

LUBRICATING COMPOSITION

Field of the Invention

5 The present invention relates to a lubricating composition, in particular to a lubricating composition for use in internal combustion engines that may be operated under sustained high load conditions, such as marine diesel engines and power applications. More particularly, the present invention relates to a
10 lubricating composition that can be used in a two-stroke crosshead diesel engine, particularly for slow speed or medium speed applications.

Background of the Invention

15 Environmental regulations for ships are established by MARPOL (the International Convention for the Prevention of Pollution from Ships). Annex VI specifies "Regulations for the Prevention of Air Pollution from Ships" and includes limitations on emissions. Since the beginning of 2015 in the so-called "Emission Controlled
20 Area", emissions of sulphur oxides must be below 0.10 wt% sulphur equivalent. This can be achieved either by exhaust gas treatment or by limiting the sulphur content of the fuel used by the ships.

25 Marine lubricants typically contain metallic organic detergents that can neutralise sulphuric acid which is formed when sulphur oxides from combusted heavy fuel oil interact with water. The neutralisation potential of the lubricant is typically reported as a Base Number (measured according to ISO 3771, ASTM D2896 or ASTM D4739
30 and expressed in mg KOH/g). To meet the emissions regulations, the amount of sulphur in the marine fuel may be reduced or exhaust gas treatment may be used. If the

amount of sulphur in a marine fuel is reduced, the Base Number of the marine lubricant must be adjusted to match the neutralisation needs of the fuel. If the Base Number is higher than required, then there is a risk that unused base reserve can contribute to increased abrasive wear on cylinder liners by forming deposits on piston lands and in ring grooves.

It is therefore desirable to provide lubricants having a lower Base Number that can be used with marine fuels having reduced sulphur content. These lubricants should exhibit good deposit formation properties (i.e. reduced build-up of deposits) and good anti-wear performance.

WO2014158855 discloses lubricating compositions for use in marine diesel engines which comprise from about 3 wt% to about 40 wt%, based upon the weight of the lubricating composition, of a sulphurised alkaline earth metal alkylphenate detergent. The lubricating composition has a total Base Number in the range of from 20 to about 100. The lubricating composition is said to have improved oxidative stability. The deposit formation properties of the lubricating compositions are not discussed.

The present inventors have sought to provide alternative lubricant formulations having effective deposit formation and anti-wear properties.

Summary of Invention

The present inventors have found that a lubricating composition that combines a particular alkaline earth metal detergent with polyisobutene as a thickener have particularly good deposit formation properties as shown by the modified Wolf Strip test and also have good anti-wear performance as shown by a wear test.

Accordingly, the present invention provides a lubricating composition having a Base Number (as measured by ISO 3771) of 30 mg KOH/g or less, comprising:

- (a) a base oil;
- 5 (b) polyisobutene;
- (c) an alkaline earth metal alkylphenate detergent.

The present invention further provides the use of a lubricating composition in an internal combustion engine, wherein the lubricating composition has a Base Number (as measured by ISO 3771) of less than 30 mg KOH/g, and
10 wherein the lubricating composition comprises:

- (a) a base oil;
- (b) polyisobutene;
- (c) an alkaline earth metal alkylphenate detergent.

15 The present invention further provides the use of a combination of polyisobutene and an alkaline earth metal alkylphenate detergent to improve the deposit formation properties of a lubricating composition.

Detailed Description of the Invention

20 The lubricating composition of the invention has a Base Number (as measured by ISO 3771) of 30 mg KOH/g or less. Preferably the Base Number is 25 mg KOH/g or less. Preferably the Base Number (as measured by ISO 3771) is at least 10 mg KOH/g, more preferably at least 15 mg
25 KOH/g. The preferred Base Number is a balance between having sufficient alkaline detergent to neutralise any sulphuric or sulphurous acid which is formed, and having excess base which may lead to increased wear. The Base Number of 30 mg KOH/g or less is likely to provide a
30 lubricating composition that is suitable for use in marine engines wherein the fuel has been designed to meet the emission requirement for sulphur oxides of less than 0.10 wt% sulphur equivalent.

The Base Number of the lubricating composition is affected by the detergents that are used in the lubricating composition, and the skilled person can choose appropriate detergents and quantities of detergents to achieve the required Base Number. The lubricating composition comprises an alkaline earth metal alkylphenate detergent, but may also comprise additional detergents. The additional detergents may include oil-soluble neutral and over-based sulphonates, phenates, sulphurised 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 additional metal detergents are neutral and over-based detergents having a Base Number (according to ISO 3771) of up to 450 mg KOH/g.

The base oil used in the lubricating composition may conveniently comprise mixtures of one or more mineral oils and/or one or more synthetic oils. The term "base oil" may refer to a mixture containing more than one type of base oil.

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

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.

Synthetic oils include hydrocarbon oils such as olefin oligomers (including poly-alpha olefin base oils; PAOs), dibasic acid esters, polyol esters, polyalkylene glycols (PAGs), alkyl naphthalenes and dewaxed waxy isomerates.

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 poly-alpha olefins are 1-octene, 1-decene, 1-dodecene and 1-tetradecene.

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.

The base oil preferably comprises at least 50 wt%, preferably at least 60 wt%, more preferably at least 70 wt% of a Group I or Group II base oil, based on the total amount of base oil. The base oil preferably comprises at least 50 wt%, preferably at least 60 wt%, more preferably at least 70 wt% of a Group I oil, based on the total amount of base oil.

The total amount of base oil in the lubricating composition is preferably from 60 to 99 wt%, more preferably from 65 to 95 wt% and most preferably from 70

to 90 wt%, with respect to the total weight of the lubricating composition.

The lubricating composition comprises polyisobutene. The molecular weight (M_n) of the polyisobutene, as measured by gel permeation chromatography and preferably by ASTM D 3536, is suitably in the range of from 500 to 5000, preferably in the range of from 1000 to 4000 and most preferably in the range of from 1500 to 3000. The polydispersity of the polyisobutene, as measured by gel permeation chromatography and preferably by ASTM D 3536, is suitably in the range of from 0.5 to 5, preferably from 1 to 3.

The amount of polyisobutene in the lubricating composition is suitably from 2 to 20 wt%, based upon the weight of the lubricating composition, preferably from 3 to 15 wt%. The preferred amount of polyisobutene is a balance between incorporating sufficient polyisobutene to obtain the desired deposit formation properties, and not so much polyisobutene that the friction force or anti-wear properties are adversely affected.

The lubricating composition comprises an alkaline earth metal alkylphenate detergent. Suitably the alkaline earth metal is calcium or magnesium. Preferably the alkaline earth metal is calcium. Suitably the alkylphenate group is a C_{10} - C_{20} group. In a preferred embodiment the alkylphenate group is sulphurised, i.e. there can be sulphur-bridging between phenate rings.

The amount of alkaline earth metal alkylphenate detergent in the lubricating composition is suitably from 3 wt% to 12 wt%, based upon the weight of the lubricating composition, preferably from 4 wt% to 10 wt%. The preferred amount of alkaline earth metal alkylphenate detergent is a balance between incorporating sufficient

alkaline earth metal alkylphenate detergent to obtain the desired anti-wear performance, and achieving the required Base Number.

5 In one embodiment of the invention, the alkaline earth metal alkylphenate detergent is the only detergent in the lubricating composition. However, it is preferable to have a combination of different detergents in the lubricating composition (always including the alkaline earth metal alkylphenate detergent) as the different
10 detergents can offer different beneficial effects to the lubricating composition. For example, it may be advantageous to incorporate a sulphonate detergent in the lubricating composition as this can offer excellent thermal stability. Alternatively or additionally, it may
15 be advantageous to include a salicylate detergent in the lubricating composition as this can offer improved oxidation stability. The total amount of detergent is determined by the detergent choice and the required Base Number of the lubricating composition.

20 The lubricating composition may further comprise one or more other additives such as anti-oxidants, anti-wear additives, dispersants, extreme pressure additives, friction modifiers, viscosity modifiers, pour point depressants, metal passivators, corrosion inhibitors,
25 demulsifiers, anti-foam agents and seal compatibility agents.

The lubricating composition suitably has a kinematic viscosity at 100 °C (according to ASTM D 445 or ASTM D 446) of above 10 mm²/s and below 30 mm²/s. The preferred
30 SAE grades are SAE 40 (having a viscosity from 12.5 to less than 16.3 mm²/s), SAE 50 (having a viscosity from 16.3 to less than 21.9 mm²/s) and SAE 60 (having a viscosity from 21.9 to less than 26.1 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).

5 The present invention further provides the use of a lubricating composition according to the invention in an internal combustion engine. The internal combustion engine is suitably an engine operated under sustained high load conditions, such as marine diesel engines and power applications. Such engines may sometimes experience low
10 load conditions. The internal combustion engine is preferably a two-stroke crosshead diesel engine. The internal combustion engine is suitably supplied with a low sulphur or distillate fuel with up to 1 wt% sulphur, preferably up to 0.5 wt% sulphur, more preferably up to
15 0.1 wt% sulphur. The fuel is suitably according to the ISO specification for marine fuels (ISO 8217:2012(E)). Alternatively, the internal combustion engine is suitably fuelled with liquefied natural gas (LNG).

In a particular embodiment the present invention
20 provides the use of a lubricating composition according to the invention in a dual fuel engine operating with either natural gas or distillate fuel with low sulphur content. The dual fuel engine is preferably a two-stroke crosshead diesel engine.

25 The present invention further provides the use of a combination of polyisobutene and an alkaline earth metal alkylphenate detergent to improve the deposit formation properties of a lubricating composition. The amount of polyisobutene is suitably from 2 to 20 wt%, based upon
30 the weight of the lubricating composition, preferably from 3 to 15 wt%. The amount of alkaline earth metal alkylphenate detergent is suitably from 3 wt% to 15 wt%,

based upon the weight of the lubricating composition, preferably from 4 wt% to 10 wt%.

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 were formulated.

The components in the compositions are described below:

Base Oil: This was a blend of two Group I base oils (HVI 160S and HVI 650, both available from Shell).

Detergent 1: Calcium long chain alkaryl sulphonate detergent (OLOA 246 SX available from Oronite)

Detergent 2: Calcium long chain alkaryl sulphonate detergent (OLOA 249 SX available from Oronite)

Detergent 3: Calcium alkylphenate detergent (OLOA 219 available from Oronite)

Detergent 4: Highly over-based calcium alkyl salicylate with anti-foam (M7125 available from Infineum)

Anti-oxidant: butylated/octylated diphenylamine (Irganox L57 from BASF)

Dispersant 1: Polyolefin polyamine succinimide (OLOA 11001 available from Oronite)

Dispersant 2: Amide/amine dispersant (C9201 from Infineum)

Polyisobutene: Indopol H-1200 available from Ineos

Tables 1 and 2 indicate 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. The components shown for Example 5 provided 100% of the

lubricating composition. The wt% values have been expressed to one decimal place.

Testing

5 The Base Number of each formulation was measured by ISO 3771. The kinematic viscosities at 100 °C and 40 °C were measured by ASTM D 445/446. The viscosity index was measured by ISO 2909.

10 The deposit formation control properties of the lubricating compositions of the present invention were tested using a modified Wolf Strip test procedure. The method determines the tendency towards formation of deposits on a test strip of the Wolf Strip Test Apparatus caused by oxidative and thermal exposure. The test oil is blended with small amount of Heavy Fuel Oil and
15 homogenised at 60°C. The blended oil (sample volume 150 ml) is pumped in the form of a thin film for 13 hours at a flow rate of 50 ± 5 ml/h over a removable metal test strip. The test strip is heated to 280°C. It is inclined at an angle of 8° to the horizontal. The sample drops from
20 the test strip into the not heated oil reservoir and is returned to the test strip by a small piston pump. At the end of the test the metal strip and deposits formed are washed in solvent and weighed.

25 The anti-wear properties of the lubricating compositions of the present invention were tested using a modified version of the ASTM G181 test in which a moving pin is reciprocated against a stationary plate to simulate piston top position under closely controlled conditions and at a load at which an insufficient lubrication will
30 create scars. The temperature was raised from 100 °C to 350 °C. If the pin created a scar on the plate that was deeper than 10 µm then the lubricant was considered to have failed the test. If the pin created a scar of less

than 10 μm then the lubricant was considered to have passed the test.

Tables 1 and 2 give the results of the testing for the formulations.

Table 1

	Comparative Example 1	Comparative Example 2	Example 1	Example 2	Comparative Example 3	Comparative Example 4	Example 3	Example 4
Base Oil Blend (Group I)	65.7	43.2	84.0	79.5	67.2	34.7	86.9	79.7
Base Oil Blend (Group I)	22.0	44.5	0	0	23.5	56.0	0	0
Detergent 1	3.0	3.0	3.0	3.0	0	0	0	0
Detergent 2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Detergent 3	7.0	7.0	7.0	7.0	7.0	7.0	7.0	7.0
Dispersant 1	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Polyisobutene	0	0	3.7	8.2	0	0	3.8	11.0
TBN value in mg KOH/g	21.0	21.8	21.3	21.4	20.6	21.7	20.7	21.0
Kinematic viscosity at 100 °C in cSt or mm ² /s	15.6	19.8	15.6	20.1	15.7	23.0	15.7	23.2
Kinematic viscosity at 40 °C in cSt or mm ² /s	164.8	236.9	196.1	220.8	166.2	287.7	157.5	266.7
Viscosity Index	96	96	77	105	97	99	101	108
Modified Wolf Strip Test	191.3	474.7	86.4	250.2	182.7	406.3	145.3	179.9
Δ weight 1 in mg	279	391.8	167.3	310.1	190.6	485.1	203	189.8
Deposits (sum Δ, in mg)	470.3	866.5	253.7	560.3	373.3	891.4	348.3	369.7

Table 2

		Comparative Example 5	Example 5
Base Oil		83.6	81.8
Detergent 2		2.9	0
Detergent 3		0.8	5.6
Detergent 4		3.0	3.0
Anti-oxidant		0.2	0.2
Dispersant 2		0.2	0.2
Polyisobutene		9.3	9.1
TBN value in mg KOH/g		25.2	25.8
Kinematic viscosity at 100 °C in cSt or mm ² /s		19.59	19.64
Kinematic viscosity at 40 °C in cSt or mm ² /s		205.9	210.2
Viscosity Index		109	107
Wear Test		Fail	Pass with constraints
Plate - Wear Scar in µm		38	1
Fail at ca. temp. in °C		320	-
Modified Wolf Strip Test	Δ weight 1 in mg	180.3	127
	Δ weight 1 in mg	167.1	105.2
	Deposits (sum Δ, in mg)	347.4	232.2

Table 1 shows the effect of including polyisobutene in the formulations. Incorporating from 3.7 to 11 wt% of polyisobutene provides better outcomes in the modified Wolf Strip test, indicating better deposit formation control, when compared to formulations that do not contain the polyisobutene (compare example 1 with comparative example 1; example 2 with comparative example 2; example 3 with comparative example 3; example 4 with comparative example 4)m. Table 2 shows the effect of including a larger amount of calcium alkylphenate

detergent (detergent 3). Incorporating 5.62 wt% of the
detergent instead of 0.79 wt% gave a better result in the
wear test, indicating better anti-wear performance and
also an improved result in the modified Wolf Strip test,
5 indicating better deposit formation control.

C L A I M S

1. A lubricating composition having a Base Number as measured by ISO 3771 of 30 mg KOH/g or less, comprising:

- (a) a base oil;
- (b) polyisobutene; and

5 (c) an alkaline earth metal alkylphenate detergent, wherein the amount of alkaline earth metal alkylphenate detergent in the lubricating composition is from 4 wt% to 10 wt%, based upon the weight of the lubricating composition.

10 2. A lubricating composition according to claim 1, having a Base Number as measured by ISO 3771 of at least 10 mg KOH/g and 25 mg KOH/g or less.

15 3. A lubricating composition according to claim 1 or claim 2, wherein the molecular weight, M_n , of the polyisobutene, as measured by ASTM D 3536, is in the range of from 500 to 5000.

20 4. A lubricating composition according to any preceding claim, wherein the amount of polyisobutene in the lubricating composition is from 2 to 20 wt%, based upon the weight of the lubricating composition.

25 5. A lubricating composition according to any preceding claim, wherein the lubricating composition has a kinematic viscosity at 100 °C according to ASTM D 445/446 of above 10 mm²/s and below 30 mm²/s.

30 6. Use of a lubricating composition according to any preceding claim in an internal combustion engine.

7. Use of a lubricating composition according to claim 6, wherein the engine is a two-stroke crosshead diesel engine.