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54 **Lubricant method and compositions.**

57 This invention concerns the lubrication of crosshead diesel engines, for example marine slow speed crosshead diesel engines. Lubrication is effected with a lubricant composition comprising a major amount of base oil and minor amounts of an anti-wear additive and of an extreme pressure additive. Good lubrication is achieved between metal surfaces at elevated temperatures and high contact pressures. Preferred compositions of the invention have a synergistic effect and include an anti-wear additive of formula $X=P(OR)$, where X represents an oxygen or a sulfur atom, and each R, which can be the same or different, represents a phenyl, tolyl or xylyl group, a halogenated derivative of such a group, tritolylphosphate, trixylylphosphate or triphenylphosphorothionate, the extreme pressure additive being an organic sulfide.

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LUBRICANT METHOD AND COMPOSITIONS

This invention concerns the lubrication of crosshead diesel engines, for example marine slow speed crosshead diesel engines.

The lubrication of crosshead diesel engines, and in particular the cylinder liners and piston rings of such engines, presents problems since the temperatures and pressures involved during their operation can lead to breakdown of the film of lubricant on the internal walls of the cylinder liners. When this occurs it leads to excessive cylinder liner and/or piston ring wear.

Various additives have been proposed for lubricant compositions for engines for the purpose of reducing engine wear. Anti-wear additives, for example, have been proposed but although they are effective at low temperatures, they tend to become ineffective at the temperatures encountered at the top of the cylinder liners of crosshead diesel engines.

Extreme pressure additives have also been proposed which function as the lubricant film breaks down between metal surfaces when they slide under high pressures. They are in particular proposed for use in gear oils. The disadvantage of using such additives in lubricant compositions for crosshead diesel engines is that under the temperature conditions at the top of the liners of such engines, cylinder liner and piston ring wear can still occur, and indeed it can be enhanced even though lubricant film breakdown does not occur.

According to the present invention there is provided a method of lubricating a crosshead diesel engine, the method comprising lubricating the engine with a lubricant composition comprising a major amount of base oil and minor amounts of an anti-wear additive and of an extreme pressure additive.

The present invention further provides a lubricant composition for lubricating a crosshead diesel engine, the composition comprising a major amount of base oil and minor amounts of an anti-wear additive and of an extreme pressure additive, the anti-wear additive comprising a compound of formula $X=P(OR)_3$, where X represents an oxygen or a sulfur atom, and each R, which can be the same or different, represents a phenyl, tolyl (e.g. 4-tolyl) or xylyl (e.g. 3,5-xylyl) group, a halogenated derivative of such a group, tritolylphosphate, trixylylphosphate or triphenylphosphorothionate, and the extreme pressure additive comprises an organic sulfide.

The present invention has enabled good lubrication to be achieved between metal surfaces at elevated temperatures and high contact pressures when compared with lubricant compositions consisting of a base oil containing either the anti-wear additive or the extreme pressure additive.

In accordance with the invention, particularly good and unexpected lubricant properties at elevated temperatures and pressures can be achieved by the use of an anti-wear additive of formula $X=P(OR)_3$, where X represents an oxygen or a sulfur atom, and each R, which can be the same or different, represents an aryl, alkaryl, alkyl or aralkyl group, or a halogenated derivative of such a group. Each R preferably represents a phenyl, tolyl (e.g. 4-tolyl) or xylyl (e.g. 3,5-xylyl) group, or a halogenated derivative of such a group. The three groups R are conveniently the same. Examples of particular anti-wear additives which can be used with advantage in accordance with the invention are the phosphorothionic acid esters described in British Patent Specification 1018307, and the analogous phosphoric acid esters having an oxygen atom in place of the sulfur atom of these esters. Specific anti-wear additives which can be used include tritolylphosphate, trixylylphosphate and triphenylphosphorothionate.

Other sulfur containing anti-wear additives can also be used, especially those containing zinc, for example zinc dihydrocarbyl dithiophosphates, e.g. primary zinc dialkyl dithiophosphates, secondary alkyl zinc dialkyl dithiophosphates and mixed alkyl-aryl zinc dithiophosphates. Zinc dihydrocarbyl dithiophosphates which can be used in accordance with the invention can be prepared as described in U.S. Patent Specification 4377527.

Preferred extreme pressure additives for use in accordance with the invention are organic sulfides. In order to have extreme pressure properties they will usually contain at least 15% by weight of sulfur. However, the sulfur content of these additives will usually be less than 55% by weight. Particularly preferred extreme pressure additives contain from 35 to 45% by weight of sulfur. The organic portion of the organic sulfides can be derived from one or more olefin, and the olefins can be straight or branched chain, or cyclic. Furthermore, the unsaturation can be terminal or internal. Preferably, the olefins contain up to eight carbon atoms. Particularly preferred extreme pressure additives are derived from olefins containing from 3 to 6 carbon atoms. Especially preferred organic sulfides which can be used as extreme pressure additives in lubricating compositions of the invention are described in British Patent Specification 1308894 and U.S. Patent Specification 4204969.

The amount of extreme pressure additive should be sufficient to provide an extreme pressure effect.

This will usually be provided by the presence of up to 5.0 percent of the additive based on the total weight of the composition. In general, at least 0.05 percent of an extreme pressure additive will need to be present, and compositions of the invention preferably contain from 0.05 to 2.0, more preferably from 0.1 to 1.5, and advantageously from 0.3 to 1.0 percent by weight of an extreme pressure additive based on the total weight of the composition.

The amount of anti-wear additive present is preferably based on the amount of extreme pressure additive present. The weight ratio of anti-wear additive to extreme pressure additive is preferably from 0.1:1 to 10:1, more preferably from 0.2:1 to 5:1, and advantageously about 0.5:1. The relative amounts of these additives is preferably adjusted to provide the compositions with good anti-wear properties under high pressures but without excessive corrosion at elevated temperatures. The amounts of anti-wear and extreme pressure additives present in order to achieve this will often be less than would be expected to provide the compositions with satisfactory low wear at high temperatures based on the known properties of the anti-wear and extreme pressure additives used.

The base oil, which can consist of a mixture of two or more oils, is preferably a hydrocarbon oil, and it can include one or more paraffinic or synthetic oils. In general, it is preferred to use a mixture of oils.

The viscosity index of the base oil should in general be at least 50, and preferably at least 70, although it will not usually be more than 180, and preferably not more than 130. The base oil preferably has a viscosity index of from 95 to 105.

Compositions used in accordance with the present invention will usually contain other additives, for example overbased additives, e.g. naphthenates, sulfonates, phenates, salicylates or carboxylates. It is generally preferred that the total base number (TBN) of the compositions is at least 40, and more preferably from 70 to 100 (as measured by ASTM D2896 in mg of KOH/g of composition). The TBN of the compositions is preferably not more than 150.

The viscosity of the compositions is preferably at least 10, and more preferably at least 15 cSt at 100 °C. However, the viscosity of the base oil will usually be not more than 35, and preferably not more than 30 cSt at 100 °C. Advantageously the viscosity of the oil will be from 17 to 25 cSt at 100 °C.

The lubricant compositions can be prepared by known methods. Thus it is generally convenient first to heat the base oil, usually to a temperature of about 60 °C, then to add any overbased additives with stirring, and finally to add the extreme pressure and anti-wear additives, again with stirring, preferably after allowing the mixture to cool.

As will be appreciated, the compositions can contain various additives used in the lubricant art, for example dispersants, antioxidants and corrosion inhibitors.

The following Examples are given by way of illustration only. All parts represent percentages by weight of the final lubricant compositions, unless stated otherwise.

Example 1

58.96 parts of 500 SN mineral oil (viscosity index 95) and 13.0 parts of mineral oil brightstock (viscosity index 95) were blended and heated to about 60 °C. 12.65 parts of overbased 250 TBN calcium phenate, 12.65 parts of overbased 300 TBN calcium sulfonate and 2.0 parts of polyalkylene succinimide were added to the blend with vigorous stirring. The resultant homogeneous mixture was cooled to about 50 °C, and 0.50 part of sulfurised olefin (containing about 38% of sulfur) and 0.24 part of tritolyl phosphate (TTP) were added with stirring.

The lubricant composition produced (TBN 70.6, viscosity index 97, and viscosity 17.2 cSt at 100 °C) was then tested on a standard IP 239/85 test "Extreme Pressure Properties : Friction and Wear Tests for Lubricants : Four-Ball Machine" modified to operate from ambient to 200 °C, the latter temperature being approximately that at the top of the cylinder liner of a slow speed crosshead diesel engine. The results obtained are shown in the accompanying Table, weld point and initial seizure values being in kg, and scar values in mm.

Example 2

In a similar manner to that described in Example 1, 59.04 parts of 500 SN mineral oil (viscosity index 95) and 13.0 parts of mineral oil brightstock (viscosity index 95) were blended and heated to about 60 °C. 12.65 parts of overbased 250 TBN calcium phenate, 12.65 parts of overbased 300 TBN calcium sulfonate and 2.0 parts of polyalkylene succinimide were added to the blend with vigorous stirring. The resultant

homogeneous mixture was cooled to about 50° C and 0.45 part of the sulfurised olefin and 0.21 part of triphenylphosphorothionate were added with stirring.

The lubricant composition produced (TBN 70.3, viscosity index 98, and viscosity 17.1 cSt at 100° C) was then tested as in Example 1, the results being shown in the accompanying Table.

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Example 3

A composition similar to that produced in Example 1 was prepared using 0.55 parts of tritolyl phosphate and 0.5 part of the sulfurised olefin, the amount of mineral oil being adjusted accordingly.

The composition was tested as in Example 1, and the results are shown in the accompanying Table.

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Example 4

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A composition similar to that of Example 1 was prepared using 0.25 part of trixylyl phosphate in place of the tritolyl phosphate, the amount of mineral oil being adjusted accordingly. The composition was tested as in Example 1, and the results are given in the accompanying Table.

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Examples 5-9

A variety of lubricant compositions was prepared using the method of Example 1 but with the amounts and types of extreme pressure and anti-wear additives shown in the accompanying Table, the amount of mineral oil being adjusted accordingly. The results of the tests carried out as described in Example 1 are also given in the Table.

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Note

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In the Table, the following apply:-

Sulfide A - Sulfurised olefin containing about 38% sulfur

Sulfide B - Organic sulfide containing about 42% of sulfur

TTP - Tritolylphosphate

35 TPPT - Triphenylphosphorothionate

TXP - Trixylylphosphate

ZDDP1 - Mixed primary zinc dialkyl dithiophosphate

ZDDP2 - Secondary alkyl zinc dialkyl dithiophosphate

ZDDP3 - Mixed alkyl-aryl zinc dithiophosphate

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TABLE

Example	Extreme pressure/anti-wear additive	Weld point	Initial seizure		1 hour wear at 200 °C
			Load	Scar	(scar)
1	0.50 Sulfide A 0.24 TTP	340	165	1.381	1.010
2	0.45 Sulfide A 0.21 TPPT	370	160	0.756	0.985
3	0.5 Sulfide A 0.55 TTP	370	170	1.641	1.085
4	0.5 Sulfide A 0.24 TXP	350	145	1.055	1.100
5	1.12 Sulfide A 0.53 TTP	460	155	0.691	1.363
6	1.57 Sulfide B 1.0 TTP	630	180	0.613	1.240
7	1.57 Sulfide B 0.9 ZDDP1	450	180	0.712	1.367
8	1.57 Sulfide B 0.9 ZDDP2	530	170	1.058	1.576
9	2.5 Sulfide B 1.57 ZDDP3	460	160	1.322	1.346

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Claims

1. A method of lubricating a crosshead diesel engine, the method comprising lubricating the engine with a lubricant composition comprising a major amount of base oil and minor amounts of an anti-wear additive and of an extreme pressure additive.

2. A method according to claim 1, wherein the anti-wear additive is a compound of formula $X=P(OR)_3$, where X represents an oxygen or a sulfur atom, and each R, which can be the same or different, represents an aryl, alkaryl, alkyl or aralkyl group, or a halogenated derivative of such a group.

3. A method according to claim 2, wherein each R represents a phenyl, tolyl (e.g. 4-tolyl) or xylyl (e.g. 3,5-xylyl) group, or a halogenated derivative of such a group.

4. A method according to claim 2 or claim 3, wherein each R has the same meaning.

5. A method according to any of the preceding claims, wherein the anti-wear additive is tritolylphosphate, trixylylphosphate or triphenylphosphorothionate.

6. A method according to any of the preceding claims, wherein the extreme pressure additive comprises an organic sulfide.

7. A method according to claim 6, wherein the organic sulfide contains from 25 to 55 percent by weight of sulfur.

8. A method according to any of the preceding claims, the composition containing up to 5.0 percent of an extreme pressure additive.

9. A method according to claim 8, wherein the composition contains from 0.05 to 2.0 percent of an extreme pressure additive.

10. A method according to claim 9, the weight ratio of anti-wear additive to extreme pressure additive being from 0.2:1 to 10:1.

11. A method according to any of the preceding claims, wherein the composition has a viscosity of from 10 to 35 cSt at 100 °C.

12. A method according to any of the preceding claims, wherein the viscosity index of the base oil is from 50 to 130.

13. A method according to any of the preceding claims, wherein the composition contains an overbased

additive.

14. A method according to any of the preceding claims, wherein the composition has a total base number (as measured by ASTM D2896 in mg of KOH/g of composition) of from 40 to 150.

15. A lubricant composition for lubricating a crosshead diesel engine, the composition comprising a major amount of base oil and minor amounts of an anti-wear additive and of an extreme pressure additive, the anti-wear additive comprising a compound of formula $X=P(OR)_3$, where X represents an oxygen or a sulfur atom, and each R, which can be the same or different, represents a phenyl, tolyl (e.g. 4-tolyl) or xylyl (e.g. 3,5-xylyl) group, a halogenated derivative of such a group, tritolylphosphate, trixylylphosphate or triphenylphosphorothionate, and the extreme pressure additive comprises an organic sulfide.

16. A composition according to claim 15, the composition being as defined in any of claims 4 and 7 to 14 as dependant from claims 1, 2, 5 and 6.

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EP 89 31 1907

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 899 432 (K. ROTHERT) * Claims 1-6 * ---	1,2,4,6 -14	C 10 M 141/10 C 10 M 163/00 //
X	US-A-4 431 552 (C.G. SALENTINE) * Claims 1-7; column 2, lines 15-61; column 3, line 36 - column 4, line 8 * ---	1-12,15 ,16	(C 10 M 141/10 C 10 M 135:04 C 10 M 137:04 C 10 M 137:10)
X	EP-A-0 239 088 (TRIBOL LUBRICANTS) * Claims 1-11; page 2, line 34 - page 3, line 5 * ---	1-16	(C 10 M 163/00 C 10 M 135:04 C 10 M 137:04 C 10 M 137:10)
X	US-A-4 137 187 (W. LOWE) * Claims 1-11; column 2, line 41 - column 3, line 5 * ---	1-12,15 ,16	C 10 M 159:24) C 10 N 30:06 C 10 N 40:25
X	US-A-3 254 027 (H.J. MATSON) * Column 1, lines 29-36; column 2, lines 3-12,38-60; column 3, lines 27-75 * ---	1-12,15 ,16	
X	GB-A- 749 678 (ESSO) * Claims 1-8 * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	EP-A-0 267 875 (CIBA-GEIGY) * Claims 1,8; page 5, lines 42-62 * -----	1	C 10 M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-02-1990	Examiner RO TSAERT L.D.C.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	