(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 194 114 A2**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
**09.06.2010 Bulletin 2010/23**

(51) Int Cl.:
***C10M 169/04*** *(2006.01)* ***C10M 171/00*** *(2006.01)*

(21) Application number: **10157050.5**

(22) Date of filing: **19.03.2010**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK SM TR**

(71) Applicant: **Shell Internationale Research Maatschappij B.V.**
**2596 HR The Hague (NL)**

(72) Inventors:
- **Paddon, Christopher Andrew**
  **Chester, Cheshire CH2 4NU (GB)**
- **Wedlock, David John**
  **Chester, Cheshire CH2 4NU (GB)**
- **De Laguno Gorria, Laura**
  **Chester, Cheshire CH2 4NU (GB)**

(54) **Lubricating composition**

(57) The present invention provides a lubricating composition comprising a base oil selected from the group consisting of a Fischer-Tropsch derived base oil and a poly-alpha olefin (PAO) base oil or a combination thereof, wherein the composition has a TBN (Total Base Number) value of from 3.5 to 70 mg KOH/g as determined according to ASTM D 2896, and wherein the composition has a soap content of from 15 to 30 mM.

EP 2 194 114 A2

## Description

**[0001]** The present invention relates to a lubricating composition comprising a base oil, in particular a Fischer-Tropsch derived base oil.

**[0002]** As is disclosed in for example as D.J. Wedlock et al., "Gas-to-Liquids Base Oils to assist in meeting OEM requirements 2010 and beyond", presented at the 2nd Asia-Pacific base oil Conference, Beijing, China, 23-25 October 2007, the use of Fischer-Tropsch derived base oils in lubricating compositions such as engine oils, transmission fluids, and industrial lubricants results in various performance benefits. Examples of performance benefits by the use of Fischer-Tropsch derived base oils mentioned in the above article are: improved oxidation properties, improved engine cleanliness, improved wear protection, improved emissions and improved aftertreatment device compatibility. Also the Fischer-Tropsch base oils allow to formulate low-viscosity energy conserving formulations.

**[0003]** Also, EP 2 159 275 discloses the use of a lubricating composition containing a Fischer-Tropsch derived base oil in order to improve anti-oxidation properties, in particular as determined by HPDSC according to ASTM D 6186-08 and/or the ROBO test according to ASTM D 7528-09.

**[0004]** Furthermore it was found that Fischer-Tropsch derived base oils, when included in crankcase lubricants for crankcase engine operation, exhibit a reduced fuel dilution effect in the lubricant. When the crankcase is cool, as during warm up, it can act as a condenser for piston blow-by gases which will contain some non-combusted fuel. This condensed fuel then dissolves and dilutes the lubricant. Also when an engine is being operated under high load conditions with associated greater blow-by, then fuel dilution of the lubricant is likely to be greater. Normally, most of the hydrocarbon components of non-combusted fuel volatilize off under normal operating temperatures. In the case of a gasoline engine, platformate which is used as a blending component in gasoline to improve octane rating of the fuel, may permanently partition into the lubricant because it is a heavy aromatic component. This will cause the used gasoline engine oil to become more toxic because of enhanced PCA (poly cyclic aromatics) content from the platformate. Similarly, in diesel engines which may use bio components (ester-based) in the diesel fuel, there can be a permanent partitioning of non-volatile fuel-derived ester components into the base oil of the lubricant. This can subsequently lead to the problems of lubricant gellation and engine damage. As Fischer-Tropsch derived base oils are essentially pure iso-paraffinc base oils with low solvency, they will thus show a lower tendency to absorb polar species such as platformate and ester in the first place - and a greater tendency to reject these components upon raising the lubricant to operating temperature thereby exhibiting a reduced fuel dilution effect in the lubricant.

**[0005]** Also it was found that catalytically dewaxed Fischer-Tropsch derived heavy base oils having a residual wax haze can be used in (e.g. marine SAE 50) cylinder lubricants without technical or aesthetic deficit. In this respect, "heavy base oils" mean base oils having a kinematic viscosity at 100°C of at least 14 cSt such as about 15 cSt. A base oil having a residual wax haze can be defined as a base oil having a cloud point of at least 15°C. The use of such high VI base oils in cylinder lubricant applications will give the added benefit of easier pumping from the lubricant oil tank under low temperature conditions, as well as higher oil film thickness under high temperature conditions within the cylinder, compared to analogous formulations based on all-mineral base oils (which will typically have a lower VI).

**[0006]** It is an object of the present invention to improve the piston deposit formation properties of a lubricating composition.

**[0007]** It is another object of the present invention to provide alternative lubricating compositions. One or more of the above or other objects can be obtained by the present invention by a lubricating composition comprising a base oil selected from the group consisting of a Fischer-Tropsch derived base oil and a poly-alpha olefin (PAO) base oil or a combination thereof, wherein the composition has a TBN (Total Base Number) value of from 3.5 to 70 mg KOH/g, as determined according to ASTM D 2896, and wherein the composition has a soap content of from 15 to 30 mM.

**[0008]** It has surprisingly been found that the lubricating compositions according to the present invention exhibit improved piston deposit formation properties, in particular as determined according to ASTM D 7097-09.

**[0009]** Preferably, the composition has a TBN value of above 4.0, more preferably above 5.5, even more preferably above 6.0 mg KOH/g, yet even more preferably above 7.0 mg KOH/g as determined according to ASTM D 2896. Typically, the composition has a TBN value of below 40, preferably below 20.0, more preferably below 15.0, even more preferably below 12.0 mg KOH/g.

**[0010]** There are no particular limitations regarding the base oil used in lubricating composition according to the present invention, and various conventional mineral oils, synthetic oils as well as naturally derived esters such as vegetable oils may be conveniently used, provided that at least a Fischer-Tropsch derived base oil or a poly-alpha olefin (PAO) base oil is present.

**[0011]** The base oil used in the present invention may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils; thus, according to the present invention, the term "base oil" may refer to a mixture containing more than one base oil. Mineral oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrofinishing processes and/or dewaxing.

**[0012]** Suitable base oils for use in the lubricating oil composition of the present invention are Group I, Group II, Group III mineral base oils, Group IV poly-alpha olefins (PAOs), Group III Fischer-Tropsch derived base oils and mixtures thereof.

**[0013]** By "Group I", Group II", "Group III" and "Group IV" base oils in the present invention are meant lubricating oil base oils according to the definitions of American Petroleum Institute (API) for category I, II, III and IV. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

**[0014]** Fischer-Tropsch derived base oils are known in the art. By the term "Fischer-Tropsch derived" is meant that a base oil is, or is derived from, a synthesis product of a Fischer-Tropsch process. A Fischer-Tropsch derived base oil may also be referred to as a GTL (Gas-To-Liquids) base oil. Suitable Fischer-Tropsch derived base oils that may be conveniently used as the base oil in the lubricating composition of the present invention are those as for example disclosed in EP 0 776 959, EP 0 668 342, WO 97/21788, WO 00/15736, WO 00/14188, WO 00/14187, WO 00/14183, WO 00/14179, WO 00/08115, WO 99/41332, EP 1 029 029, WO 01/18156 and WO 01/57166.

**[0015]** Synthetic oils include hydrocarbon oils such as olefin oligomers (including polyalphaolefin base oils; PAOs), dibasic acid esters, polyol esters, polyalkylene glycols (PAGs), alkyl naphthalenes and dewaxed waxy isomerates. Synthetic hydrocarbon base oils sold by the Shell Group under the designation "Shell XHVI" (trade mark) may be conveniently used.

**[0016]** Poly-alpha olefin base oils (PAOs) and their manufacture are well known in the art. Preferred poly-alpha olefin base oils that may be used in the lubricating compositions of the present invention may be derived from linear $C_2$ to $C_{32}$, preferably $C_6$ to $C_{16}$, alpha olefins. Particularly preferred feedstocks for said poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

**[0017]** According to the present invention, the base oil as used in the lubricating composition according to the present invention comprises at least a base oil selected from the group consisting of a poly-alpha olefin base oil and a Fischer-Tropsch derived base oil or a combination thereof.

**[0018]** There is a strong preference for using a Fischer-Tropsch derived base oil over a PAO base oil, in view of the high cost of manufacture of the PAOs. Thus, preferably, the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%. most preferably more than 90 wt.% Fischer-Tropsch derived base oil. In an especially preferred embodiment not more than 5 wt.%, preferably not more than 2 wt.%, of the base oil is not a Fischer-Tropsch derived base oil. It is even more preferred that 100 wt.% of the base oil is based on one or more Fischer-Tropsch derived base oils. Preferably the base oil or base oil blend comprising the Fischer-Tropsch derived base oil has a kinematic viscosity at 100°C of between 2 and 30 cSt, preferably between 2.5 and 10 cSt (according to ASTM D 445).

**[0019]** The total amount of base oil incorporated in the lubricating composition of the present invention is preferably present in an amount in the range of from 60 to 99 wt.%, more preferably in an amount in the range of from 65 to 90 wt. % and most preferably in an amount in the range of from 70 to 85 wt.%, with respect to the total weight of the lubricating composition.

**[0020]** According to a preferred embodiment of the present invention, the composition comprises a detergent. There are no particular limitations regarding the detergent used in the lubricating composition according to the present invention, and various conventional detergents may be used. Examples of detergents that may be used include oil-soluble neutral and overbased sulfonates, phenates, sulfurized phenates, thiophosphonates, salicylates and naphthenates and other oil-soluble carboxylates of a metal, particularly the alkali or alkaline earth metals, e.g. sodium, potassium, lithium, and in particular calcium and magnesium. Preferred metal detergents are neutral and overbased detergents having a TBN (Total Base Number; according to ASTM D2896) of from 20 to 450 mg KOH/g. According to a preferred embodiment, the detergent has a TBN value below 500 mg KOH/g, such as in the range of from 60 to 350, preferably below 240 mg KOH/g, more preferably below 200 mg KOH/g. Combinations of detergents, whether overbased or neutral or both, may be used.

**[0021]** Typically the detergent, or mixture of detergents, is present in the lubricating composition according to the present invention in an amount of from 0.01 to 9.0 wt.%, preferably from 1.0 to 6.0 wt.%, more preferably from 3.5 to 5.5 wt.%, based on the total weight of the fully formulated lubricating oil composition.

**[0022]** According to a preferred embodiment of the present invention, the detergent is a salicylate-type detergent. Examples of suitable salicylate-type detergents include the products available from Infineum under the trade designations "Infineum C9012", "Infineum M7101" "Infineum M7102", "Infineum M7105", "Infineum M7121" and "Infineum M7125".

**[0023]** Further it is preferred according to the present invention that the composition comprises an amine compound. There are no particular limitations regarding the amine compound used in the lubricating composition according to the present invention, and various conventional amine compounds may be used. Examples of suitable amine compounds include monamines, diamines, and polyamines.

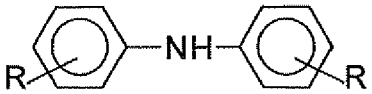
**[0024]** According to a preferred embodiment of the present invention, the amine compound is an aromatic amine compound. Examples of suitable aromatic amine compounds include diphenylamines, alkylated diphenylamines, phenyl-$\alpha$-naphthylamines (PANA), phenyl-$\beta$-naphthylamines, and alkylated $\alpha$-naphthylamines. Preferably the aromatic amine is selected from an optionally alkylated diphenylamine and an optionally alkylated phenyl-alpha-naphthylamine, more

preferably an optionally alkylated diphenylamine.

**[0025]** The above-mentioned (optionally alkylated) diphenylamine (DPA) compounds are known in the art and widely commercially available. Examples of suitable diphenylamines and phenyl-alpha-naphthylamines that may be used include, but are not limited to, diphenylamine (DPA), butyldiphenylamine, dibutyldiphenylamine, octyldiphenylamine, dioctyldiphenylamine, nonyldiphenylamine, dinonyldiphenylamine, heptyldiphenylamine, diheptyldiphenylamine, methylstyryldiphenylamine, mixed butyl/octyl alkylated diphenylamines, mixed butyl/styryl alkylated diphenylamines, mixed nonyl/ethyl alkylated diphenylamines, mixed octyl/styryl alkylated diphenylamines, mixed ethyl/methylstyryl alkylated diphenylamines, phenyl-alpha-naphthylamine, octylphenyl-beta-naphtnylamine, t-octylphenyl-alpha-naphthylamine, phenyl-beta-naphthylamine, p-octylphenyl-alpha-naphthylamine, 4-octylphenyl-1-octyl-beta-naphthylamine, n-t-dodecylphenyl-1-naphthylamine, N-hexylphenyl-2-naphthylamine, and mixed alkylated phenyl-alpha-naphthylamines. Commercial examples of diphenylamines and phenyl-naphthylamines are available from CIBA Speciality Chemicals under the trade designations Irganox L-06 and Irganox L-57; from Chemtura under the trade designations Naugalube AMS, Naugalube 438, Naugalube 438R, Naugalube 438L, Naugalube 640, Naugalube 680, Naugalube APAN and Naugard PANA; from R.T. Vanderbilt Company, Inc under the trade designations Vanlube DND, Vanlube NA, Vanlube PNA, Vanlube SL, Vanlube SLHP, Vanlube SS, Vanlube 81, Vanlube 848, and Vanlube 849; from Albemarle under the trade designation AN-1225.

**[0026]** Typically, the amine compounds are present in an amount in the range of from 0.1 to 10.0 wt.%, preferably from 0.1 to 5.0 wt.%, more preferably from 0.2 to 4.0 wt.%, most preferably from 0.3 to 1.5 wt%, based on the total weight of the fully formulated lubricating oil composition.

**[0027]** According to an especially preferred embodiment of the present invention, the aromatic amine compound is a diphenylamine having the general formula (I)




(I)

wherein each R is independently an alkyl group having from 1 to 16 carbon atoms, preferably from 3 to 14 carbon atoms, more preferably from 4 to 12 carbon atoms.

**[0028]** The lubricating composition according to the present invention may further comprise one or more additives such as anti-oxidants, anti-wear additives, dispersants, detergents, overbased detergents, extreme pressure additives, friction modifiers, viscosity index improvers, pour point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc.

**[0029]** As the person skilled in the art is familiar with the above and other additives, these are not further discussed here in detail. Specific examples of such additives are described in for example Kirk-Othmer Encyclopedia of Chemical Technology, third edition, volume 14, pages 477-526. The above-mentioned additives are typically present in an amount in the range of from 0.01 to 35.0 wt.%, based on the total weight of the lubricating composition, preferably in an amount in the range of from 0.05 to 25.0 wt.%, more preferably from 1.0 to 20.0 wt.%, based on the total weight of the lubricating composition.

**[0030]** The lubricating compositions of the present invention may be conveniently prepared by admixing the one or more additives with the base oil(s).

**[0031]** According to an especially preferred embodiment of the present invention, the composition has a soap content of from 18 to 26 mM, preferably from 20 to 24 mM, more preferably from 20 to 23 mM.

**[0032]** Furthermore it is preferred that the composition comprises at least 1.0 wt.% of a PIB succinimide compound, based on the total weight of the composition. PIB succinimide compounds are known as dispersant additives in the art of PCMO and HDDEO engine oils and therefore not further described here; suitable PIB succinimides can be obtained from e.g. Infineum International Ltd (Abingdon, UK). Typically, the composition comprises less than 12.0 wt.% of the PIB succinimide, preferably less than 10.0 wt.%, more preferably less than 9.0 wt.%, based on the total weight of the composition. Also it is preferred that the composition comprises at least 5.0 wt.% of the PIB succinimide, based on the total weight of the composition.

**[0033]** The lubricating compositions according to the present invention preferably are so-called "low SAPS" (SAPS = sulphated ash, phosphorus and sulphur), "mid SAPS" or "regular SAPS" formulations.

**[0034]** For Passenger Car Motor Oil (PCMO) engine oils the above ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 0.5 wt.% (low SAPS), up to 0.8 wt.% (mid SAPS) and up to 1.5 wt.% (high SAPS), respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.05 wt.% (low SAPS), up to 0.08 wt.% (mid SAPS)

and typically up to 0.1 wt.% (high SAPS), respectively; and

- a sulphur content (according to ASTM D 5185) of up to 0.2 wt.% (low SAPS), up to 0.3 wt.% (mid SAPS) and typically up to 0.5 wt.% (high SAPS), respectively.

**[0035]** For Heavy Duty Diesel Engine Oils the above SAPS ranges mean:

- a sulphated ash content (according to ASTM D 874) of up to 1 wt.% (low SAPS), up to 1 wt.% (mid SAPS) and up to 2 wt.% (high SAPS), respectively;
- a phosphorus content (according to ASTM D 5185) of up to 0.08 wt.% (low SAPS) and up to 0.12 wt.% (mid SAPS), respectively; and
- a sulphur content (according to ASTM D 5185) of up to 0.3 wt.% (low SAPS) and up to 0.4 wt.% (mid SAPS), respectively.

**[0036]** The lubricating composition may meet the above SAPS ranges for engine oils, even if the lubricating composition is intended for a different application.

**[0037]** Also, the lubricating composition may meet certain industry standards such as SAE J300 Specifications (as revised in January 2009). Preferably the lubricating composition according to the present invention meets the specifications of SAE J300 0W-20, 5W-30, 5W-40 and 10W-40 crankcase engine oils, preferably those of 10W-40. SAE stands for Society of Automotive Engineers.

**[0038]** It is especially preferred according to the present invention that the composition has:

- a dynamic viscosity at -25°C (according to ASTM D 5293) of below 7000 cP;
- a kinematic viscosity at 100°C (according to ASTM D 445) of at least 12.5 cSt and typically below 16.3;
- a high temperature, high shear viscosity ("HTHS"; according to ASTM D 4683) of at least 3.5 cP; and
- a Noack volatility (according to ASTM D 5800) of below 14 wt.%, preferably below 13.0 wt.%, more preferably below 11.0 wt.%, even more preferably below 10.5 wt.%, most preferably below 10.0 wt.%.

**[0039]** The lubricating composition according to the present invention may be used in various applications, such as in internal combustion engines (as an engine oil), as a transmission oil, a grease, a hydraulic oil, a turbine oil, compressor oil, etc.

**[0040]** In another aspect, the present invention provides the use of a lubricating composition as described herein, in order to improve deposit reduction properties, in particular as determined according to ASTM D 7097-09.

**[0041]** The present invention is described below with reference to the following Examples, which are not intended to limit the scope of the present invention in any way.

Examples

Lubricating Oil Compositions

**[0042]** Various combinations of additives and base oils were formulated. Table 1 indicates the properties of the base oils used. Tables 2-4 indicate the amounts of additives as incorporated in the respective base oils ("Base oil 1" or "Base oil 2"). All the compositions except for "Blank 1" in Table 2 and Table 4, and "Blank 3" and "Blank 4" in Table 3 contained 500 ppm of an anti-oxidant additive (additive "A0"); the amounts of the additives (the remainder being base oil & 500 ppm A0) are given in wt.%, based on the total weight of additive(s) plus base oil. "Blank 2" in Table 2 and Table 4 contained no other additive in addition to 500 ppm of the above-mentioned A0. For ease of reference, Table 2 and Table 4 also includes references to "Mixtures 1-38" containing a combination of base oil, additive A0, and two or more other additives.

**[0043]** "Base oil 1" (or "BO1" or "GTL 4") was a Fischer-Tropsch derived base oil having a kinematic viscosity at 100°C (ASTM D445) of approx. 3.9 cSt ($mm^2s^{-1}$). Base oil 1 may be conveniently manufactured by the process described in e.g. WO-A-02/070631, the teaching of which is hereby incorporated by reference.

**[0044]** "Base oil 2" (or "BO2") was a commercially available Group III base oil having a kinematic viscosity at 100°C (ASTM D445) of approx. 4.3 cSt. Base oil 2 is commercially available from e.g. SK Energy (Ulsan, South Korea) under the trade designation "Yubase 4".

Table 1

| | Base oil 1 (GTL 4) | Base oil 2 (Yubase 4) |
|---|---|---|
| Kinematic viscosity at 40°C[1] [cSt] | 16.91 | 19.49 |
| Kinematic viscosity at 100°C[1] [cSt] | 3.90 | 4.26 |
| VI Index[2] | 127 | 126 |
| Pour point[3] [°C] | -39 | -18 |
| Noack volatility[4] [wt.%] | 12.2 | 14.2 |
| Saturates[5] [wt.%] | 99.2 | 99.3 |
| Dynamic viscosity at -20°C[6] [cP] | n.d. | 713 |
| Dynamic viscosity at -25°C[6] [cP] | 704 | 931 |
| [1]According to ASTM D 445<br>[2]According to ASTM D 2270<br>[3]According to ASTM D 5950<br>[4]According to CEC L-40-A-93 / ASTM D 5800<br>[5]According to IP 368 (modified)<br>[6]According to ASTM D 5293<br>n.d. = not determined | | |

**[0045]** The following additives A0-A17 were used:

- A0: Octylated/butylated diphenylamine (DPA), available from CIBA Speciality Chemicals (Basel, Switzerland) under the trade designation "Irganox L-57".
- A1: Low BI (Basicity Index) salicylate detergent (Ca-based) available from Infineum International Ltd (Abingdon, UK) under the trade designation "Infineum M7102". Properties: Vk40 (270); Vk100 (19); TBNE (Total Base Number Equivalent (ASTM D 2896); mgKOH/g) = 64; Ca (wt.%) = 2.3.
- A2: Medium BI salicylate detergent (Ca-based) available from Infineum International Ltd. under the trade designation "Infineum M7121". Properties: Vk40 (1130); Vk100 (95); TBNE (mgKOH/g) = 225; Ca (wt.%) = 8.0%; Mg (wt.%) = 0.24.
- A3: High BI salicylate detergent (Ca-based) available from Infineum International Ltd. under the trade designation "Infineum M7125". Properties: Vk40 (835); Vk100 (100); TBNE (mgKOH/g) = 350; Ca (wt.%) = 12.5; Mg (wt.%) = 0.3.
- A4: Reaction product of an acidic organic compound, a boron compound, and basic organic compound, available from Chemtura. See e.g. US 2005/0172543 and in particular paragraphs [0025]-[0077] thereof.
- A5: Sulfonate detergent available from Infineum International Ltd. under the trade designation "Infineum C9350".
- A6: Phenate detergent available from Infineum International Ltd. under the trade designation "Infineum C9380".
- A7: Overbased calcium sulfonate detergent available from Chevron Oronite S.A. (Levallois-Perret, France) under the trade designation "OLOA 249 SX".
- A8: Phenate detergent available from Infineum International Ltd. under the trade designation "Infineum C9394".
- A9: Zinc dialkyl dithiophosphate (ZDTP) available from Infineum International Ltd. under the trade designation "Infineum C9417".
- A10: PIB Succinimide dispersant available from Infineum International Ltd. under the trade designation "Infineum C9280".
- A11: A borated low MW ashless dispersant available from Infineum International Ltd. under the trade designation "Infineum C9230".
- A12: A high MW borated ashless dispersant available from Infineum International Ltd. under the trade designation "Infineum C9260".
- A13: A Mg salicylate detergent available from Infineum International Ltd. under the trade designation "C9012".
- A14: A sulfonate detergent available from Infineum International Ltd. under the trade designation "Infineum C9330".
- A15: A poly(hydroxycarboxylic acid) amide salt derivative available from Shanghai Sanzheng Polymer Company under the trade designation "CH-5".
- A16: A poly(hydroxycarboxylic acid) amide salt derivative available from Shanghai Sanzheng Polymer Company under the trade designation "CH-7".
- A17: A phenate detergent available from Chevron Oronite S.A. under the trade designation "OLOA 219C".

Table 2

| Additive | [wt.%] | Soap[1] [mM] | TBN[2] [mg.KOH/g] | Total Deposits (mg) | |
|---|---|---|---|---|---|
| | | | | In BO1 (GTL 4) | In BO2 (Yubase 4) |
| Blank 1 (without 0.05 wt.% | - | - | - | 176.4 | 133.4 |
| A0) Blank 2 (with 0.05 wt.% A0) | - | - | - | 144.9 | 173.9 |
| A1* | 6.6 | 26.9 | 4.3 | 27.0 | 35.9 |
| A2* | 1.9 | 12.7 | 4.3 | n.d. | n.d. |
| A2** | 3.05 | 20.4 | 6.9 | 43.9 | 52.4 |
| A2*** | 3.8 | 25.5 | 8.6 | n.d. | n.d. |
| A3* | 1.2 | 4.8 | 4.3 | 78.2 | 51.4 |
| A3*** | 2.45 | 9.6 | 8.6 | 48.1 | 55.0 |
| A1 + A2 [Mixture 1]* | 4.55 + 0.25 | 22.8 | 4.2 | n.d. | n.d. |
| A1 + A2 +A3 [Mixture 2]* | 4.5 + 0.25 + 0.25 | 21.1 | 4.4 | 52.3 | 55.2 |
| A1 + A2 + A3 [Mixture 3]* | 1.0 + 1.25 + 0.25 | 13.5 | 4.3 | 106.0 | 83.5 |
| A1 + A3 [Mixture 4]* | 2.25 + 0.5 | 13.2 | 3.5 | n.d. | n.d. |
| A1 + A2 + A3 [Mixture 5]* | 0.5 + 1.25 + 0.35 | 11.8 | 4.4 | 95.5 | 67.7 |
| A2 + A3 [Mixture 6]* | 1.5 + 0.45 | 10.0 | 4.4 | 54.9 | 54.8 |
| A2 + A3 [Mixture 7] | 2.0 + 1.0 | 17.3 | 8.0 | n.d. | n.d. |
| A2 + A3 [Mixture 8] | 2.3 + 2.5 | 25.2 | 13.9 | n.d. | n.d. |
| A2 + A3 [Mixture 9] | 5.25 + 3.6 | 50.0 | 14.2 | n.d. | n.d. |
| A1+ A3 [Mixture 10]* | 0.5 + 1.0 | 6.0 | 3.8 | 64.2 | 98.4 |
| A1 + A2 [Mixture 11]** | 3.0 + 2.15 | 26.7 | 6.8 | 40.6 | n.d. |
| A1 + A2 + A3 [Mixture 12]** | 2.75 + 1.25 + 0.5 | 21.6 | 6.4 | 38.1 | 47.4 |
| A1 + A2 + A3 [Mixture 13]** | 1.0 + 1.25 + 1.0 | 16.4 | 7.0 | 52.1 | 61.7 |
| A1 + A2 [Mixture 14]*** | 4.5 + 2.5 | 35.2 | 8.6 | 24.3 | n.d. |
| A1 + A2 + A3 [Mixture 15]*** | 3.5 + 1.25 + 1.0 | 26.6 | 8.6 | 36.0 | 39.4 |
| A1 + A2 + A3 [Mixture 16]*** | 0.5 + 2.5 + 1.0 | 22.7 | 9.5 | 26.5 | 36.6 |
| A1 + A2 + A3 [Mixture 17]*** | 0.8 + 1.25 + 1.5 | 17.5 | 8.6 | 42.6 | 63.3 |
| A4 | 2.0 | - | - | 177.4 | 167.5 |
| A4 | 5.0 | - | - | 93.6 | 103.9 |
| A5 + A6 [Mixture 18] | 2.5 + 1.5 | - | 2.6 | 99.2 | 82.4 |
| A5 + A7 [Mixture 19] | 3.0 + 1.0 | - | 4.7 | n.d. | n.d. |

(continued)

| Additive | [wt.%] | Soap[1] | TBN[2] | Total Deposits (mg) | |
|---|---|---|---|---|---|
| A7 + A8 [Mixture 20] | 0.5 + 2.5 | - | 7.5 | n.d. | n.d. |
| A8 | 4.0 | - | 10.4 | n.d. | n.d. |
| A1 + A2 + A3 + A9 [Mixture 21]* | 4.2 + 0.2 + 0.1 + 0.6 | 19.0 | 3.5 | n.d. | n.d. |
| A1 + A2 + A3 + A9 [Mixture 22]** | 2.75 + 1.1 + 0.4 + 1.0 | 20.2 | 5.7 | n.d. | n.d. |
| A1 + A2 + A3 + A9 | 0.5 + 2.5 + | 21.7 | 8.6 | n.d. | n.d. |
| [Mixture 23]*** | 0.75 + 1.5 | | | | |
| A2 + A13 [Mixture 24] | 1.5 + 1.5 | 16.2 | 8.6 | n.d. | n.d. |
| A10 | 6.0 | - | - | 126.4 | 140.8 |
| A1 + A2 + A10 25]* | 3.0 + 0.75 + 6.0 | 17.3 | 3.6 | 47.1 | 52.1 |
| [Mixture A1 + A2 + A3 + A9 + A10 26]* | 4.2 + 0.2 + 0.1 + 0.6 + 6.0 | 19.0 | 3.5 | n.d. | n.d. |
| [Mixture A5 + A14 [Mixture 27] | 1.5 + 3.5 | - | 10.8 | n.d. | n.d. |
| A11 | 4.0 | - | - | 126.3 | 143.0 |
| A7 + A17 [Mixture 28] | 6.0 + 14.0 | - | 60.0 | n.d. | n.d. |
| A12 | 4.0 | - | - | 136.1 | 128.5 |
| A1 + A2 + A3 + A10 [Mixture 29]** | 2.75 + 1.25 + 0.5 + 6.0 | 21.6 | 6.4 | 34.4 | n.d. |
| A1 + A2 + A3 + A9 + A10 [Mixture 30]** | 2.75 + 1.1 + 0.4 + 1.0 + 6.0 | 20.2 | 5.7 | 29.6 | 52.2 |
| A1 + A2 + A3 + A10 [Mixture 31]*** | 0.5 + 2.5 + 1.0 + 6.0 | 22.7 | 9.5 | 19.1 | 27.0 |
| A1 + A2 + A3 + A9 + A10 [Mixture 32]*** | 0.5 + 2.5 + 0.75 + 1.5 + 6.0 | 21.7 | 8.6 | n.d. | n.d. |
| A4 + A10 [Mixture 33] | 2.0 + 6.0 | - | - | n.d. | n.d. |
| A4 + A10 [Mixture 34] | 5.0 + 6.0 | - | - | n.d. | n.d. |
| A2 + A3 + A9 + A10 [Mixture 35] | 2.0 + 0.8 + 1.0 + 9.0 | 16.5 | 7.3 | n.d. | n.d. |
| A2 + A13 + A9 + A10 [Mixture 36] | 1.5 + 1.5 + 1.0 + 9.0 | 16.1 | 8.6 | n.d. | n.d. |
| A5 + A14 + A9 + A10 [Mixture 37] | 1.5 + 3.5 + 1.5 + 9.0 | - | 10.8 | n.d. | n.d. |
| A8 + A9 + A10 [Mixture 38] | 4.0 + 1.5 + 9.0 | - | 10.4 | n.d. | n.d. |

[1]Soap content has been calculated.
[2]As determined according to ASTM D 2896.
n.d. = total deposits value not determined for this sample
*Low SAPS (PCMO)
**Mid SAPS (PCMO)
***High SAPS (PCMO)

TEOST MHT Test

**[0046]** In order to demonstrate the improved piston deposit properties of the lubricating compositions according to the present invention, measurements were performed using the standard test method for determination of moderately high temperature piston deposits by thermo-oxidation engine oil simulation test (TEOST MHT) according to ASTM D 7097-09. This test determines the mass of deposits formed on a specially constructed test rod exposed to repetitive passage of 8.5 g of engine oil over the rod in a thin-film under oxidative and catalytic (0.1 g Pb/Fe/Sn/ liquid naphthenes) conditions at 285°C. The measured values for total deposits (filter deposits + rod deposits) as obtained using the standard conditions as outlined in ASTM D 7097-09 are indicated in Table 2 above.

Cam Baffle Bench Screener Test

**[0047]** In order to demonstrate deposit control properties of the lubricating compositions, measurements were performed using the Bench Screener Test as described in WO 2007/128740 (see page 28, line 11 - page 29, line 4), except that the following ratings were used: Black = no cleaning at all, + = clean and ++ = completely clean. The measured ratings are indicated in Table 3 below.

**[0048]** The same base oils BO1 and BO2 as used above were used. Also, the definitions for the additives has been given above.

Table 3

| Base Oil | Additive | Wt.% of additive | 0 h | 24 h | 120 h | 144 h |
|---|---|---|---|---|---|---|
| BO1 | "Blank 3": w/o A0 | - | Black | Black | Black | Black |
| BO2 | "Blank 4": w/o A0 | - | Black | Black | Black | Black |
| BO1 | A15 | 0.5 | Black | Black | + | ++ |
| BO1 | A15 | 3.5 | Black | + | ++ | ++ |
| BO1 | A6 + A15 | 1.0 + 0.5 | Black | Black | + | ++ |
| BO1 | A6 + A15 | 1.5 + 3.5 | Black | + | ++ | ++ |
| BO1 | A2 + A16 | 1.5 + 0.5 | Black | Black | + | + |
| BO1 | A2 + A16 | 1.5 + 3.5 | Black | ++ | ++ | ++ |
| BO1 | A4 + A15 | 2.0 + 0.5 | Black | + | ++ | ++ |
| BO1 | A4 + A15 | 2.0 + 3.5 | Black | ++ | ++ | ++ |
| BO1 | A11 | 4.0 | Black | + | + | + |
| BO2 | A11 | 4.0 | Black | + | + | ++ |
| BO1 | A11 + A15 | 1.0 + 2.0 | Black | ++ | ++ | ++ |
| BO2 | A11 + A15 | 1.0 + 2.0 | Black | + | + | ++ |
| BO1 | A12 | 4.0 | Black | + | + | ++ |
| BO2 | A12 | 4.0 | Black | Black | + | + |

Komatsu Hot Tube Test

**[0049]** In order to demonstrate the improved piston deposit properties of the lubricating compositions according to the present invention at high temperatures, measurements were also performed using the standard Komatsu Hot Tube Test ("KHTT", according to JPI-5S-55-99; JPI is the Japanese Petroleum Institute). The measured ratings are indicated in Table 4 below.

**[0050]** The same base oils BO1 and BO2 as used above were used. Also, the definitions for the additives have been given above.

Table 4

| Additive | [wt.%] | Soap[1] [mM] | TBN[2] [mg.KOH/g] | Average rating (0-10) | |
|---|---|---|---|---|---|
| | | | | In BO1 (GTL 4) | In BO2 (Yubase 4) |
| Blank 1 (without 0.05 wt.% A0) at 280°C | - | - | - | 4.5 | 1.0 |
| Blank 1 (without 0.05 wt.% A0) at 290°C | - | - | - | 1.0 | n.d. |
| Blank 2 (with 0.05 wt.% A0) at 280°C | - | - | - | 6.4 | 0.5 |
| Blank 2 (with 0.05 wt.% A0) at 290°C | - | - | - | 1.0 | n.d. |
| A2 + A3 [Mixture 7]* at 280°C | 2.0 + 1.0 | 17.3 | 8.0 | 6.5 | 5.9 |
| A2 + A3 [Mixture 8]** at 280°C | 2.3 + 2.5 | 25.2 | 13.9 | 9.0 | 7.0 |
| A2 + A3 [Mixture 8]** at 290°C | 2.3 + 2.5 | 25.2 | 13.9 | 9.0 | 6.5 |
| A2 + A3 [Mixture 9]** at 280°C | 5.25 + 3.6 | 50.0 | 14.2 | 9.0 | 9.0 |
| A8 at 280°C | 4.0 | - | 10.4 | 9.0 | 2.0 |
| A2 + A9 [Mixture 24]* at 280°C | 1.5 + 1.5 | 16.2 | 8.6 | 4.5 | 5.0 |
| A5 + A10 [Mixture 27] at 290°C | 1.5 + 3.5 | - | 10.8 | 4.0 | n.d. |
| A7 + A17 [Mixture 28] at 280°C | 6.0 + 14.0 | - | 60.0 | 8.8 | 2.0 |
| A7 + A17 [Mixture 28] at 290°C | 6.0 + 14.0 | - | 60.0 | 8.8 | 1.3 |
| A2 + A3 + A9 + A10 [Mixture 35]* at 280°C | 2.0 + 0.8 + 1.0 + 9.0 | 16.5 | 7.3 | 1.0 | 9.5 |
| A2 + A3 + A9 + A10 [Mixture 35]* at 290°C | 2.0 + 0.8 + 1.0 + 9.0 | 16.5 | 7.3 | 1.0 | 9.0 |
| A2 + A13 + A9 + A10 [Mixture 36]* at 280°C | 1.5 + 1.5 + 1.0 + 9.0 | 16.1 | 8.6 | 0.5 | 9.8 |
| A2 + A13 + A9 + A10 [Mixture 36]* at 290°C | 1.5 + 1.5 + 1.0 + 9.0 | 16.1 | 8.6 | 1.5 | 0.8 |

(continued)

| Additive | [wt.%] | Soap[1] [mM] | TBN[2] [mg.KOH/g] | Average rating (0-10) | |
|---|---|---|---|---|---|
| | | | | In BO1 (GTL 4) | In BO2 (Yubase 4) |
| A8 + A9 + A10 [Mixture 38] | 4.0 + 1.5 + 9.0 | - | 10.4 | 4.0 | 1.0 |

[1]Soap content has been calculated.
[2]As determined according to ASTM D 2896.
n.d. = total deposits value not determined for this sample
*Low SAPS (HDDEO); **High SAPS (HDDEO)

SAE J1899 (Grade 50) Formulations

**[0051]** In addition, various compositions meeting the SAE J1899 (Grade 50) specification (as revised in August 2005) for use in aviation piston engines were formulated.

**[0052]** Table 5 indicates the composition of the lubricating compositions that were tested (Examples 1 and 2 and Comparative Examples 1 and 2); the amounts of the components are given in wt.%, based on the total weight of the compositions.

**[0053]** "Base oil 3" was a commercially available Group I base oil having a kinematic viscosity at 100°C (ASTM D445) of approx. 31.6 cSt ($mm^2s^{-1}$). Base oil 3 is commercially available from e.g. Shell Canada Products, (Brockville, Ontario, Canada) under the trade designation "HVI 650".

**[0054]** "Base oil 4" was a Fischer-Tropsch derived base oil ("GTL 8") having a kinematic viscosity at 100°C (ASTM D445) of approx. 8 cSt ($mm^2s^{-1}$). This GTL base oil may be conveniently manufactured similar to the process as described in e.g. WO 02/070631, the teaching of which is hereby incorporated by reference.

**[0055]** "Base oil 5" was a Fischer-Tropsch derived base oil ("GTL 5") having a kinematic viscosity at 100°C (ASTM D445) of approx. 5 cSt; this GTL base oil may be conveniently manufactured similar to the process as described in e.g. above-mentioned WO 02/070631.

**[0056]** "CH-5" was a poly(hydroxycarboxylic acid) amide salt derivative, commercially available from Shanghai Sanzheng Polymer Company under the trade designation "CH-5". "CH-5" has a TBN value of approximately 2.0 mg.KOH/g, as measured by ASTM D 4739. Furthermore, "CH-5" has a sulphur content of approximately 0.86 wt.%, as measured by ICP-AES.

**[0057]** "Syn-O-Ad 8485" was a product commercially available from Supresta (Akzo Nobel; Amersfoort, The Netherlands) under the trade designation "Syn-O-Ad 8485". Syn-O-Ad 8485 contains a mixture of triaryl esters including up to 60 wt.% trialkylated triaryl phosphate esters.

**[0058]** The "Additive package" (the same in all SAE J1899 (Grade 50) formulations) contained a conventional combination of additives including a phenolic anti-oxidant, a viscosity modifier, a pour point depressant, a triazole-type corrosion inhibitor, a glycerol mono-oleate type friction modifier and an antifoam agent.

**[0059]** The compositions of Examples 1-2 and Comparative Examples 1-2 were obtained by mixing the base oils with the additive package and other additives using conventional lubricant blending procedures.

Table 5

| Component [wt.%] | Comp. Ex. 1 | Comp. Ex. 2 | Ex. 1 | Ex. 2 |
|---|---|---|---|---|
| Base oil 3 (Group I) | 69.8 | 53.8 | 67.6 | 52.2 |
| Base oil 4 (GTL 8) | - | 41.0 | - | 39.7 |
| Base oil 5 (GTL 5) | 25.0 | - | 24.3 | - |
| "CH-5" product | - | - | 3.0 | 3.0 |
| "Syn-O-Ad 8485" product | 1.6 | 1.6 | 1.6 | 1.6 |
| Additive package | 3.6 | 3.6 | 3.6 | 3.6 |
| TOTAL | 100 | 100 | 100 | 100 |

**[0060]** The SAE J1899 (Grade 50) formulations according to Examples 1 and 2 (containing CH-5) appeared to result in improved lead dispersion properties.

Discussion

**[0061]** As can be learned from Table 2, the improvement of anti-deposit properties for compositions according to the present invention having a TBN value of from 3.5 to 70 mg KOH/g and a soap content of 15 to 30 mM in a Fischer-Tropsch derived base oil (Base oil 1) are improved when compared with the same formulations based on a mineral derived base oil (Base oil 2).

**[0062]** Also, it was found that a SAE 75W-80 transmission fluid containing Fischer-Tropsch derived base oil and using API GL-5 type of additive chemistry resulted in no visible wear on gear and bearing parts, no sludge and no deposits when running a gear box for about 600,000 km. Oil analysis showed no significant oil degradation and only low metal wear rates.

## Claims

1. A lubricating composition comprising a base oil selected from the group consisting of a Fischer-Tropsch derived base oil and a poly-alpha olefin (PAO) base oil or a combination thereof,
wherein the composition has a TBN (Total Base Number) value of from 3.5 to 70 mg KOH/g as determined according to ASTM D 2896, and wherein the composition has a soap content of from 15 to 30 mM.

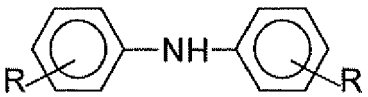
2. Lubricating composition according to claim 1, wherein the base oil contains more than 50 wt.%, preferably more than 60 wt.%, more preferably more than 70 wt.%, even more preferably more than 80 wt.%, most preferably more than 90 wt.% Fischer-Tropsch derived base oil.

3. Lubricating composition according to claim 1 or 2, wherein the composition comprises a detergent, preferably a salicylate-type detergent.

4. Lubricating composition according to claim 3, wherein the detergent has a TBN value below 500 mg KOH/g, preferably in the range of from 60 to 350 mg KOH/g.

5. Lubricating composition according to any one of claims 1 to 4, comprising an amine compound, preferably an aromatic amine compound, more preferably selected from a diphenylamine and a phenyl-alpha-naphthylamine.

6. Lubricating composition according to claim 5, wherein the aromatic amine compound is a diphenylamine having the general formula (I)




(I)

wherein each R is independently an alkyl group having from 1 to 16 carbon atoms, preferably from 3 to 14 carbon atoms, more preferably from 4 to 12 carbon atoms.

7. Lubricating composition according to any one of claims 1 to 6, wherein the composition has a soap content of from 18 to 26 mM, preferably from 20 to 24 mM.

8. Lubricating composition according to any one of claims 1 to 7, wherein the composition comprises at least 1.0 wt. % of a PIB succinimide compound, based on the total weight of the composition.

9. Lubricating composition according to any one of claims 1 to 8, wherein the composition has:

- a sulphated ash content of up to 1.0 wt.%;
- a phosphorus content of up to 0.08 wt.%; and
- a sulphur content of up to 0.3 wt.%.

10. Use of a lubricating composition according to any one of claims 1 to 9, in order to improve deposit reduction properties,

in particular as determined according to ASTM D 7097-09.

## REFERENCES CITED IN THE DESCRIPTION

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

### Patent documents cited in the description


- EP 2159275 A **[0003]**
- EP 0776959 A **[0014]**
- EP 0668342 A **[0014]**
- WO 9721788 A **[0014]**
- WO 0015736 A **[0014]**
- WO 0014188 A **[0014]**
- WO 0014187 A **[0014]**
- WO 0014183 A **[0014]**
- WO 0014179 A **[0014]**
- WO 0008115 A **[0014]**
- WO 9941332 A **[0014]**
- EP 1029029 A **[0014]**
- WO 0118156 A **[0014]**
- WO 0157166 A **[0014]**
- WO 02070631 A **[0043] [0054] [0055]**
- US 20050172543 A **[0045]**
- WO 2007128740 A **[0047]**


### Non-patent literature cited in the description


- **D.J. Wedlock et al.** Gas-to-Liquids Base Oils to assist in meeting OEM requirements 2010 and beyond. *2nd Asia-Pacific base oil Conference,* 23 October 2007 **[0002]**
- API Publication 1509. April 2002 **[0013]**
- **Kirk-Othmer.** Encyclopedia of Chemical Technology. vol. 14, 477-526 **[0029]**