one embodiment, the phenyl rings of Formula II or Formula III are substituted at the ortho, para or meta positions.

Preferred PNAs that can be employed in the present invention include, for example, octyl alkylated phenyl-\( \alpha \)-naphthylamine, dodecyl phenyl-\( \alpha \)-naphthylamine and mixed alkylated phenyl-\( \alpha \)-naphthylamines. Examples of commercially produced substituted PNAs are Naugalube® PANA and Irganox® L60.

Preferred commercially produced PNAs that can be utilized in the present invention include, for example, Naugard® PANA.

In one embodiment of the invention, there is a composition comprising a mixture of two or more PNAs selected from the structures and compounds identified above.

In one embodiment of the invention, the sulfur-containing phenol comprises sulfur-containing phenols of Formula IV:

\[
\text{Formula IV}
\]

wherein \( R_1 \) is a sulfur-containing alkyl or aryl group, or a sulfur-containing alkene or carboxylic acid; and

wherein \( R_3 \) and \( R_4 \) are alkyl or aryl.

Preferred sulfur-containing phenols that can be employed in the present invention include, for example, 2,2'-thiodiethylenedioxy bis(3,5-di-t-butyl-4-hydroxyphenyl)propiionate, 2,2'-thiodi(4-methyl-6-t-butyl-phenol), 4,4'-thiodi(bis(4-methyl-6-t-butyl-phenol), 4,4'-thiodi(bis(4-tert-butyl-3-methyl-phenoxy) propane, 2,2'-thiodiethylenedioxy bis(3,5-di-t-butyl-4-hydroxyphenyl)propiionate, 2,2'-thiodi(4-methyl-6-t-butyl-phenol), 4,4'-thiodi(bis(4-methyl-6-t-butyl-phenol), 4,4'-thiodi(bis(4-tert-butyl-3-methyl-phenoxy) propane.
(2-t-butyl-5-methylphenol) and iso(C10-C14)alkyl(3,5-di tert-butyl-4-hydroxyphenyl)methylthioacetate.

Preferred commercially produced sulfur-containing phenols that can be utilized in the present invention include, for example, Naugalube® 15, Naugalube® 16 and Naugalube® 18 from Chemtura Corporation; Irganox® R115, Irganox® R118, Irganox® R1035, Irganox® R1081 and Irganox® R1415 for Ciba Specialty chemicals. In one embodiment of the invention, the additive package is prepared by mixing Naugalube® 438L with Naugard® PNA and a sulfur-containing phenol. Mixing is carried out at 65°C and under nitrogen protection. The mixing may be carried out for at least 5 minutes, e.g., at least 10 minutes, at least 15 minutes, at least 25 minutes, or at least 60 minutes. It should be appreciated by those of ordinary skill in the art that the mixing time will vary based on the quantities of each of the materials. The resultant mixture was a free-flowing liquid at room temperature having a viscosity, measured at 40°C, of less than about 100,000 cP, e.g., less than about 50,000 cP, less than about 40,000 cP, less than about 25,000 cP or less than about 10,000 cP. In other embodiments, the resultant mixture was dark reddish in color.

In a preferred embodiment of the invention, the additive package comprises butyl and octylated diphenylamine, octyl alkylated phenyl-alpha-naphthylamine and 2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate. In another preferred embodiment of the invention, the additive package comprises butyl and octylated diphenylamine, octyl alkylated phenyl-alpha-naphthylamine and 2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate.

Additional embodiments utilize the combinations of ADPA, PNA and sulfur-containing phenol listed in TABLE 3. This listing is not exclusive of all preferred embodiments.

<table>
<thead>
<tr>
<th>Exemplary Combination</th>
<th>ADPA</th>
<th>PNA</th>
<th>Sulfur-containing Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed mono- and di-cetyl DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed mono- and di-cetyl DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed mono- and di-nonyl DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
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<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed mono- and di-styryl DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed mono- and di-styryl DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed butyl/styryl alkylated DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
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</tr>
<tr>
<td>Mixed butyl/styryl alkylated DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
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<tr>
<td>Mixed octyl/styryl alkylated DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed octyl/styryl alkylated DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed butyl/styryl alkylated DPAs</td>
<td>Octyl alkylated phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
<tr>
<td>Mixed butyl/styryl alkylated DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
</tbody>
</table>

Exemplary ADPA, PNA and sulfur-containing phenol candidates are listed in TABLE 4. This listing is not exclusive.

<table>
<thead>
<tr>
<th>ADPA</th>
<th>PNA</th>
<th>Sulfur-containing Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixed mono- and di-cetyl DPAs</td>
<td>Phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
</tr>
<tr>
<td>Mixed mono- and di-cetyl DPAs</td>
<td>Octyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
</tr>
<tr>
<td>Mixed mono- and di-styryl DPAs</td>
<td>Dodecyl phenyl-alpha-naphthylamine</td>
<td>2,2'-thiodiethylene bis (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
</tr>
<tr>
<td>Mixed butyl/styryl alkylated DPAs</td>
<td>Iso(C10-C14)alkyl (3,5-di-t-butyl-4-hydroxyphenyl)propionate</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4-continued

<table>
<thead>
<tr>
<th>ADPA</th>
<th>PNA</th>
<th>Sulfur-containing Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkylated DPAs</td>
<td>tert-butyl-4-hydroxyphenyl</td>
<td>methylthioacetate</td>
</tr>
<tr>
<td>Mixed octyl/styryl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>alkylated DPAs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed butyl/octyl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>alkylated DPAs</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Additional additives may be incorporated in the compositions of the invention to enable them to meet particular requirements. Examples of additives that may be included in the lubricating oil compositions are dispersants, detergents, metal rust inhibitors, viscosity index improvers, corrosion inhibitors, oxidation inhibitors, friction modifiers, other dispersants, anti-foaming agents, anti-wear agents, and pour point depressants. Some are discussed in further detail below.

Lubricating oil compositions of the present invention can further contain one or more ashless dispersants, which effectively reduce formation of deposits upon use in gasoline and diesel engines, when added to lubricating oils. Ashless dispersants useful in the compositions of the present invention comprise an oil soluble polymeric long chain backbone having functional groups capable of associating with particles to be dispersed. Typically, such dispersants comprise amine, alcohol, amide or ester polar moieties attached to the polymer backbone, often via a bridging group. The ashless dispersant can be, for example, selected from oil soluble salts, esters, amido-esters, amides, imides, and oxazolines of long chain hydrocarbon-substituted mono- and polyalkylcylic acids or anhydrides thereof; thioalkoxyalkylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having polyamine moieties attached directly thereto; and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine.

Preferred dispersants include polyamine-derivatized poly alpha-olefin, dispersants, particularly ethylene/butene alpha-olefin and polyisobutylene-based dispersants. Particularly preferred are ashless dispersants derived from polyisobutylene substituted with succinic anhydride groups and reacted with polyethylene amines, e.g., polyethylene diamine, tetraethylenetetramine; or a polyoxyalkylene polyamine, e.g., polyoxypropylene diamine, trimethylolaminononmethane; or a hydroxy compound, e.g., pentaerythritol; and combinations thereof. One particularly preferred dispersant combination is a combination of (A) polyisobutylene substituted with succinic anhydride groups and reacted with (B) a hydroxy compound, e.g., pentaerythritol; (C) a polyoxyalkylene polylamine, e.g., polyoxypropylene diamine, or (D) a polyalkylene diamine, e.g., polyethylene diamine and tetraethylene pentamine using about 0.3 to about 2 moles of (B), (C) and/or (D) per mole of (A). Another preferred dispersant combination comprises a combination of (A) polyisobutylene succinic anhydride with (B) a polyalkylene polylamine, e.g., tetraethylene pentamine, and (C) a polyhydroxy alcohol or polyhydroxy-substituted aliphatic primary amine, e.g., pentaerythritol or trimethylolaminononmethane, as described in U.S. Pat. No. 3,632,511.

Another class of ashless dispersants comprises Mannich base condensation products. Generally, these products are prepared by condensing about one mole of an alkyl-substituted mono- or polyhydroxy benzene with about 1 to 2.5 moles of carbonyl compound(s) (e.g., formaldehyde and paraformaldehyde) and about 0.5 to 2 moles of polyalkylene polyamine, as disclosed, for example, in U.S. Pat. No. 3,442,808. Such Mannich base condensation products can include a polymer product of a metallocone catalyzed polymerization as a substituent on the benzene group, or can be reacted with a compound containing such a polymer substituted on a succinic anhydride in a manner similar to that described in U.S. Pat. No. 3,442,808. Examples of functionalized and/or derivatized olefin polymers synthesized using metallocone catalyst systems are described in the publications identified supra.

The dispersant can be further post treated by a variety of conventional post treatments such as boration, as generally taught in U.S. Pat. Nos. 3,087,936 and 3,254,025. Boration of the dispersant is readily accomplished by treating an acyl nitrogen-containing dispersant with a boron compound, such as boron oxide, boron halide boron acids, and esters of boron acids, in an amount sufficient to provide from about 0.1 to about 20 atomic proportions of boron for each mole of acylated nitrogen composition. Useful dispersants contain from about 0.05 to about 2.0 wt. %, e.g., from about 0.05 to about 0.7 wt. % boron. The boron, which appears in the product as dehydrated boric acid polymers (primarily \(\text{H}_2\text{BO}_3\)), is believed to attach to the dispersant imides and dimides as amine salts, e.g., the metabolite salt of the dimide. Boration can be performed by adding from about 0.5 to 4 wt. %, e.g., about 1 to about 3 wt % (based on the mass of acyl nitrogen compound) of a boron compound, preferably boric acid, usually as a slurry, to the acyl nitrogen compound and heating with stirring at from about 135°C to about 190°C, e.g., 140°C to 170°C, for from about one to about five hours, followed by nitrogen stripping. Alternatively, the boron treatment can be conducted by adding boric acid to a hot reaction mixture of the dicarboxylic acid material and amine, while removing water. Other post reaction processes commonly known in the art can also be applied.

The dispersant can also be further post treated by reaction with a so-called “capping agent.” Conventionally, nitrogen-containing dispersants have been “capped” to reduce the adverse effect such dispersants have on the fluorocarbon engine seals. Numerous capping agents and methods are known. Of the known “capping agents,” those that convert basic dispersant amino groups to non-basic moieties (e.g., amido or imido groups) are most suitable. The reaction of a nitrogen-containing dispersant and alkyl acetacetate (e.g., ethyl acetacetate (EAA)) is described, for example, in U.S. Pat. Nos. 4,839,071, 4,839,072, and 4,579,675. The reaction of a nitrogen-containing dispersant and formic acid is described, for example, in U.S. Pat. No. 3,185,704. The reaction product of a nitrogen-containing dispersant and other suitable capping agents are described in U.S. Pat. No. 4,663,064 (glycolic acid); U.S. Pat. Nos. 4,612,132, 5,334,321, 5,356,552, 5,716,912, 5,849,676, and 5,861,363 (alkyl and alkylene carbonates, e.g., ethylene carbonate); U.S. Pat. No. 5,328,622 (mono-epoxide); U.S. Pat. No. 5,026,495; U.S. Pat. Nos. 5,085,788, 5,259,906, 5,407,591 (poly (e.g., bis-epoxides)); and U.S. Pat. No. 4,686,054 (maleic anhydride or succinic anhydride). The foregoing list is not exhaustive, and other methods of capping nitrogen-containing dispersants are known to those skilled in the art.

For adequate piston deposit control, a nitrogen-containing dispersant can be added in an amount providing the
lubricating oil composition with from about 0.03 wt % to about 0.15 wt %, preferably from about 0.07 to about 0.12 wt %, of nitrogen.

[0059] Metal-containing or ash-forming detergents function both as detergents to reduce or remove deposits and as acid neutralizers or rust inhibitors, thereby reducing wear and corrosion and extending engine life. Detergents generally comprise a polar head with a long hydrophobic tail, with the polar head comprising a metal salt of an acidic organic compound. The salts can contain a substantially stoichiometric amount of the metal, in which case they are usually described as normal or neutral salts, and would typically have a total base number or TBN (as can be measured by ASTM D2896) of from 0 to 80. A large amount of a metal base can be incorporated by reacting excess metal compound (e.g., an oxide or hydroxide) with an acidic gas (e.g., carbon dioxide). The resulting overbased detergent comprises neutralized detergent as the outer layer of a metal base (e.g. carbonate) micelle. Such overbased detergents can have a TBN of 150 or greater and typically will have a TBN of from 250 to 450 or more.

[0060] Detergents that can be used include oil-soluble neutral and overbased sulfonates, phenates, sulfonated phenates, thiophosphonates, salts, naphthenates, and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g., sodium, potassium, lithium, calcium, and magnesium. The most commonly used metals are calcium and magnesium, which can both be present in detergents used in a lubricant, and mixtures of calcium and/or magnesium with sodium. Particularly convenient metal detergents are neutral and overbased calcium sulfonates having TBN of from 20 to 450 TBN, and neutral and overbased calcium phenates and sulfonated phenates having TBN of from 50 to 450. Combinations of detergents, whether overbased or neutral or both, can be used.

[0061] Sulfonates can be prepared from sulfonic acids which are typically obtained by the sulfonation of alkyl substituted aromatic hydrocarbons such as those obtained from the fractionation of petroleum or by the alkylation of aromatic hydrocarbons. Examples include those obtained by alkylation benzene, toluene, xylene, naphthalene, diphenyl, or their halogen derivatives such as chlorobenzene, chlorotoluene and chloronaphthalene. The alkylation can be performed in the presence of a catalyst with alkylation agents having from about 3 to more than 70 carbon atoms. The alkylar sulfonates usually contain from about 9 to about 80 or more carbon atoms, preferably from about 16 to about 60 carbon atoms, per alkyl substituted aromatic moiety.

[0062] The oil soluble sulfonates or alkyl sulfonic acids can be neutralized with oxides, hydroxides, alkoxides, carbonates, carboxylate, sulfides, hydrosulfides, nitrates, borates, and ethers of the metal. The amount of metal compound is chosen having regard to the desired TBN of the final product but typically ranges from about 100 to 220 wt. % (preferably at least 125 wt. %) of that stoichiometrically required.

[0063] Metal salts of phenols and sulfonated phenols are prepared by reaction with an appropriate metal compound such as an oxide or hydroxide, and neutral or overbased products can be obtained by methods well known in the art. Sulfurized phenols can be prepared by reacting a phenol with sulfur or a sulfur containing compound such as hydrogen sulfide, sulfur monohalide, or sulfur dihalide, to form products which are generally mixtures of compounds in which two or more phenols are bridged by sulfur containing bridges.

[0064] Dihydrocarbaryl dithiophosphate metal salts are frequently used as antiwear and antioxidant agents. The metal can be an alkali or alkaline earth metal, or aluminum, lead, tin, molybdenum, manganese, nickel or copper. The zinc salts are most commonly used in lubricating oil in amounts of 0.1 to 10 wt %, preferably 0.2 to 2 wt %, based upon the total weight of the lubricating oil composition. They can be prepared in accordance with known techniques by first forming a dihydrocarbaryl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P2S5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid can be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbaryl groups on one are entirely secondary in character and the hydrocarbaryl groups on the others are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could be used, but the oxides, hydroxides, and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to the use of an excess of the basic zinc compound in the neutralization reaction.

[0065] The preferred zinc dihydrocarbaryl dithiophosphates are oil soluble salts of dihydrocarbaryl dithiophosphoric acids and can comprise zinc dialkyl dithiophosphates. The present invention can be particularly useful when used with passenger car diesel engine lubricant compositions containing phosphorus levels of from about 0.02 to about 0.12 wt %, such as from about 0.03 to about 0.10 wt %, or from about 0.05 to about 0.08 wt %, based on the total mass of the composition and heavy duty diesel engine lubricant compositions containing phosphorus levels of from about 0.02 to about 0.16 wt %, such as from about 0.05 to about 0.14 wt %, or from about 0.08 to about 0.12 wt %, based on the total mass of the composition. In one preferred embodiment, lubricating oil compositions of the present invention contain zinc dialkyl dithiophosphate derived predominantly (e.g., over 50 mol. %, such as over 60 mol. %) from secondary alcohols.

[0066] Oxidation inhibitors or antioxidants reduce the tendency of mineral oils to deteriorate in service. Oxidative deterioration can be evidenced by sludge in the lubricant, varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include hindered phenols, alkaline earth metal salts of alkylphenolthioketones having preferably C8 to C15 alkyl side chains, calcium nonylephenoxy sulfide, oil soluble phenates and sulfonated phenates, phosphosulfurized or sulfonized hydrocarbons, phosphorous esters, metal thiocarbamates, oil soluble copper compounds as described in U.S. Pat. No. 4,867,890, and molybdenum-containing compounds.

[0067] Typical oil soluble aromatic amines having at least two aromatic groups attached directly to one amine nitrogen contain from 6 to 16 carbon atoms. The amines can contain more than two aromatic groups. Compounds having a total of at least three aromatic groups, in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a —CO—, —SO2— or alkylene group) and two are directly attached to one amine nitrogen, are also considered aromatic amines having at least two aromatic groups attached directly to the nitrogen. The aromatic rings are typically substituted by one or more substituents.
selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups.

[0068] Preferably, lubricating oil compositions useful in the practice of the present invention, particularly lubricating oil compositions useful in the practice of the present invention that are required to contain no greater than 1200 ppm of phosphorus, contain ashless antioxidants other than benzenediamines, in an amount of from about 0.1 to about 5 wt. %, preferably from about 0.3 wt. % to about 4 wt. %, more preferably from about 0.5 wt. % to about 3 wt. %. Where the phosphorus content is required to be lower, the amount of ashless antioxidant other than benzenediamine will preferably increase accordingly.

[0069] Representative examples of suitable viscosity modifiers are polyisobutylene, copolymers of ethylene and propylene, polymethacrylates, methacrylate copolymers, copolymers of an unsaturated dicarboxylic acid and a vinyl compound, interpolymers of styrene and acrylic esters, and partially hydrogenated copolymers of styrene/isoprene, styrenel butadiene, and isoprene/butadiene, as well as the partially hydrogenated homopolymers of butadiene and isoprene.

[0070] A viscosity index improver dispersant functions both as a viscosity index improver and as a dispersant. Examples of viscosity index improver dispersants include reaction products of amines, for example, polyamines, with a hydrocarbyl-substituted mono- or dicarboxylic acid in which the hydrocarbyl substituent comprises a chain of sufficient length to impart viscosity index improving properties to the compounds. In general, the viscosity index improver dispersant can be, for example, a polymer of a C₄ to C₂₄ unsaturated ester of vinyl alcohol or a C₃ to C₁₀, unsaturated mono-carboxylic acid or a C₄ to C₁₀ di-carboxylic acid with an unsaturated nitrogen-containing monomer having 4 to 20 carbon atoms; a polymer of a C₂ to C₂₀ olefin with an unsaturated C₂ to C₁₀ mono- or di-carboxylic acid neutralized with an amine, hydroxymeine or an alcohol; or a polymer of ethylene with a C₃ to C₂₀ olefin further reacted either by grafting a C₄ to C₂₀ unsaturated nitrogen-containing monomer thereon or by grafting an unsaturated acid onto the polymer backbone and then reacting carboxylic acid groups of the grafted acid with an amine, hydroxy amine, or alcohol.

[0071] Friction modifiers and fuel economy agents that are compatible with the other ingredients of the final oil can also be included. Examples of such materials include glyceryl monoesters of higher fatty acids, for example, glyceryl monostearate; esters of long chain polycarboxylic acids with diols, for example, the butane diol ester of a dimethylized unsaturated fatty acid; oxazoline compounds; and alkoxylated alkyl-stabilized mono-amines, diamines and alkyl ether amines, for example, ethoxylated tallow amine and ethoxylated tallow ethyl amine.

[0072] Other known friction modifiers comprise oil-soluble organo-tungsten compounds. Such organo-tungsten friction modifiers also provide antioxidant and antiwear credits to a lubricating oil composition. Examples of such oil soluble organo-tungsten compounds include dithiocarbamates, dithiophosphates, dithiophosphinates, xanthates, thioxanthates, sultidies, and the like, and mixtures thereof. Particularly preferred are molybdenum dithiocarbamates, dialkyldithiophosphates, alkyl xanthates, and alkylthioxanethanes.

[0073] Additionally, the molybdenum compound can be an acidic molybdenum compound. These compounds will react with a basic nitrogen compound as measured by ASTM test D-664 or D-2896 titration procedure and are typically hexavalent. Included are molybdic acid, ammonium molybdate, sodium molybdate, potassium molybdate, and other alkaline metal molybdates and other molybdenum salts, e.g., hydrogen sodium molybdate, MoOC₂H₅, MoO₂Br₂, MoO₂Cl₂, molybdenum trioxide or similar acidic molybdenum compounds.

[0074] Another group of organo-tungsten compounds useful in the lubricating compositions of this invention are trinuclear molybdenum compounds, especially those of the formula Mo₉SₓLₓQₓ and mixtures thereof wherein the L are independently selected ligands having organo groups with a sufficient number of carbon atoms to render the compound soluble or dispersible in the oil, n is from 1 to 4, k varies from 4 through 7, Q is selected from the group of neutral electron donating compounds such as water, alcohols, amines, ethers, phosphines, and esters, and z ranges from 0 to 5 and includes non-stoichiometric values. At least 21 total carbon atoms should be present among all the ligand organo groups, such as at least 25, at least 30, or at least 35 carbon atoms.

[0075] Pour point depressants, otherwise known as lube oil flow improvers (LOFI), lower the minimum temperature at which the fluid will flow or can be poured. Such additives are well known. Typical of those additives that improve the low temperature fluidity of the fluid are C₅ to C₁₂ dialkyl fumarate/vinyl acetate copolymers, and polymethacrylates. Foam control can be provided by an antifoamant of the polysiloxane type, for example, silicone oil or polydimethylsiloxane.

[0076] Some of the above-mentioned additives can provide a multiplicity of effects; thus, for example, a single additive can act as a dispersant-oxidation inhibitor. This approach is well known and need not be further elaborated herein.

[0077] In the present invention it may be necessary to include an additive that maintains the stability of the viscosity of the blend. Thus, although polar group-containing additives achieve a suitably low viscosity in the pre-blending stage, it has been observed that some compositions increase in viscosity when stored for prolonged periods. Additives which are effective in controlling this viscosity increase include the long chain hydrocarbons functionalized by reaction with mono- or dicarboxylic acids or anhydrides which are used in the preparation of the ashless dispersants as hereinbefore disclosed.

[0078] When lubricating compositions contain one or more of the above-mentioned additives, each additive is typically blended into the base stock in an amount that enables the additive to provide its desired function. Representative effect amounts of such additives, when used in crankcase lubricants, are listed below in TABLE 5. All the values listed are exemplary and are stated as weight percent active ingredient.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Wt % (Desirable)</th>
<th>Wt % (Preferred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal Detergents</td>
<td>0.1-15</td>
<td>0.2-9</td>
</tr>
<tr>
<td>Corrosion Inhibitor</td>
<td>0.0-0.5</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Metal Dihydrocarbyl</td>
<td>0.1-0.6</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>Dithiophosphate</td>
<td>0.0-0.5</td>
<td>0.01-0.3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.0-0.5</td>
<td>0.01-0.1</td>
</tr>
<tr>
<td>Pour Point Depressant</td>
<td>0.01-0.5</td>
<td>0.01-0.1</td>
</tr>
<tr>
<td>Antifoaming Agent</td>
<td>0.0-0.5</td>
<td>0.001-0.15</td>
</tr>
<tr>
<td>Supplemental Antiwear Agents</td>
<td>0.0-0.1</td>
<td>0.0-0.5</td>
</tr>
</tbody>
</table>
### TABLE 5-continued

<table>
<thead>
<tr>
<th>ADDITIVE</th>
<th>Wt % (Desirable)</th>
<th>Wt % (Preferred)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction Modifier</td>
<td>0.0-5</td>
<td>0.0-1.5</td>
</tr>
<tr>
<td>Viscosity Modifier</td>
<td>0.01-0.10</td>
<td>0.25-3</td>
</tr>
<tr>
<td>Diamine</td>
<td>0.01-0.10</td>
<td>0.1-5</td>
</tr>
<tr>
<td>Base stock</td>
<td>Balance (i.e.)</td>
<td>Balance (i.e.)</td>
</tr>
</tbody>
</table>

-47.5-99.8                      -75.9-99.4

[0079] Fully formulated passenger car diesel engine lubricating oil (PCDO) compositions of the present invention preferably have a sulfur content of less than about 0.4 wt %, such as less than about 0.35 wt %, more preferably less than about 0.03 wt %, such as less than about 0.15 wt %. Preferably, the Noack volatility of the fully formulated PCDO oil (oil of lubricating viscosity plus all additives) will be no greater than 13, such as no greater than 12, preferably no greater than 10. Fully formulated PCDOs of the present invention preferably have no greater than 1200 ppm of phosphorus, such as no greater than 1000 ppm of phosphorus, or no greater than 800 ppm of phosphorins. Fully formulated PCDOs of the present invention preferably have a sulfated ash (SASH) content of about 1.0 wt % or less.

[0080] Fully formulated heavy duty diesel engine (HDD) lubricating oil compositions of the present invention preferably have a sulfur content of less than about 1.0 wt %, such as less than about 0.6 wt %, more preferably less than about 0.4 wt %, such as less than about 0.15 wt %. Preferably, the Noack volatility of the fully formulated HDD lubricating oil composition (oil of lubricating viscosity plus all additives) will be no greater than 20, such as no greater than 15, preferably no greater than 12. Fully formulated HDD lubricating oil compositions of the present invention preferably have no greater than 1600 ppm of phosphorus, such as no greater than 1400 ppm of phosphorus, or no greater than 1200 ppm of phosphorus. Fully formulated HDD lubricating oil compositions of the present invention preferably have a sulfated ash (SASH) content of about 1.0 wt % or less.

[0081] Examples of phenol anti-oxidants include 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4,6-di-tert-butylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-di-cyclopropyl-4-methylphenol, 2-(α-methylcyclohexyl)-4,6-dimethylphenol, 2,4,6-tri-cyclohexylylphenol, 2,6-di-tert-butyl-4-methoxyphenol, 2,6-di-tert-butyl-4-methyloxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octdecyloxyphenol, 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis(4,6-dimethylcyclohexylphenol), 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(4-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethyldienebis(4,6-di-tert-butylphenol), 2,2'-ethyldienebis(6-tert-butyl-4-isobutylphenol or 5-isopropylphenol, 2,2'-methylenebis(6-a-methylbenzyl)-4-nonylphenol), 2,2'-ethyldienebis(6-(α,α-dimethylbenzyl)-4-nonylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenyl)butane, 2,6-di(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(3-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3′-tert-butyl-4′-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopenta diene, bis[2-(3′-tert-butyl-2′-hydroxy-5-methylbenzyl]-6-tert-butyl-4-methylphenyl)terephthalate, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, bis(3,5-di-tert-butyl-4-hydroxybenzyl)dithiol terephthalate, 1,5,5-tri(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(3,5-di-tert-butyl-2-hydroxy-6-dimethyl benzyl)isocyanurate, dicarbonate 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, monoethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate calcium salt, 4-hydroxyauranilide, 4-hydroxyxestearilide, 2,4-bis-oc tylmepropaeto-6-(3,5-di-tert-butyl-4-hydroxyanilino)-s-triazine, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate, esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid and/or esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with monohydric or polyhydric alcohols, for example with methanol triethylene glycol octadeceanol tri-hydroxethyl isocyanurate 1,6-hexanediol bis-hydroxyethyl oxalic acid diamide neopentyl glycol diethyleneglycol, amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, for example, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionylhexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionyltrimethylsilylamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propionyltrimethylamine.

[0082] Examples of amine anti-oxidants include, N,N'-disopropyl-p-phenylenediamine, N,N'-di-isopropyl-3,4-phenylenediamine, N,N'-bis(1,4-phenylenediamine), N,N'-bis(1-ethyl-3-methylphenyl)-p-phenylenediamine, N,N'-bis(1-methylethyl)-p-phenylenediamine, N,N'-dicycloyxethyl-p-phenylenediamine, N,N'-di(2-naphthyl)-p-phenylenediamine, 4-(4-toluene-sulfonamido) diphenylamine, N,N'-dimethyl-N,N'-di-isopropyl-p-phenylenediamine, 4-a-butylaminophenol, 4-butylaminophenol, 4-nonylanilinophenol, 4-dodecanylanilinophenol, 4-octadecanylanilinophenol, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4-diaminophenylmethane, 4,4′-diaminophenylmethane, N,N,N'-tetramethy1-4,4′-diaminophenylmethane, 1,2-dif(2-methylphenyl)aminolnaphthalene, 1,2-di(phenylamine)propane (o-toly)biguanide, di[4-(1,3′-dimehylbutyl)phenyl]amine, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzoxazine, phenothiazine, N-allylphenothiazine.

[0083] Examples of further anti-oxidants include esters of thiophosphoronic acid or of thioldiacetic acid and salts of thiocarbamide acid or thiophosphoric acid.

[0084] Examples of metal deactivators include triazoles, benzotriazoles and their derivatives, tolutriazoles and their derivatives, 2-mercaptobenzothiazole, 2-mercaptobenzotriazole, 2,5-dimercaptobenzothiazole, 5,5′-methylenebisbenzotriazoles, 4,5,6,7-tetrahydrobenzothiazole, salicylidene dipropylenediamine, salicylaminoguanidine and their salts.

[0085] Examples of rust inhibitors include a) organic acids and esters, metal salts and anhydrides thereof, for example: N-octylsarcosine, sorbitol monooleate, lead napthenate, alkenysuccinimide, for example dodecanylbenzic anhydride, alkenysuccinic acid hemester and hemi-amides, and 4-nonylphenoxycetic acid; b) Nitrogenous compounds, for example, primary, secondary or tertiary aliphatic or cycloaliphatic amines and amine salts of organic and inorganic.
ganic acids, for example oil-soluble alkylammonium carboxylates; heterocyclic compounds, for example, substituted imidazolines and oxazolines, c) Phosphorus compounds, for example, amine salts of partial esters of phosphoric acid or partial esters of phosphoric acid, zinc dialkylidithiophosphates, d) Sulfur compounds, for example, barium dinonyl-naphthalenesulfonates, calcium petroleum sulfonates.

Examples of viscosity index improvers include polyacrylates, polymethacrylates, vinylpyrrolidone/methacrylic acid copolymers, polyvinylpyrrolidones, polybutenes, olefin copolymers, styreneacrylate copolymers, polyethylenes. Examples of pour-point depressants include polymethacrylate and alkylated naphthalene derivatives.

Examples of dispersants/surfactants include polybutenylsuccinimides or -imides, polybutenylphosphonanic acid derivatives, basic magnesium, calcium and barium sulfonates.

Anti-oxidants include compounds containing sulfur and/or phosphorus and/or halogen, such as sulfurized vegetable oils, zinc dialkylidithiophosphates, triSOURCEpyrrolidone, chlorinated paraffins, alkyl sulfides, ar dy sulfides and aryl trisulfides, triphenyIphospho-

Examples of lubricant compositions of the present invention improve the oxidative stability of materials that are subject to oxidative, thermal, and/or light-induced degradation. These organic materials can be natural or synthetic. These organic materials can include "functional fluids," lubricating oils, greases, and fuels, as well as automatic and manual transmission fluids, power steering fluid, hydraulic fluids, gas turbine oils, compressor lubricants, automotive and industrial gear lubricants and heat transfer oils.

In one embodiment, in food grade lubricants are used as base stocks. Such base stocks are those that could have incidental food contact. These are sometimes referred to as "above the line" lubricants. Such stocks may be used on food-processing equipment as a protective antitrust film, as a release agent on gaskets or seals of tank closures and as a lubricant for machine parts and equipment in locations where the lubricated part is potentially exposed to food. In one embodiment of the invention, the amount used is the smallest needed to accomplish the desired technical effect on the equipment.

Preferred commercially produced Hi food grade lubricants that can be utilized in the present invention include Tri-Flow® and Spray-on®711® from Krylon Products Group and NEVASTANE® lubricants from TOTAL Lubricants USA, Inc.

In one embodiment of the invention, base stocks of lubricating viscosity useful in the context of the present invention are selected from natural lubricating oils, synthetic lubricating oils, and mixtures thereof. The lubricating oil can range in viscosity from light distillate mineral oils to heavy lubricating oils, such as gasoline engine oils, mineral lubricating oils, and heavy duty diesel oils. Generally, the viscosity of the oil ranges from about 1 centistokes to about 400 centistokes, especially from about 4 centistokes to about 20 centistokes, as measured at 100°C.

In one embodiment of the invention, the diesel fuel is a petroleum-based fuel oil, especially a middle distillate fuel oil. Such distillate fuel oils generally boil within the range of from 110°C to 500°C, e.g., 150°C to 400°C. The fuel oil may comprise atmospheric distillate or vacuum distillate, cracked gas oil, or a blend in any proportion of straight run and thermally and/or refinery streams such as catalytically cracked and hydro-cracked distillates.

Examples of base stocks include Fischer-Tropsch fuels. Fischer-Tropsch fuels, also known as FT fuels, include those described as gas-to-liquid (GTL) fuels, biomass-to-liquid (BTL) fuels and coal conversion fuels. To make such fuels, syngas (CO+H₂) is first generated and then converted to normal paraffins by a Fischer-Tropsch process. The normal paraffins can then be modified by processes such as catalytic cracking/ reforming or isomerization, hydrocracking and hydroisomerization to yield a variety of hydrocarbons such as iso-paraffins, cyclo-paraffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types. Also suitable are diesel fuels derived from plant or animal sources. These can be used alone or in combination with other types of fuel.

Oils and fats derived from plant or animal materials are increasingly finding application as fuels and, in particular, as partial or complete replacements for petroleum derived middle distillate fuels such as diesel. Commonly, such fuels are known as "biodiesel." Biodiesel may be derived from many sources. Among the most common are the alkyl, esters of fatty acids extracted from plants, such as rapeseed, sunflower, and the like. These types of fuel are often referred to as FAME (fatty acid methyl esters).

Base stocks may include natural oils including animal oils and vegetable oils, e.g., tallow oil, castor oil, liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic, and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils. Other examples of oils and fats derived from animal or vegetable material are rapeseed oil, corn oil, soya bean oil, cottonseed oil, sunflower oil, castor oil, olive oil, peanut oil, maize oil, almon oil, canola oil, jojoba oil, palm kernel oil, coconut oil, mustard seed oil, jatropha oil, beef tallow, and fish oils. Further examples include oils derived from corn, jute, sesam, shea nut, ground nut, and inseed oil, and may be derived therfrom by methods known in the art. Rapeseed oil, which is a mixture of fatty acids and glycerol, is available in large quantities and can be obtained in a simple way by pressing from rapeseed. Recycled oils such as used kitchen oils are also suitable.

Base stocks are, for example, alkyl esters of fatty acids, which include commercial mixtures of the ethyl, propyl, butyl and especially methyl esters of fatty acids with 12 to 22 carbon atoms. For example, lauric acid, myristic acid, palmitic acid, palmitoleic acid, stearic acid, oleic acid, elaidic acid, petroselic acid, ricinoleic acid, elaeostearic acid, linoleic acid, linolenic acid, eicosanoic acid, gadoleic acid, docosanoic acid, or erucic acid are useful and have an iodine number from 50 to 150, especially 90 to 125. Mixtures with particularly advantageous properties are those which contain mainly, i.e., at least 50 wt. %, methyl esters of fatty acids with 16 to 22 carbon atoms and 1, 2, or 3 double bonds. The preferred lower alkyl esters of fatty acids are the methyl esters of oleic acid, linoleic acid, linolenic acid, and erucic acid.

Commercial mixtures of the stated kind are obtained for example by cleavage and esterification of animal and vegetable fats and oils by their transesterification with lower
aliphatic alcohols. For production of alkyl esters of fatty acids, it is advantageous to start from fats and oils which contain low levels of saturated acids, less than 20%, and which have an iodine number of less than 130. Blends of the following esters or oils are suitable, e.g., rapeseed, sunflower, coriander, castor, soya bean, peanut, cotton seed, beef tallow, and the like. Alkyl esters of fatty acids based on a new variety of rapeseed oil, the fatty acid component of which comprises more than 80 wt. % unsaturated fatty acids with 18 carbon atoms, are preferred.

[0100] Particularly preferred base stocks are oils capable of being utilized as biofuels. Biofuels, i.e., fuels derived from animal or vegetable material, are believed to be less damaging to the environment on combustion and are obtained from a renewable source. It has been reported that on combustion less carbon dioxide is formed by the equivalent quantity of petroleum distillate fuel, e.g., diesel fuel, and very little sulfur dioxide is formed. Certain derivatives of vegetable oil, e.g., those obtained by saponification and re-esterification with a monohydric alkyl alcohol, can be used as a substitute for diesel fuel.

[0101] Preferred biofuels are vegetable oil derivatives, of which particularly preferred biofuels are alkyl ester derivatives of rapeseed oil, cottonseed oil, soya bean oil, sunflower oil, olive oil, or palm oil, rapeseed oil methyl ester being especially preferred, either alone or in admixture with other vegetable oil derivatives, e.g., mixtures in any proportion of rapeseed oil methyl ester and palm oil methyl ester.

[0102] At present, biofuels are most commonly used in combination with petroleum-derived oils. The present invention is applicable to mixtures of biofuel and petroleum-derived fuels in any ratio. For example, at least 5%, preferably at least 25%, more preferably at least 50%, and most preferably at least 95% by weight of the oil, may be derived from a plant or animal source.

[0103] Synthetic base stock lubricating oils include hydrocarbon oils and halogen-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylene, propylene-propylenes, propylene-isobutylene copolymers, chlorinated polybutylene, poly (1-hexene), poly(1 octene), poly(1-decene)); alkylbenzenes (e.g., dodecylbenzene, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulfides and derivatives, analogs, and homologs thereof. Also useful are synthetic oils derived from a gas to liquid process from Fischer-Tropsch synthesized hydrocarbons, which are commonly referred to as gas to liquid or “GTL” base oils.

[0104] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methylpolyisopropylene glycol) either having a molecular weight of 1000 or diphenyl ether of polyethylene glycol having a molecular weight of 1000 to 1500), and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₈-C₁₈ fatty acid esters, and C₁₅ oxo acid diester of tetraethylene glycol.

[0105] Another suitable class of synthetic base stock lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alky1 succinic acids and alkyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodceyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl)sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisododecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosy1 sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2 ethylhexanoic acid.

[0106] Esters useful as synthetic oils also include those made from C₆ to C₁₄ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylol propane, pentaerythritol, dipentaerythritol and tripentaerythritol. Silicone-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxiloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids, polymeric tetrahydrofurans, poly-α-olefins, and the like.

[0107] Silicone-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxiloxane oils and silicate oils comprise another useful class of synthetic base stock lubricants; such oils include tetraethyl silicate, tetrasiropropy silicate, tetra(2-ethylhexyl)silicate, tetra(4-methyl-2-ethylhexyl)silicate, tetra(p-tert-butyl phenyl) silicate, hexa(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl) siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0108] The lubricating oil may be derived from unrefined, refined, reprocessed, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar and bitumen) without further purification or treatment. Examples of unrefined oils include a shale oil obtained directly from a retorting operation, a petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to unrefined oils, except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, percolation, and the like, all of which are well-known to those skilled in the art. Refined oils are obtained by treating refined oils in processes similar to those used to obtain the refined oils. Those refined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

[0109] Lubricating oil base stocks derived from the hydroisomerization of wax may also be used, either alone or in combination with the aforesaid natural and/or synthetic base stocks. Such wax isomerate oil is produced by the hydroisomerization of natural or synthetic waxes or mixtures thereof over a hydroisomerization catalyst. Natural waxes are typically the slack waxes recovered by the solvent dewatering of mineral oils; synthetic waxes are typically the wax produced by the Fischer-Tropsch process. The resulting isomer-
ate product is typically subjected to solvent dewaxing and fractionation to recover various fractions having a specific viscosity range. Wax isomerate is also characterized by possessing very high viscosity indices, generally having a viscosity index of at least 130, preferably at least 135 or higher and, following dewaxing, a pour point of about −20°C or lower.

[0110] The base stock of lubricating viscosity can comprise a Group I, Group II, or Group III base stock or base oil blends of the aforementioned base stocks. Preferably, the oil of lubricating viscosity is a Group II or Group III base stock, or a mixture thereof, or a mixture of a Group I base stock and one or more of a Group II and Group III. Preferably, a major amount of the oil of lubricating viscosity is a Group II, Group III, Group IV, or Group V base stock, or a mixture thereof. The base stock, or base stock blend, preferably has a saturate content of at least 65%, e.g., at least 75% or at least 85%. Most preferably, the base stock, or base stock blend, has a saturate content of greater than 90%.

[0111] Preferably the volatility of the oil or base oil, as measured by the Noack volatility test (ASTM D5880), is less than or equal to 30%, preferably less than or equal to 25%, more preferably less than or equal to 20%, most preferably less than or equal to 15%. Preferably, the viscosity index (VI) of the oil or base oil is at least 85, preferably at least 100, and most preferably from about 105 to 140.

[0112] Definitions for the base stocks and base oils in this invention are the same as those found in the American Petroleum Institute (API) publication “Engine Oil Licensing and Certification System,” Industry Services Department (14th ed., December 1996), Addendum 1, Dec. 1998. This publication categorizes base stocks as follows.

(a) Group I base stocks contain less than 90 percent saturates (as determined by ASTM D 2007) and/or greater than 0.03 percent sulfur (as determined by ASTM D2622, ASTM D 4294, ASTM D 4927 and ASTM D 3120) and have a viscosity index greater than or equal to 80 and less than 120 (as determined by ASTM D 2270).

(b) Group II base stocks contain greater than or equal to 90 percent saturates (as determined by ASTM D 2007) and less than or equal to 0.03 percent sulfur (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4927 and ASTM D 3120) and have a viscosity index greater than or equal to 80 and less than 120 (as determined by ASTM D 2270).

(c) Group III base stocks contain greater than or equal to 90 percent saturates (as determined by ASTM D 2007) and less than or equal to 0.03 percent sulfur (as determined by ASTM D 2622, ASTM D 4294, ASTM D 4927 and ASTM D 3120) and have a viscosity index greater than or equal to 120 (as determined by ASTM D 2270).

(d) Group IV base stocks are polyalphaolefins (PAO).

(e) Group V base stocks include all other base stocks not included in Groups I, II, III, or IV.

[0118] In one embodiment of the invention, the additive package is added to the base stock in the form of an additive package concentrate. The total amount of additive components in the concentrates generally varies from 20 to 95 wt. % or more, with the balance being diluent oil. The diluent oil may be the base stocks of the invention, as defined above, or a hydrocarbon, preferably aromatic, solvent or mixtures thereof. The concentrates may contain other additives, as listed below. Typically, the additive package concentrates are added to the base stock in an amount sufficient to provide the proper weight % of ADPA, PNA and/or sulfur-containing phenol to the finished lubricating oil composition.

[0119] Embodiments of the invention will become more evident in view of the following non-limiting examples.

Mid-High Temperature Thermo-Oxidation Engine Oil Simulation Test (TEOST MHT)

[0120] ASTM D7097 is the “Standard Test Method for Determination of Moderately High Temperature Piston Deposits by Thermo-oxidation Engine Oil Simulation Tests,” approved December 2004, which is incorporated by reference in its entirety for any purpose. ASTM D7097 is a new standard lubricant industry test for the evaluation of the oxidation and carbonaceous deposit-forming characteristics of engine oils. The test is designed to simulate high temperature deposition formation in the piston ring belt area of modern engines.

[0121] The test is also a useful tool for studying the formation of volatile organic molecules upon oxidation of an engine oil. It is generally understood that the formation of volatile organic molecules upon oxidation of a lubricant are detrimental because they lead to an increase in emissions, and can also promote further polymerization of the lubricant. Polymerization of the lubricant leads to viscosity increase, which is also undesirable. The additive combination of this invention is effective at controlling both deposit formation and the formation of volatile organic molecules. Typically, polar volatile organic molecules are formed by decomposition of an organic peroxide in the lubricant. This decomposition produces an organic alkoxyl radical that can react with another oil molecule to produce an alcohol, or that can degrade to form aldehydes and ketones. The degradation of aldehydes and ketones generally lowers molecular weight and thus provides more volatile fragments, which are pollutants and are also active precursors to oligomers and polymers that thicken the lubricant. It is therefore highly desirable to prevent or eliminate the formation of these polar volatile organic molecules.

[0122] The TEOST MHT determines the mass of deposit formed on a specially constructed, pre-weighed steel depositor rod. The fully formulated lubricant (8.4 g) and an organo-metallic catalyst (about 0.1 g) are added to a flask equipped with a Teflon stirring bar and stirred for 20-60 minutes without heating. The depositor rod, sample flask, oil inlet, air inlet, and volatiles collection vial are fitted to the TEOST apparatus according to manufacturers specifications. The pump is started at a high flow rate and run until the test oil reaches the connection of the pump and oil feed tube, at which point the pump flow is turned to zero. The heater switch is turned on and when the depositor rod temperature controller is between 200-210°C, the pump speed increased to achieve a sample delivery of 0.25±0.02 g/min, making sure that the oil is flowing down the depositor rod and is not leaking. The temperature is allowed to stabilize at 285±2°C. and the test is run under these conditions for 24 hrs.

[0123] Three test tubes are prepared with cyclohexane or another suitable hydrocarbon solvent for extraction of oil from the depositor rod. The test instrument is disassembled as per manufacturer’s instructions and the depositor rod is transferred to a weighing boat and kept under cover. The depositor rod is placed successively for 10 minutes each in each of the three test tubes prepared with a hydrocarbon solvent. The rod is placed in tared weighing boat and allowed to sit for 10 minutes to insure evaporation of the hydrocarbon solvent.
The rod and the boat are weighed, verifying that a constant mass has been achieved. The contents of the three test tubes, along with the lower-end cap deposits and glass mantle deposits, are washed into a common container which is then filtered using a glass funnel equipped with a filter cartridge. After completing the filtering, the filter cartridge is dried under vacuum and weighed, until a constant mass is achieved. The total mass of the deposits from the depositor rod and filter deposits is then determined.

[0124] During the 24 hour duration of the test, the volatile compounds in the formulated oil that are there originally or those formed during the test, are flushed off the depositor rod. These volatiles condense on the glass mantle and are collected on a continuous basis in a small, weighed vial. The vial and volatiles are measured at the end of the 24 hour test period and the amount of volatiles is calculated by subtracting the original weight of the vial.

Pressurized Differential Scanning Calorimeter (PDSC) Testing

[0125] PDSC testing can be used to measure the oxidation induction time (OIT) of materials. The samples discussed in this application were tested in accordance with the parameters listed in TABLE 1 (displayed above). Further, the PDSC instrument used was a Mettler DSC27HP manufactured by Mettler-Toledo, Inc. The PDSC method employs a steel cell under constant oxygen pressure throughout each run. The instrument has a typical repeatability of ±5.0 minutes with 95 percent confidence for an OIT of 200 minutes. At the beginning of a PDSC run, the PDSC steel cell is pressurized with oxygen and heated at a rate of 40°C per minute to the isothermal temperature listed in TABLE 1. The induction time is measured from the time the sample reaches its isothermal temperature until the enthalpy change is observed. The longer the oxidation induction time, the better the oxidative stability of the oil, i.e., longer OITs indicate more stable compositions. For every 50 grams of test oil prepared, 40 µL of oil soluble ferric naphthenate (6 weight percent in mineral oil) was added, prior to PDSC testing, to facilitate 50 ppm of iron in oil.

[0126] The antioxidant effect of the present invention may preferably be demonstrated in, for example, a low phosphorus-containing SAE 5W20 fully formulated engine oil. Such an engine oil was used in the PDSC testing discussed herein. The SAE 5W20 engine oil formulation was pre-blended with the components shown in TABLE 6, all of which are commercially available. The antioxidant package was subsequently added to the engine oil pre-blend. The PDSC testing was carried out at 185°C.

<p>| TABLE 6 |</p>
<table>
<thead>
<tr>
<th>Composition</th>
<th>Amounts in composition, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overbased Calcium Sulfonate Detergents</td>
<td>2.5</td>
</tr>
<tr>
<td>ZDDP</td>
<td>0.5</td>
</tr>
<tr>
<td>Succinimide Dispersant</td>
<td>6.4</td>
</tr>
<tr>
<td>Pour Point Depressant</td>
<td>0.1</td>
</tr>
<tr>
<td>OCP VI Improver</td>
<td>5.0</td>
</tr>
<tr>
<td>Base oil, API Group II</td>
<td>Balance</td>
</tr>
</tbody>
</table>

TABLE 7

<table>
<thead>
<tr>
<th>Examples 1-6</th>
<th>ADPA-Naugahyde 438L</th>
<th>PNA-Naugard PNA</th>
<th>Sulfur-containing phenol-Naugahyde-15</th>
<th>OIT, minutes</th>
<th>Expected OIT, minutes</th>
<th>TEOST MHT, mg</th>
<th>Expected TEOST MHT, mg</th>
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Comparative Examples A-C

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<th></th>
<th>A</th>
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<td>Expected TEOST MHT, mg</td>
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[0128] Each of additive packages 1-6 and A-C was blended with base stock at a weight ratio of about 99:1, base stock to additive package, to produce lubricant oil compositions. Example blends 1-6 are representative embodiments of the invention. Example blends A-C are comparative. The lubricant oil compositions were tested for OIT and TEOST MHT. The results are shown in TABLE 7.

[0129] As shown above, Comparative Examples A, B, and C represent pure ADPA, PNA, and sulfur-containing phenol, respectively. These blends demonstrated OIT values of 37.0, 52.0, and 3.8 minutes, respectively, and TEOST MHT values of 55.0, 63.7, and 63 grams of deposits, respectively. The expected OITs for additive packages may be calculated by adding the OITs of pure ADPA, PNA and sulfur-containing phenol according to the appropriate weight percentages of the respective mixture. The expected TEOST MHT values for additive packages may be calculated in a similar manner. The expected OITs and the expected TEOST MHT values are also shown in TABLE 7.

[0130] Surprisingly and unexpectedly, the lubricating oil blend 1, which is representative of the present invention,
demonstrates TEOST MHT values below 40. In addition, the additive packages of the embodiments of the invention demonstrate OIT values that are greater than 38 minutes, when tested according to the parameters mentioned above.

In addition, the additive packages of the embodiments of the invention surprisingly and unexpectedly demonstrate superior OIT's when compared to the expected values—in most cases, greater than 13% increases. Further, these additive packages show superior TEOST MHT values when compared to the expected values—in most cases, greater than 20% decreases, which are also surprising and unexpected.

Any feature described or claimed with respect to any disclosed implementation may be combined in any combination with any one or more other feature(s) described or claimed with respect to any other disclosed implementation or implementations, to the extent that the features are not necessarily technically incompatible, and all such combinations are within the scope of the present invention. Furthermore, the claims appended below set forth some non-limiting combinations of features within the scope of the invention, but also contemplated as being within the scope of the invention are all possible combinations of the subject matter of any two or more of the claims, in any possible combination, provided that the combination is not necessarily technically incompatible.

What is claimed is:

1. A lubricant oil composition comprising:
   (A) a base stock; and
   (B) a liquid additive package,
   wherein the additive package comprises:
   (i) an alkylated diphenylamine;
   (ii) at least about 5 weight percent of a phenyl naphthylamine, based on the weight of the additive package; and
   (iii) a sulfur-containing phenol.

2. The composition of claim 1, wherein the composition comprises the phenyl naphthylamine in an amount ranging from about 1 to about 50 weight percent, based on the weight of the additive package.

3. The composition of claim 1, wherein the composition comprises the phenyl naphthylamine an amount ranging from about 10 to about 20 weight percent, based on the weight of the additive package.

4. The composition of claim 1, wherein the composition comprises the sulfur-containing phenol in an amount ranging from about 5 to about 50 weight percent, based on the weight of the additive package.

5. The composition of claim 1, wherein the composition comprises the sulfur-containing phenol in an amount ranging from about 10 to about 20 weight percent, based on the weight of the additive package.

6. The composition of claim 1, wherein the composition comprises the alkylated diphenylamine in an amount of at least about 10 weight percent, based on the weight of the additive package.

7. The composition of claim 1, wherein the composition comprises the alkylated diphenylamine in an amount at least about 50 weight percent, based on the weight of the additive package.

8. The composition of claim 1, wherein the composition comprises the alkylated diphenylamine in an amount ranging from about 50 to about 99 weight percent, based on the weight of the additive package.

9. The composition of claim 1, wherein the composition comprises the alkylated diphenylamine in an amount at least about 50 wt %, based on the weight of the additive package, and the sulfur-containing phenol in an amount of at least about 1 wt %, based on the weight of the additive package.

10. The composition of claim 1, wherein the composition comprises the alkylated diphenylamine in an amount at least about 70 wt %, based on the weight of the additive package, and the phenyl naphthylamine in an amount of at least about 10 wt % and the sulfur-containing phenol in an amount of at least about 5 wt %, based on the weight of the additive package.

11. The composition of claim 1, wherein the additive package has a viscosity ranging from about 100 to about 50,000 cP at 25°C.

12. The composition of claim 1, wherein the additive package has a viscosity ranging from about 1,000 to about 25,000 cP at 25°C.

13. The composition of claim 1, wherein the weight ratio of alkylated diphenylamine to sulfur-containing phenol in the additive package is at least about 6:1.

14. The composition of claim 13, wherein the weight ratio of alkylated diphenylamine to phenyl naphthylamine in the additive package is at least about 4:1.

15. The composition of claim 1, wherein the weight ratio of phenyl naphthylamine to sulfur-containing phenol in the additive package ranges from about 1:5 to about 5:1.

16. The composition of claim 1, wherein the weight ratio of alkylated diphenylamine and phenyl naphthylamine, combined, to sulfur-containing phenol is at least about 4:1.

17. The composition of claim 1, wherein the composition comprises the base stock in an amount at least about 50 weight percent, based on the weight of the lubricating oil composition, and the additive package in an amount at least about 0.1 weight percent based on the weight of the lubricating oil composition.

18. The composition of claim 1, wherein the composition comprises the base stock in an amount at least about 90 weight percent, based on the weight of the lubricating oil composition, and the additive package in an amount at least about 0.5 weight percent based on the weight of the lubricating oil composition.

19. The composition of claim 1, wherein the weight ratio of base stock to additive package ranges from about 50:50 to about 99.9:0.1.

20. The composition of claim 1, wherein the base stock is selected from a group consisting of natural lubricating oil, synthetic lubricating oil, lard oil, vegetable oil, oleic soybean oil, high oleic soybean oil, rapeseed oil, palm oil, jojoba oil, canola oil, castor oil, sunflower oil, petroleum oil, mineral oil, and oils derived from coal or shale, oils obtained by isomerization of synthetic wax and wax, white oils, hydrocrackate oils produced by hydrocracking the aromatic and polar components of crude oil, polymerized and interpolymerized olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, alkyene oxide polymers, interpolymers, copolymers, and derivatives thereof, esters of carboxylic acids, silicon-based oils, liquid esters of phosphorus-containing acids, polymeric tertbutydropuruns, poly-α-olefins and mixtures thereof.

21. The composition of claim 1, wherein the alkylated diphenylamine is selected from a group consisting of diphenylamine, monoalkylated diphenylamine, dialkylated diphenylamine, trialkylated diphenylamine, 3-hydroxiphenylamine, 4-hydroxyphenylamine, mono- and/or di-tert-butyl diphenylamine.
diphenylamine, mono- and or di-dieptyldiphenylamine, mono- and/or di-octyldiphenylamine, di-octyl diphenylamine, mono- and/or dononyldiphenylamine, mono- and/or di-dodecyl diphenylamine, hexadecyl diphenylamine, ecosenyl diphenylamine, tetracosyl diphenylamine, octacosyl diphenylamine, polyisobutyl diphenylamine, mono and/or di-(α-methylstyryl) diphenylamine, mono- and/or distyryldiphenylamine, 4-(p-toluenesulfonylamido)diphenylamine, 4-isoproxydiphenylamine, t-octylated N-phenyl-1-naphthylamine, mixtures of mono- and di-alkylated t-butyl t-octyldiphenylamine and mixtures thereof.

22. The composition of claim 1, wherein the sulfur-containing phenol is represented by Formula II

![Formula II](image)

wherein $R_1$ is a sulfur-containing alkyl, a sulfur-containing aryl group, a sulfur-containing alkene or a sulfur-containing carboxylic acid; and wherein $R_2$ and $R_3$ are alkyl, aryl or hydrogen.

23. The composition of claim 1, wherein the base stock is a food grade lubricant.

24. The composition of claim 1, wherein the composition exhibits a pressurized differential scanning calorimeter oxidation induction time at least about 25 minutes.

25. The composition of claim 1, wherein the composition exhibits a pressurized differential scanning calorimeter oxidation induction time of about 40 minutes.

26. The composition of claim 1, wherein the composition has a Thermo-Oxidation Engine Oil Simulation Test value of less than about 50 milligrams.

27. The composition of claim 1, wherein the composition has a Thermo-Oxidation Engine Oil Simulation Test value of less than about 40 milligrams.

28. The composition of claim 1, wherein the composition comprises:

(A) about 99 weight percent of the base stock, based on the weight of the lubricating oil composition; and

(B) about 1 weight percent of the additive package, based on the weight of the lubricating oil composition,

wherein the additive package comprises:

(i) about 70 weight percent of alkylated diphenylamine, based on the weight of the additive package;

(ii) about 15 weight percent of phenyl-α-naphthylamine, based on the weight of the additive package; and

(iii) about 15 weight percent of sulfur-containing phenol, based on the weight of the additive package.

29. A liquid additive package comprising:

(A) an alkylated diphenylamine;

(B) at least 5 weight percent of a phenyl naphthylamine, based on the weight of the additive package; and

(C) a sulfur-containing phenol.

30. The additive package of claim 29, wherein the composition comprises the phenyl naphthylamine in an amount ranging from about 1 to about 20 weight percent, based on the weight of the additive package.

31. The additive package of claim 29, wherein the composition comprises the phenyl naphthylamine in an amount ranging from about 10 to about 20 weight percent, based on the weight of the additive package.

32. The additive package of claim 29, wherein the composition comprises the sulfur-containing phenol in an amount ranging from about 5 to about 50 weight percent, based on the weight of the additive package.

33. The additive package of claim 29, wherein the composition comprises the sulfur-containing phenol in an amount ranging from about 10 to about 20 weight percent, based on the weight of the additive package.

34. The additive package of claim 29, wherein the composition comprises the sulfur-containing phenol in an amount of at least about 10 weight percent, based on the weight of the additive package.

35. The additive package of claim 29, wherein the composition comprises the alkylated diphenylamine in an amount at least about 50 weight percent, based on the weight of the additive package.

36. The additive package of claim 29, wherein the composition comprises the alkylated diphenylamine in an amount ranging from about 50 to about 99 weight percent, based on the weight of the additive package.

37. The additive package of claim 29, wherein the composition comprises the alkylated diphenylamine in an amount at least about 50 wt %, based on the weight of the additive package, and the sulfur-containing phenol in an amount of at least about 1 wt %, based on the weight of the additive package.

38. The additive package of claim 29, wherein the composition comprises the alkylated diphenylamine in an amount ranging from about 70 to about 85 weight percent, based on the weight of the additive package, the phenyl naphthylamine in an amount of at least about 10 wt % and the sulfur-containing phenol in an amount of at least about 5 wt %, based on the weight of the additive package.

39. The additive package of claim 29, wherein the weight ratio of alkylated diphenylamine to sulfur-containing phenol in the additive package at least about 6:1.

40. The additive package of claim 29, wherein the weight ratio of alkylated diphenylamine to phenyl naphthylamine in the additive package is at least about 6:1.

41. The additive package of claim 29, wherein the weight ratio of alkylated diphenylamine to phenyl naphthylamine in the additive package is at least about 4:1.

42. The additive package of claim 29, wherein the weight ratio of phenyl naphthylamine to sulfur-containing phenol in the additive package ranges from about 1.5 to about 5:1.

43. The additive package of claim 29, wherein the weight ratio of phenyl naphthylamine to sulfur-containing phenol in the additive package is at least about 4:1.

44. The additive package of claim 29, wherein the weight ratio of alkylated diphenylamine and phenyl naphthylamine, combined, to sulfur-containing phenol is at least about 4:1.

45. A method of producing a liquid additive package comprising:

combining:

(i) alkylated diphenylamine;

(ii) at least about 5 weight percent of a phenyl naphthylamine, based on the weight of the additive package; and

(iii) a sulfur-containing phenol.
46. The method of claim 45, wherein the combining is performed under nitrogen.

47. The method of claim 45, wherein the ratio of phenyl naphthylamine to alkylated diphenylamine ranges from about 1:20 to about 1:3.

48. A method of producing a lubricating oil composition comprising:
   (A) providing a base stock; and
   (B) blending with the base stock a liquid additive package comprising:
   (i) alkylated diphenylamine;
   (ii) at least 5 weight percent of a phenyl naphthylamine, based on the weight of the additive package; and
   (iii) a sulfur-containing phenol.

49. The method of claim 48, wherein the base stock base stock is in an amount at least about 90 weight percent, based on the weight of the lubricating oil composition, and the additive package is in amount at least about 0.5 weight percent based on the weight of the lubricating oil composition.

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