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(54) Titre : COMPOSITION DE LUBRIFIANT
(54) Title: LUBRICANT COMPOSITION

(57) Abrégé/Abstract:

A marine diesel cylinder lubricant composition for a marine diesel engine running on fuel having a sulphur content of less than 1.5%, the composition having a total base number, as determined according to ASTM D2896, of more than 30 and less than 70, and comprising at least 40 wt% of an oil of lubricating viscosity, and at least one detergent prepared from at least two surfactants, one of which is a salicylate. The marine diesel cylinder lubricant composition demonstrates good ability to reduce deposit formation, especially on pistons. The marine diesel cylinder lubricant composition also demonstrates good lubrication at temperatures above 250°C.

ABSTRACT

A marine diesel cylinder lubricant composition for a marine diesel engine running on fuel having a sulphur content of less than 1.5%, the composition having a total base number, as determined according to ASTM D2896, of more than 30 and less than 70, and comprising at least 40 wt% of an oil of lubricating viscosity, and at least one detergent prepared from at least two surfactants, one of which is a salicylate.

The marine diesel cylinder lubricant composition demonstrates good ability to reduce deposit formation, especially on pistons. The marine diesel cylinder lubricant composition also demonstrates good lubrication at temperatures above 250°C.

Lubricant Composition

This invention concerns a lubricant composition, in particular, a marine diesel cylinder lubricant (MDCL) composition. Marine diesel cylinder lubricant compositions are total loss lubricants and their purpose is to provide a strong oil film between the cylinder liner and the piston rings and to neutralise acids formed by combustion of sulphur compounds in the fuel.

Fuels used for diesel engines generally have a high sulphur content, which results in exhaust gases from diesel engines containing large amounts of sulphur oxides (SO_x). The sulphur oxides react with moisture also present in the exhaust gases to form sulphuric acid which corrodes the engine. Marine diesel cylinder lubricant compositions therefore include overbased metallic detergents to neutralise the sulphuric acid. Commercial marine diesel cylinder lubricant compositions generally have a total base number ('TBN') of at least 70 (as determined using ASTM D2896).

There is growing environmental pressure to reduce the amount of sulphur in fuels. Therefore, a marine diesel cylinder lubricant composition having a TBN less than 70 could be used. However, the applicants have found that if a marine diesel cylinder lubricant composition is diluted with base oil to lower the total base number to less than 70, the ability of the lubricant to prevent deposit formation, particularly on the pistons, is significantly reduced.

The aim of the present invention is to provide a marine diesel cylinder lubricant composition having a base number lower than 70 without reducing the ability of the lubricant to prevent deposit formation, particularly on the pistons.

In accordance with the present invention there is provided a marine diesel cylinder lubricant composition for a marine diesel engine running on fuel having a sulphur content of less than 1.5%, the composition having a total base number, as determined according to ASTM D2896, of more than 30 and less than 70, and comprising:

- at least 40 wt% of an oil of lubricating viscosity, and
- at least one detergent prepared from at least two surfactants, one of which is a salicylate.

The inventor has found that the marine diesel cylinder lubricant composition defined above is capable of preventing deposit formation, particularly on the pistons, and is also capable of improving resistance to high temperature-induced wear (i.e. scuffing).

The marine diesel cylinder lubricant composition has a total base number (TBN) of less than 70, preferably less than 60, and most preferably less than 50. Furthermore, the marine diesel cylinder lubricant composition preferably has a total base number (TBN) of more than 32, more preferably more than 35.

In accordance with the present invention there is also provided a method of operating a marine diesel cylinder engine running on fuel having at most 1.5% sulphur, the method including the step of using the marine diesel cylinder lubricant composition defined above to lubricate the engine.

In accordance with the present invention there is also provided use of the marine diesel cylinder lubricant composition defined above to reduce deposits in a marine diesel cylinder engine running on fuel having at most 1.5% sulphur.

In accordance with the present invention there is also provided use of the marine diesel cylinder lubricant composition defined above to provide lubricity in a marine diesel cylinder engine running on fuel having at most 1.5% sulphur and running at cylinder liner temperatures above 250°C, preferably above 300°C.

Oil of Lubricating Viscosity

The oil of lubricating viscosity (sometimes referred to as lubricating oil) may be any oil suitable for the lubrication of a marine engine. The lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as a naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tridecyl adipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutene and poly-alpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60, typically greater than 70, mass % of the composition, and typically have a kinematic viscosity at 100ºC of from 2 to 40, for example for 3 to 15, mm^2s^{-1} and a viscosity index of from 80 to 100, for example from 90 to 95.

Another class of lubricating oils is hydrocracked oils, where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have a kinematic viscosity at 100ºC of from 2 to 40, for example from 3 to 15, mm^2s^{-1} and a viscosity index typically in the range of from 100 to 110, for example from 105 to 108.

The oil may include 'brightstock' which refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at 100ºC of from 28 to 36 mm^2s^{-1} and are typically used in a proportion of less than 40, preferably less than 30, more preferably less than 20, mass %, based on the mass of the composition.

The marine diesel cylinder lubricant composition preferably includes at least 50 wt% of oil of lubricating viscosity, more preferably at least 60 wt% of oil of lubricating viscosity.

Complex/Hybrid Detergent

A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it has acid-neutralising properties and is capable of keeping finely divided solids in suspension. It is based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

The detergent comprises a polar head with a long hydrophobic tail. Large amounts of a metal base are included by reacting an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide to give an overbased detergent which comprises neutralised detergent as the outer layer of a metal base (e.g. carbonate) micelle.

The detergent is a complex/hybrid detergent including at least two surfactants, one of which is a salicylate. The complex detergent preferably includes at least 5 mass% of salicylate, more preferably at least 10 mass% of salicylate. The amount of salicylate in the complex detergent can be determined using techniques such as chromatography, spectroscopy and/or titration, well known to persons skilled in the art. The other surfactant may be a sulphonate, a phenate, a sulphurized phenate, a thiophosphate, a naphthenate, or an oil-soluble carboxylate. The other surfactant is preferably a phenate. The complex detergent preferably includes at least 5 mass% of phenate. The complex detergent may also include at least 5 mass% of sulphonate. The surfactant groups are incorporated during the overbasing process. The metal may be an alkali metal or an alkaline earth metal such as sodium, potassium, lithium, calcium and magnesium. Calcium is preferred.

Examples of complex detergents are described in WO 97/46645 and WO 97/46646.

Preferably, the detergent has a TBN in the range of 250 to 500, more preferably 260 to 450.

<u>Dispersants</u>

The marine diesel cylinder lubricant composition may include at least one dispersant. A dispersant is an additive for a lubricating composition whose primary function in cylinder lubricants is to accelerate neutralization of acids by the detergent system.

A noteworthy class of dispersants are "ashless", meaning a non-metallic organic material that forms substantially no ash on combustion, in contrast to metal-containing, hence ash-forming, materials. Ashless dispersants comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g. an O, P or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed.

Examples of ashless dispersants are succinimides, e.g. polyisobutene succinic anhydride; and polyamine condensation products that may be borated or unborated.

Anti-wear Additive

The marine diesel cylinder lubricant composition may include at least one anti-wear additive. The anti-wear additive may be metallic or non-metallic, preferably the former.

Dihydrocarbyl dithiophosphate metal salts are examples of the anti-wear additives. The metal in the dihydrocarbyl dithiophosphate metal may be an alkali or alkaline earth metal, or aluminium, lead, tin, molybdenum, manganese, nickel or copper. Zinc salts are preferred, preferably in the range of 0.1 to 1.5, preferably 0.5 to 1.3, mass %, based upon the total mass of the lubricating oil composition. They may be prepared in accordance with known techniques by firstly forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 and then neutralizing the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reacting mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared comprising both hydrocarbyl groups that are entirely secondary and hydrocarbyl groups that are entirely primary. To make the zinc salt, any basic or neutral zinc compound may be used but the oxides, hydroxides and carbonates are most generally employed. Commercial additives frequently contain an excess of zinc due to use of an excess of the basic zinc compound in the neutralisation reaction.

The preferred zinc dihydrocarbyl dithiophosphates are oil-soluble salts of dihydrocarbyl dithiophosphoric acids and may be represented by the following formula:

$$[(RO)\,(R^1O)\,P(S)S]_2\,Zn$$

where R and R^1 may be the same or different hydrocarbyl radicals containing from 1 to 18, preferably 2 to 12, carbon atoms and including radicals such as alkyl, alkenyl, aryl, arylalkyl, alkaryl and cycloaliphatic radicals. Particularly preferred as R and R^1 groups are alkyl groups of 2 to 8 carbon atoms. Thus, the radicals may, for example, be ethyl, n-propyl, I-propyl, n-butyl, I-butyl, sec-butyl, amyl, n-hexyl, I-hexyl, n-octyl, decyl, dodecyl, octadecyl, 2-ethylehexyl, phenyl, butylphenyl, cyclohexyl, methylcyclopentyl, propenyl, butenyl. In order to obtain oil-solubility, the total number of carbon atoms (i.e. in R and R^1) in the dithiophoshoric acid will generally be 5 or greater. The zinc dihydrocarbyl dithiophosphate can therefore comprise zinc dialkyl dithiophosphates.

Anti-oxidants

The marine diesel cylinder lubricant composition may include at least one anti-oxidant. The anti-oxidant may be aminic or phenolic. As examples of amines there may be mentioned secondary aromatic amines such as diarylamines, for example diphenylamines wherein each phenyl group is alkyl-substituted with an alkyl group having 4 to 9 carbon atoms. As examples of anti-oxidants there may be mentioned hindered phenols, including mono-phenols and bis-phenols.

Preferably, the anti-oxidant, if present, is provided in the composition in an amount of up to 3 mass %.

Other additives such as pour point depressants, anti-foamants, and/or demulsifiers may be provided, if necessary.

The terms 'oil-soluble' or 'oil-dispersable' as used herein do not necessarily indicate that the compounds or additives are soluble, dissolvable, miscible or capable of being suspended in the oil in all proportions. These do mean, however, that they are, for instance, soluble or stably dispersible in oil to an extent sufficient to exert their intended effect in the environment in which the oil is employed. Moreover, the additional incorporation of other additives may also permit incorporation of higher levels of a particular additive, if desired.

The lubricant compositions of this invention comprise defined individual (i.e. separate) components that may or may not remain the same chemically before and after mixing.

The present invention is illustrated by, but in no way limited to, the following examples.

Examples

A marine diesel cylinder lubricant composition was prepared using a commercial additive package and commercial base oils. The lubricant composition had a total base number of approximately 70 and comprised: an overbased complex calcium detergent having a base number of 410 and including phenate and sulphonate surfactants; a calcium phenate having a base number of 250; a dispersant; and an anti-wear agent. It is noted that this marine diesel cylinder lubricant composition has been approved by marine diesel engine manufacturers because it exhibits good performance in engine field tests. The lubricant was subjected to the Panel Coker Test (details of which are shown below) for piston deposit control testing. The lubricant was then diluted to give a TBN of approximately 40 and also tested using the Panel Coker Test. The test results are shown below in Table 1:

Table 1

	Comparative Example 1	**Comparative Example 2**
Total Base Number	74.1	43.6
Vk 100	18.7	17.0
Panel Coker Test Results		
Merit Rating	4.34	2.28
Deposits (mg)	34.1	50.7

As shown in Table 1, when the marine diesel cylinder lubricant composition is diluted to give a TBN of approximately 40, the merit rating and the amount of deposits produced are worse.

Example 3 and Comparative Example 4 were then prepared (see Table 2 below) and tested using the Panel Coker Test. Example 3 included a complex detergent having a TBN of 350; the complex detergent included salicylate, phenate and sulphonate surfactants. Example 4 included a complex detergent having a TBN of 410; the complex detergent included phenate and sulphonate surfactants. It is noted that the complex detergent used in Comparative Example 4 is the same as the complex detergent used in Comparative Example 1.

Table 2

	Example 3	**Comparative Example 4**
Complex detergent including salicylate, sulphonate and phenate surfactants	7.15	
Complex detergent including sulphonate and phenate surfactants		6.10
Additive Package comprising a 250 overbased calcium phenate, a borated dispersant, ZDDP and Group I diluent base oil	8.60	8.60
Base Oil, APE 2500 available from ExxonMobil	20.00	20.00

Base Oil, APE 600 available from ExxonMobil	64.25	65.30
Vk 100	17.2	16.8
BN	42.9	41.0
Panel Coker Test Results		
Merit Rating	5.06	2.46
Deposits (mg)	28.5	61.6

As shown above in Table 2, Example 3 has a base number of approximately 40 but it still exhibits good results in the Panel Coker Test. Furthermore, the results are better than those produced by Comparative Example 1, which has received approval by the marine diesel engine manufacturers.

Comparative Example 4 shows that if the complex detergent does not include any salicylate, the Panel Coker Test results are poor. Therefore, the complex detergent including phenate and sulphonate as the surfactants is only suitable for use in marine diesel cylinder lubricant compositions having a TBN of at least 70.

The results in Table 2 clearly show that it is possible to formulate a marine diesel cylinder lubricant composition having a base number less than 70 without adversely affecting the amount of deposits produced by the use of a complex detergent including salicylate as one of the surfactants.

<u>The Panel Coker Test</u>

This test involves splashing a lubricating oil composition on to a heated test panel to see if the oil degrades and leaves any deposits that might affect engine performance. The test uses a panel coker tester (model PK-S) supplied by

Yoshida Kagaku Kikai Co, Osaka, Japan. The test starts by heating the lubricating oil composition to a temperature of 100°C through an oil bath. A test panel made of aluminium alloy, which has been cleaned using acetone and heptane and weighed, is placed above the gas engine lubricating oil composition and heated to 320°C using an electric heating element. When both temperatures have stabilised, a splasher splashes the gas engine lubricating oil composition on to the heated test panel in a discontinuous mode: the splasher splashes the oil for 15 seconds and then stops for 45 seconds. The discontinuous splashing takes place over 1 hour, after which the test is stopped, everything is allowed to cool down, and then the aluminium test panel is weighed and rated visually. The difference in weight of the aluminium test panel before and after the test, expressed in mg, is the weight of deposits. The visual rating is made from 0 to 10, with 0 being for a completely black panel and 10 being for a completely clean panel.

This test is used for simulating the ability of a lubricant composition to prevent deposit formation on pistons. Comparative Example 1 has been approved by marine diesel engine manufacturers. Therefore, its performance in this test is considered to be acceptable. A better lubricant composition would produce a higher merit rating and a lower amount of deposits.

<u>High Temperature HFRR Test</u>

The HFRR Test, or High Frequency Reciprocating Rig Test, is a measure of in-use lubricity and the test rig is described in CEC PF 06-T-94 or ISO/TC22/SC7/WG6/N188. In these examples, the friction coefficient is monitored at temperatures up to 350°C. When the friction coefficient reaches a minimum, the temperature is recorded as the temperature of scuffing initiation, i.e. the temperature at which adhesive wear ('scuffing') begins.

This test is used for assessing the ability of a lubricant composition to control adhesive wear in large bore crosshead engines. The result given for Comparative Example 1 is considered to be acceptable by manufacturers of marine diesel engines. A better lubricant composition would produce a higher temperature of scuffing initiation.

Example 3 and Comparative Examples 1 and 2 were tested using the HFRR test. The test results are shown below:

Table 3

	Example 3	**Comparative Example 1**	**Comparative Example 2**
Temperature of Scuffing Initiation (degrees C)	338	270	277

As shown above, Example 3 provides ‘scuff-free’ lubrication up to 338°C, whereas Comparative Examples 1 and 2 only provide ‘scuff-free’ lubrication up to 270°C and 277°C respectively. These results show that marine diesel cylinder lubricant compositions of the present invention having a total base number below 70 can provide lubrication at higher temperatures than commercially available lubricant compositions having total base numbers of at least 70.

Claims

1. A marine diesel cylinder lubricant composition for a marine diesel engine running on fuel having a sulphur content of less than 1.5%, the composition having a total base number, as determined according to ASTM D2896, of more than 30 and less than 70, and comprising:

   - at least 40 wt% of an oil of lubricating viscosity, and
   - at least one detergent prepared from at least two surfactants, one of which is a salicylate.

2. The marine diesel cylinder lubricant composition as claimed in claim 1, wherein the detergent includes at least 5 mass% of salicylate, preferably at least 10 mass% of salicylate.

3. The marine diesel cylinder lubricant composition as claimed in claims 1 or 2, wherein the detergent further includes at least 5 mass% of phenate and optionally at least 5 mass% of sulphonate.

4. The marine diesel cylinder lubricant composition as claimed in any one of the preceding claims, wherein the lubricant has a base number of less than 60, and preferably less than 50; and preferably more than 32, more preferably more than 35.

5. The marine diesel cylinder lubricant composition as claimed in any one of the preceding claims, further including at least one of the following: a dispersant, an anti-wear agent, an anti-oxidant, a pour point depressant, an anti-foamant and a demulsifier.

6. A method of operating a marine diesel engine running on fuel having at most 1.5% sulphur, the method including the step of using the marine diesel

cylinder lubricant composition claimed in any one of claims 1-5 to lubricate the engine.

7. Use of the marine diesel lubricant composition as claimed in any one of claims 1-5 to reduce deposits in a marine diesel cylinder engine running on fuel having at most 1.5% sulphur.

8. Use of the marine diesel cylinder lubricant composition as claimed in any one of claims 1-5 to provide lubricity in a marine diesel engine running on fuel having at most 1.5% sulphur and running at temperatures above 250°C, preferably above 300°C.