

LUBRICATING COMPOSITION

The present invention relates to a lubricating composition, in particular to lubricating compositions for use in internal combustion engines operated under sustained high load conditions, such as marine diesel engines and power applications. More particularly, the present invention relates to a marine lubricant.

Marine lubricants are known in the art. As an example, EP 1 086 195 discloses a marine cylinder oil composition comprising a lubricating base oil and an over-based detergent component, the composition having a TBN of 50-90, and the detergent component comprising an over-based calcium sulphonate having a viscosity of at least 180 cSt at 100°C and a TBN of about 400 or more.

Lubricating compositions for use in internal combustion engines are subject to high levels of stress. It is important that the lubricating composition provides good lubrication properties under a variety of conditions, and amongst other properties, helps to keep the engine clean, to be thermally and oxidatively stable, to provide good wear, corrosion protection and to carry heat away from the engine.

Lubricating compositions used in marine diesel engines are subject to particularly high levels of stress due to the fact that marine engines are usually run continuously at near full load conditions for long periods of time, often in remote locations. In addition, the lubricating compositions are expected to have long lifetimes since there is often little or no opportunity for changing the lubricating compositions in a marine engine.

It will be appreciated in the art that the term "marine" does not restrict such engines to those used in

water-borne vessels. That is to say, in addition said term also includes engines used for power generation applications. These highly rated, fuel efficient, slow- and medium-speed marine and stationary diesel engines operate at high pressures, high temperatures and long-strokes.

It is an object of the present invention to improve the deposit formation properties of a lubricating composition, especially for use in an internal combustion engine such as a marine diesel engine.

It is another object of the present invention to provide alternative lubricating compositions for use in an internal combustion engine.

One or more of the above or other objects can be obtained by the present invention by providing a lubricating composition at least comprising:

- a base oil; and
- a detergent;

wherein the detergent comprises at least 30 mol%, based on the total amount of detergent, of a sulphonate detergent having a BN (Base Number) of from 0.1 to 80 mg KOH/g;

wherein the detergent comprises from 30 to 70 mol%, based on the total amount of detergent, of a phenate detergent;

wherein the lubricating composition comprises at least 4 wt.% of detergent, based on the total weight of the composition; and

wherein the lubricating composition has a TBN (total base number) (according to ASTM D 2896) of at least 10 mg KOH/g.

It has now surprisingly been found according to the present invention that the lubricating compositions according to the present invention exhibit improved

deposit formation control properties as determined according to DIN 51392 and the Komatsu Hot Tube Test.

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.

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.

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

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 categories I-IV. These API categories are defined in API Publication 1509, 15th Edition, Appendix E, April 2002.

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.

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.

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 C₂ to C₃₂, preferably C₆ to C₁₆, alpha olefins. Particularly preferred feedstocks for said poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

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 98 wt.% and most preferably in an amount in the range of from 70 to 95 wt.%, with respect to the total weight of the lubricating composition.

According to a preferred embodiment of the present invention the base oil comprises at least 50 wt.%, preferably at least 60 wt.%, more preferably at least 70 wt.% of a Group II base oil, based on the total amount of base oil.

There are no particular limitations regarding the detergent as used in lubricating compositions according to the present invention (provided that the requirements

of claim 1 are met) and various conventional detergents may be conveniently used. The term "detergent" may refer to a single detergent, but also to a mixture containing two or more different detergents. Examples of detergents that may be used include oil-soluble neutral and over-based sulphonates, phenates, sulphurized 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 over-based detergents having a TBN (Total Base Number; according to ASTM D2896) of up to 450 mg KOH/g. Combinations of detergents, whether over-based or neutral or both, may be used.

As mentioned earlier, in compositions according to the present invention, the detergent comprises at least 30 mol%, based on the total amount of detergent, of a sulphonate detergent having a BN (Base Number) of from 0.1 to 80 mg KOH/g. This type of sulphonate detergents having a relatively low BN are well known in the art; as an example WO 96/26919 discloses low BN calcium sulphonates, and the preparation thereof.

According to a preferred embodiment of the present invention the detergent comprises at least 35 mol% of the sulphonate detergent, preferably at least 40 mol%, more preferably at least 45 mol%, even more preferably at least 50 mol.%, most preferably at least 55 mol%. Also it is preferred that the sulphonate detergent has a BN of at most 50 mg KOH/g, more preferably at most 40 mg KOH/g.

As mentioned earlier, in compositions according to the present invention, the detergent comprises from 30 to 70 mol%, based on the total amount of detergent, of a phenate detergent. Preferably, the detergent comprises at least 35 mol% of the phenate detergent; preferably the

detergent comprises at most 65 mol% of the phenate detergent, more preferably at most 60 mol%, even more preferably at most 55 mol%, yet even more preferably at most 50 mol%, most preferably at most 45 mol% of the phenate detergent. Also it is preferred that the phenate detergent is an over-based detergent having a BN of at least 190 mg KOH/g, preferably at least 200, more preferably at least 220, most preferably at least 240 mg KOH/g. Such detergents are well-known in the art.

The total amount of the detergent in the compositions of the invention is typically at most 35.0 wt.%, based on the total weight of the lubricating composition. The composition of the present invention comprises at least 4 wt.%, preferably at least 8 wt.%, more preferably at least 12 wt.% of detergent, based on the total weight of the composition.

The lubricating composition according to the present invention may further comprise one or more other additives such as anti-oxidants, anti-wear additives, dispersants, other detergents, extreme pressure additives, other friction modifiers, viscosity modifiers, pour point depressants, metal passivators, corrosion inhibitors, demulsifiers, anti-foam agents, seal compatibility agents and additive diluent base oils, etc. Preferably, in addition to the detergent, at least a dispersant is present in the compositions according to the present invention; more preferably, at least a dispersant and an anti-wear additive are present.

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 0.5 to 30.0 wt.%, based on the total weight of the lubricating composition. More preferably, the lubricating composition according to the present contains less than 5.0 wt.% of

any other additives than one or more detergents. Preferably, the composition contains no other additives than one or more detergents, one or more dispersants and one or more anti-wear agents.

5 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,
10 volume 14; pages 477-526.

Preferably, the composition has a Total Base Number (TBN) value of at most 75 mg KOH/g, preferably at most 70 mg KOH/g, more preferably at most 65 mg KOH/g, even more preferably at most 60 mg KOH/g (in particular according
15 to ASTM D 2896). The composition has a total base number (TBN) value (according to ASTM D 2896) of at least 10 mg KOH/g.

Further, it is preferred that the composition has a kinematic viscosity at 100°C (according to ASTM D 445) of
20 above 5.6 mm²/s and below 21.9 mm²/s, preferably above 12.5 mm²/s, more preferably above 16.3 mm²/s.

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

25 In another aspect, the present invention provides the use of a lubricating composition according to the present invention in order to improve deposit formation control properties, in particular as determined according to DIN 51392.

30 The lubricating compositions according to the present invention are useful for lubricating apparatus generally, but in particular for use as engine oils for internal combustion engines. These engine oils include passenger car engines, diesel engines, marine diesel engines, gas
35 engines, two- and four-cycle engines, etc., and in

particular marine diesel engines.

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

Various lubricating compositions for use as marine cylinder oils in a marine diesel engine were formulated.

Table 1 indicates the composition and properties of the formulations that were tested; the amounts of the components are given in wt.%, based on the total weight of the fully formulated formulations.

All tested marine diesel engine oil formulations were formulated as SAE 50 formulations meeting the so-called SAE J300 Specifications (as revised in January 2009; SAE stands for Society of Automotive Engineers). All the tested formulations had a kinematic viscosity at 100°C (according to ASTM D 445) of above 16.3 mm²/s and below 21.9 mm²/s.

All the tested marine cylinder oil formulations contained a combination of a base oil, a detergent combination and a dispersant.

"Base oil 1" was a base oil blend of a Group I base oil and Bright Stock, commercially available from Shell Chemicals Ltd. (London, United Kingdom) under the trade designation "Catenex".

"Base oil 2" was a base oil blend containing a thickener and 75 wt.% of a Group II base oil; the blend is commercially available from Chevron Products Company (San Ramon, CA, USA) under the trade designation "Chevron 600 R".

"Detergent 1" was an over-based sulphonate detergent having a TBN of 417 mg KOH/g (according to ASTM D 2896) and a soap content of 236 mM Ca²⁺, commercially available

from Chevron Oronite (Windsor, UK) under the trade designation "OLOA 249SX".

"Detergent 2" was an over-based sulphonate detergent having a TBN of 375 mg KOH/g and a soap content of 317 mM Ca^{2+} , commercially available from JinZhou KangTai Lubricant Additives Co. Ltd. (Liaoning, China) under the trade designation "T106".

"Detergent 3" was an over-based phenate detergent having a TBN of 246 mg KOH/g and a soap content of 397 mM Ca^{2+} , commercially available from Lubrizol (Wickliffe, Ohio, USA) under the trade designation "Lubrizol 6499".

"Detergent 4" was an over-based phenate detergent having a TBN of 250 mg KOH/g and a soap content of 282 mM Ca^{2+} , commercially available from Chevron Oronite under the trade designation "OLOA 219C".

"Detergent 5" was a low BN sulphonate detergent having a TBN of 16 mg KOH/g and a soap content of 410 mM Ca^{2+} , commercially available from Chevron Oronite under the trade designation "OLOA 246S".

"Detergent 6" was a low BN sulphonate detergent having a TBN of 34 mg KOH/g and a soap content of 395 mM Ca^{2+} , commercially available from Chemtura Corporation (Middlebury, USA) under the trade designation "LOBASE C-4503".

"Detergent 7" was an over-based sulphonate detergent having a TBN of 9 mg KOH/g and a soap content of 441 mM Ca^{2+} , commercially available from Chemtura Corporation under the trade designation "LOBASE C-4506".

The "dispersant" was a high MW polyisobutene succinimide, commercially available from Afton Chemical Corporation (Richmond, VA, USA) under the trade designation "HiTEC".

The compositions of Examples 1-10 and Comparative Examples 1-2 were obtained by mixing the base oils with the detergents, dispersant using conventional lubricant

blending procedures.

The following methods as referred to in Table 1 were used:

¹TBN value has been determined according to ASTM D 2896;

²Detergent content (or "soap content") of the individual detergents was determined by TAN measurement (according to ASTM D 664) of the soap fraction of the detergents after the isolation procedure as described in the article of V.A. Zakupra and S.V. Timoshenko (All-Union Scientific-Research and Design Institute of the Petroleum Refining and Petrochemical Industry (VNIIPKneftekhim), USSR), "Separation of lube oil detergent additives on silica gel", in Khimiya i Tekhnologiya Topliv i Masel, No. 2, pp. 48-52, February, 1980. The measured value for the soap content has been expressed as equivalents of millimol Ca^{2+} per kg of the detergent additive (see the soap contents as determined for the Detergents 1-7 above). The detergent (molar) content of each detergent type (e.g. low BN sulphonates) is obtained by addition of the individual detergent additive contribution (on wt.% basis) in the total formulation multiplied by the individual detergent content.

³The detergent proportion has been determined by calculation (each detergent component divided by the total) and is expressed in mol%. In the Examples, the phenate proportion and sulphonate proportion add up to 100%; the proportion of Low BN sulphonate (i.e. sulphonates having a BN of from 0.1 to 80 mg KOH/g, preferably 0.1 to 50 mg KOH/g) is a subset of the sulphonate proportion.

⁴Normalized deposits have been based on the total deposits values as determined after testing according to DIN 51392. Normalized deposits (rather than total deposits) have been indicated, whilst taking Comparative

Example 3 as the reference, to better reflect the relative values.

Table 1

Component [wt.%]	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Base oil 1 (Group I + BS)	83.4	81.1	83.9	82.5	-	-	76.1
Base oil 2 (Group II + thickener)	-	-	-	-	79.5	81.7	-
Detergent 1 (Over-based sulphonate)	-	-	-	-	-	-	-
Detergent 2 (Over-based sulphonate)	-	-	1.0	-	-	-	1.9
Detergent 3 (Over-based phenate)	-	-	7.2	7.0	7.0	1.5	-
Detergent 4 (Over-based phenate)	7.4	7.4	-	1.5	-	6.5	13.0
Detergent 5 (Low BN sulphonate)	-	-	-	-	-	8.8	-
Detergent 6 (Low BN sulphonate)	7.7	10.0	-	-	12.0	-	-
Detergent 7 (Low BN sulphonate)	-	-	6.4	7.5	-	-	7.5
Dispersant	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TOTAL	100	100	100	100	100	100	100
Properties of total composition							
TBN value ¹ [mg KOH/g]	21.12	21.90	22.04	21.65	21.30	21.35	40.30
Over-based sulphonate	-	-	3.17	-	-	-	6.02

content ² [mM Ca ²⁺ /kg]							
Phenate content ² [mM Ca ²⁺ /kg]	20.87	20.87	28.58	32.02	27.79	24.29	36.66
Low BN sulphonate content ² [mM Ca ²⁺ /kg]	30.42	39.50	28.22	33.08	47.40	36.08	33.08
Total detergent content ² [mM Ca ²⁺ /kg]	51.28	60.37	59.98	65.10	75.19	60.37	75.76
Phenate proportion ³ [mol.%]	41	35	48	49	37	40	48
Low BN sulphonate proportion ³ [mol.%]	59	65	47	51	63	60	44
Sulphonate proportion ³ [mol.%]	59	65	52	51	63	60	52
Normalised deposits ⁴	32.66	30.20	34.68	31.54	28.41	21.25	34.45

Table 1 (continued)

Component [wt.%]	Ex.8	Comparative Ex. 1	Comparative Ex. 2	Ex. 9	Ex. 10
Base oil 1 (Group I + BS)	86.2	88.8	82.0	85.6	78.5
Base oil 2 (Group II + thickener)	-	-	-	-	-
Detergent 1 (Over-based sulphonate)	-	1.5	2.0	-	-
Detergent 2 (Over-based sulphonate)	-	-	-	1.0	-
Detergent 3 (Over-based phenate)	8.8	6.2	-	7.1	-
Detergent 4 (Over-based phenate)	-	-	5.0	-	8.0
Detergent 5 (Low BN sulphonate)	-	-	-	4.8	-
Detergent 6 (Low BN sulphonate)	-	-	-	-	-
Detergent 7 (Low BN sulphonate)	3.5	2.0	9.5	-	12.0
Dispersant	1.5	1.5	1.5	1.5	1.5

TOTAL	100	100	100	100	100
Properties of total composition					
TBN value ¹ [mg KOH/g]	21.96	21.69	21.70	21.98	21.08
Over-based sulphonate content ² [mM Ca ²⁺ /kg]	-	3.54	4.72	3.17	-
Phenate content ² [mM Ca ²⁺ /kg]	34.94	24.61	14.10	28.19	22.56
Low BN sulphonate content ² [mM Ca ²⁺ /kg]	15.44	8.82	41.90	19.68	52.92
Total detergent content ² [mM Ca ²⁺ /kg]	50.37	36.97	60.72	51.04	75.48
Phenate proportion ³ [mol.%]	69	67	23	55	30
Low BN sulphonate proportion ³ [mol.%]	31	24	69	39	70
Sulphonate proportion ³ [mol.%]	31	33	77	45	70
Normalised deposits ⁴	63.09	86.13	100.00	49.44	56.38

Wolf Strip Test

In order to demonstrate the deposit formation control properties of the present invention, measurements were performed using the Wolf Strip Test procedure according to DIN 51392 (test duration; 12 hours; plate temperature at 280°C). In the test, the following test conditions were used: 150 ml of oil flow in a closed loop was used; the oil under test was pumped in the form of a thin film for 12 hours at 280°C at a flow rate of 50 (±5) ml/h over a removable test strip which strip was inclined at an angle of 8° to the horizontal.

The measured normalized deposits are indicated in Table 1 above, indicating the relative amount compared to the example having the highest amount of total deposits (viz. Comparative Example 3).

Komatsu Hot Tube Test

In an alternative test to demonstrate the deposit formation control properties of the present invention, measurements were performed using the Komatsu Hot Tube Test procedure according to the visual rating as explained in the Swiss Testing procedure No. STS Nr. 452. The Komatsu Hot Tube Test evaluates the high temperature stability of a lubricant. Oil droplets are pushed up by air inside a heated narrow glass capillary tube and the thin film oxidative stability of the lubricant is measured by the degree of lacquer formation on the glass tube, the resulting colour of the tube being rated on a scale of 0-10. A rating of 0 refers to heavy deposit formation and a rating of 10 means a clean glass tube at the end of the test. The method is also described in SAE paper 840262. The level of lacquer formation in the tube reflects the high temperature stability of the oil and its tendency during service to form deposits in high temperature areas of the engine. The measured ratings (at 290 and 320°C) are indicated in Table 2 below.

Table 2

	Ex. 2	Ex. 3	Ex. 5	Ex. 6	Comp. Ex. 1
290°C	9.5	9.5	9.5	9.5	8.5
320°C	5.0	5.0	8.5	8.5	blocked

Discussion

As can be learned from Table 1, the deposit formation control properties for the compositions according to the present invention were significantly improved when compared with Comparative Examples 1-2.

From the comparison of the deposit formation control properties of Examples 1 to 10 it can be learned – amongst others – that according to the present invention there is a preference for embodiments wherein at least 40 mol.% of the detergent is a low BN sulphonate detergent (i.e. having a BN number of from 0.1 to 80, preferably below 50 mg KOH/g) and at the same time more than 35 mol.% of the total amount of detergent is a phenate detergent (Examples 1-7). Further there is a special preference for Examples 5 and 6 as these exhibit smaller amount of deposits. Also, it is preferred that the base oil comprises at least 50 wt.% of a Group II base oil.

The desirable deposit formation control properties according to the present invention were confirmed in the Komatsu hot tube test (see Table 2). Examples 2, 3, 5 and 6 received exceptionally good ratings (9.5 out of 10) at 290°C and still acceptable (5.0 for Examples 2 and 3) to good (8.5 for Examples 5 and 6) values at 320°C, whilst Comparative Example 1 did not pass the test at 320°C ("blocked").

CLAIMS

1. A lubricating composition at least comprising:

- a base oil; and
- a detergent;

wherein the detergent comprises at least 30 mol%, based on the total amount of detergent, of a sulphonate detergent having a BN (Base Number) of from 0.1 to 80 mg KOH/g; wherein the detergent comprises from 30 to 70 mol%, based on the total amount of detergent, of a phenate detergent, wherein the phenate detergent is an over-based detergent having a BN of at least 190 mg KOH/g; wherein the lubricating composition comprises at least 8 wt.% of detergent, based on the total weight of the composition; and wherein the lubricating composition has a TBN (total base number) according to ASTM D 2896 of at least 10 mg KOH/g.

2. Lubricating composition according to claim 1, wherein the detergent comprises at least 35 mol% of the sulphonate detergent.

3. Lubricating composition according to claim 1 or 2, wherein the sulphonate detergent has a BN of at most 50 mg KOH/g.

4. Lubricating composition according to any of claims 1 to 3, wherein the detergent comprises at least 35 mol% of the phenate detergent.

5. Lubricating composition according to any of claims 1 to 4, wherein the phenate detergent is an over-based detergent having a BN of at least at least 200mg KOH/g.

6. Lubricating composition according to any of claims 1 to 5, wherein the composition comprises at least 12 wt.% of detergent, based on the total weight of the composition.

7. Lubricating composition according to any of claims 1 to 6, wherein the composition has a TBN (Total Base Number) value of at most 75 mg KOH/g.

8. Lubricating composition according to any of claims 1 to 7, wherein the base oil comprises at least 50 wt.% of a Group II base oil, based on the total amount of base oil.

9. Lubricating composition according to any of claims 1 to 8, wherein the composition is a marine diesel engine oil.

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