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(54) **USE OF DETERGENT FOR INTERNAL COMPUSTION ENGINE OIL COMPOSITIONS**

(57) Oxyalkylated sulfurized alkylphenol detergent additives are used in an internal combustion engine lubricant to provide control of and/or improvement of wear performance of the lubricant.

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Description**FIELD OF THE INVENTION**

[0001] This invention relates to the lubrication of internal combustion engines.

BACKGROUND OF THE INVENTION

[0002] EP-A-2 682 451 ("451") describes overbased sulphurised calcium phenate detergent additives having oxyalkylated phenolic functional groups from unreacted alkylphenol starting material and lubricating compositions (including MDCL's) comprising the same. See Abstract and paragraph 0046. These are stated to be for a range of internal combustion engines (spark-ignited or compression-ignited) such as motor vehicle engines and marine engines. The latter include two-stroke marine diesel engines and marine trunk piston engines. There is, however, no mention of the additives having antiwear properties; in fact, "451" refers to antiwear functionality being provided by different additives. See paragraph 0045.

SUMMARY OF THE INVENTION

[0003] It is now found that the use of additives exemplified by oxyalkylated sulfurized alkylphenol detergents in internal combustion engine lubricants provide valuable antiwear properties.

[0004] Thus, the present invention provides in one aspect the use of an oxyalkylated sulfurized alkylphenol detergent additive in an internal combustion engine lubricant for providing control of and/or improvement of the wear performance of the lubricant, such as when lubricating the engine cylinder of a marine diesel two-stroke cross-head engine.

[0005] In a second aspect the invention provides a method of operating an internal combustion engine comprising supplying to the engine, in operation of the engine, an internal combustion lubricant comprising an oxyalkylated sulfurized alkylphenol detergent additive wherein the detergent additive provides control of and/or improvement in the engine's wear performance.

[0006] In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

"active ingredients" or "(a.i.)" refers to additive material that is not diluent or solvent;

"comprising" or any cognate word specifies the presence of stated features, steps, or integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof; the expressions "consists of" or "consists essentially of" or cognates may be embraced within "comprises" or cognates, wherein "consists essentially of" permits inclusion of substances not materially affecting the characteristics of the composition to which it applies;

"Hydrocarbyl" means a substituent or group (such as an alkyl group) having a carbon atom directly attached to the remainder of a molecule and a predominantly hydrocarbon character. Hetero atoms may be present provided they do not alter the essentially hydrocarbon nature of the group.

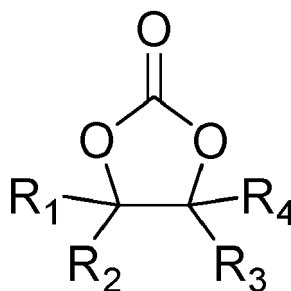
"major amount" means 40 or 50 mass % or more of a composition, preferably 60 mass % or more, even more preferably 70 mass % or more;

"minor amount" means less than 50 mass % of a composition, preferably less than 40 mass %, even more preferably less than 30 mass %;

"TBN" means total base number as measured by ASTM D2896.

"Oxyalkylation" or any cognate word means the addition of an oxyalkyl group of the general formula $-(R'O)_n-$ to a nucleophilic compound.

"Alkylene carbonate" means a compound that has the general structure:



where R₁, R₂, R₃ and R₄ are independently hydrogen or a hydrocarbyl group.

[0007] Furthermore in this specification, if and when used:

"calcium content" is as measured by ASTM 4951;

"phosphorus content" is as measured by ASTM D5185;

"sulphated ash content" is as measured by ASTM D874;

"sulphur content" is as measured by ASTM D2622;

"KV100" means kinematic viscosity at 100°C as measured by ASTM D445.

[0008] Also, it will be understood that various components used, essential as well as optimal and customary, may react under conditions of formulation, storage or use and that the invention also provides the product obtainable or obtained as a result of any such reaction.

[0009] Further, it is understood that any upper and lower quantity, range and ratio limits set forth herein may be independently combined.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The features of the invention will now be discussed in more detail below.

OIL OF LUBRICATING VISCOSITY

[0011] The lubricant composition contains a major amount of an oil of lubricating viscosity. Such lubricating oils may range in viscosity from light distillate mineral oils to heavy lubricating oils. Generally, the viscosity of the oil ranges from 2 to 40, such as 3 to 15, mm²/sec, as measured at 100°C, and has a viscosity index of 80 to 100, such as 90 to 95. The lubricating oil may comprise a major amount of the composition as defined above.

[0012] Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil); liquid petroleum oils and hydrorefined, solvent-treated or acid-treated mineral oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale also serve as useful base oils.

[0013] Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymerized olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes)); alkybenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols); and alkylated diphenyl ethers and alkylated diphenyl sulphides and derivatives, analogues and homologues thereof.

[0014] Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc., constitute another class of known synthetic lubricating oils. These are exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and the alkyl and aryl ethers of polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having a molecular weight of 1000 or diphenyl ether of polyethylene glycol having a molecular weight of 1000 to 1500); and mono- and polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ oxo acid diester of tetraethylene glycol.

[0015] Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric

acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol). Specific examples of such esters includes dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

[0016] Esters useful as synthetic oils also include those made from C₅ to C₁₂ monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

[0017] Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy- or polyaryloxysilicone oils and silicate oils comprise another useful class of synthetic lubricants; such oils include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl)silicate, tetra-(4-methyl-2-ethylhexyl)silicate, tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-ethylhexyl)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

[0018] Unrefined, refined and re-refined oils can be used in lubricants of the present invention. Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations; petroleum oil obtained directly from distillation; or ester oil obtained directly from esterification and used without further treatment are unrefined oils.

[0019] The American Petroleum Institute (API) publication "Engine Oil Licensing and Certification System", Industry Services Department, Fourteenth Edition, December 1996, Addendum 1, December 1998 categorizes base stocks as follows:

a) Group I base stocks contain less than 90 percent saturates and/or greater than 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

b) Group II base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in Table E-1.

c) Group III base stocks contain greater than or equal to 90 percent saturates and less than or equal to 0.03 percent sulphur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1.

d) Group IV base stocks are polyalphaolefins (PAO).

e) Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[0020] Analytical Methods for Base Stock are tabulated below:

Table E-1

PROPERTY	TEST METHOD
Saturates	ASTM D 2007
Viscosity Index	ASTM D 2270
Sulphur	ASTM D 2622
	ASTM D 4294
	ASTM D 4927
	ASTM D 3120

[0021] The present invention preferably embraces Group I or Group II base stocks or oils. Preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more of said basestocks. It may contain 60, such as 70, 80 or 90, mass % or more of said basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all of said basestock or a mixture thereof. The invention is not however limited to use of the above-mentioned base stocks; thus it may, for example, include use of Group III, IV or V basestocks and of bright stock. They also include basestocks derived from hydrocarbons synthesised by the Fischer-Tropsch process. In the Fischer-Tropsch process, synthesis gas containing carbon monoxide and hydrogen (or 'syngas') is first generated and then converted to hydrocarbons using a Fischer-

Tropsch catalyst. These hydrocarbons typically require further processing in order to be useful as a base oil. For example, they may, by methods known in the art, be hydroisomerized; hydrocracked and hydroisomerized; dewaxed; or hydroisomerized and dewaxed. The syngas may, for example, be made from gas such as natural gas or other gaseous hydrocarbons by steam reforming, when the basestock may be referred to as gas-to-liquid ("GTL") base oil; or from gasification of biomass, when the basestock may be referred to as biomass-to-liquid ("BTL" or "BMTL") base oil; or from gasification of coal, when the basestock may be referred to as coal-to-liquid ("CTL") base oil.

[0022] Preferably, the oil of lubricating viscosity in this invention contains 50 mass % or more of said basestocks. It may contain 60, such as 70, 80 or 90, mass % or more of said basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all of said basestock or a mixture thereof.

DETERGENT ADDITIVE

[0023] A detergent is an additive that is based on compounds comprising a polar moiety and a hydrophobic tail, sometimes referred to as surfactants. If the polar moiety of the surfactant is acidic then it can optionally be neutralised in the presence of a metal base to form detergents comprising metal salts.

[0024] Large amounts of a metal base are optionally 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 surfactant as the outer layer of a metal base (e.g. carbonate) micelle. In this invention, the detergent may be a surfactant, partially neutralised surfactant, fully neutralised surfactant or overbased neutralised surfactant.

[0025] If neutralised, the detergent is preferably an alkali metal or alkaline earth metal additive such as a neutral or overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a phenol, wherein any overbasing is provided by an oil-insoluble salt of the metal, e.g. carbonate, basic carbonate, acetate, formate, hydroxide or oxalate, which is stabilized in an oleaginous diluent by the oil-soluble salt of the surfactant. Preferably the metal is calcium.

[0026] The TBN of the detergent may be low, i.e. less than 50 mg KOH/g, medium, i.e. 50 to 150 mg KOH/g, or high, i.e. over 150 mg KOH/g, on an active ingredients basis as determined by ASTM D2896.

[0027] In this invention, the sulfurised alkylphenol detergent additive may have been oxyalkylated by reaction with 10 to 50, such as 15 to 40 or 20 to 30, % by mass of an alkylene carbonate relative to the detergent additive on an active ingredients basis.

[0028] When the lubricant is a marine diesel cylinder lubricant, the TBN of the lubricant is preferably in the range of 5 to 160, and the total detergent concentration in the additive package is preferably from greater than 50 up to 99, such as 60 to 98 or 70 to 95, as a percentage by mass of the total active ingredient.

[0029] The lubricant may further comprise an overbased sulfonate (preferably calcium) detergent, for example having a TBN in the range of 250 to 800 on an active ingredients basis and, for example, in a concentration of 20 to 95, such as 30 to 90 or 40 to 85, % as a percentage by mass of the total active ingredient.

[0030] The lubricant may further comprise a non-sulfurized oxyalkylated alkylphenol such as in a concentration of 0.01 to 10% as a percentage by mass of the total active ingredient.

[0031] The lubricant may further comprise a borated or non-borated dispersant additive, such as a polyalkenyl succinimide.

ENGINES

[0032] The invention is applicable to lubricants for a range of internal combustion engines (spark-ignited or compression-ignited) such as motor vehicle engines and marine engines. Of the latter, there may be mentioned two-stroke marine diesel cross-head engines and marine trunk piston engines.

[0033] Cross-head engines are slow engines with a high to very high power range. They include two separately-lubricated parts: the piston/cylinder assembly lubricated, with total-loss lubrication, by a highly viscous oil (an MDCL); and the crankshaft lubricated by a less viscous lubricant, usually referred to as a system oil. The MDCL lubricates the inner walls of the engine cylinder and the piston ring pack.

[0034] Marine cylinder lubricants are routinely formulated with high base number metal detergents as the main additive constituents to neutralise the acid produced from the high sulfur fuels used in operation of the engines.

[0035] Wear has become more of a problem due to changes in cross-head diesel engine design. Thus, the MDCL needs to withstand varying engine operating temperatures and increased combustion pressure, which may impact on how well the lubricant film is maintained on the cylinder liner walls. This, in consequence, may lead to excessive wear. An additive with antiwear properties and that is compatible with the MDCL environment would be of high value in the lubricant industry.

EXAMPLES

[0036] The invention will now be illustrated in the following non-limiting examples.

Additive Components*Non-Borated Dispersant*

[0037] A dispersant is an additive whose primary function is to hold solid and liquid contaminations in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. For example, a dispersant maintains in suspension oil-insoluble substances that result from oxidation during use of the lubricant, thus preventing sludge flocculation and precipitation or deposition on metal parts of the engine.

[0038] Dispersants are usually "ashless", being non-metallic organic materials that form substantially no ash on combustion. They comprise a long hydrocarbon chain 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 backbone.

[0039] A preferred class of olefin polymers is constituted by polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a C₄ refinery stream.

[0040] Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, examples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants is constituted by hydrocarbon-substituted succinimides, made, for example, by reacting the above acids (or derivatives) with a nitrogen-containing compound, advantageously a polyalkylene polyamine, such as a polyethylene polyamine. Particularly preferred are the reaction products of polyalkylene polyamines with alkenyl succinic anhydrides, such as described in US-A-3,202,678 ; - 3,154,560 ; - 3,172,892 ; - 3,024,195 ; - 3,024,237 , - 3,219,666 ; and - 3,216,936.

Borated Dispersant

[0041] Hydrocarbon-substituted succinimides such as those described above may be post-treated to improve their properties, such as through boration (as described in US-A-3,087,936 and - 3,254,025). For example, boration may be accomplished by treating an acyl nitrogen-containing dispersant with a boron compound selected from boron oxide, boron halides, boron acids and esters of boron acids.

Sulfonate Detergent

[0042] Sulfonate detergents are metal salts and may contain a substantially stoichiometric amount of the metal when they are usually described as normal or neutral salts and would typically have a total base number or TBN (as may be measured by ASTM D2896) of from 0 to 80. Large amounts of a metal base can be included by reaction of an excess of a metal compound, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide. The resulting overbased detergent comprises neutralised detergent as an outer layer of a metal base (e.g. carbonate) micelle. Such overbased sulfonate detergents may have a TBN of 150 or greater, and typically of from 250 to 800 or more on an active ingredient basis.

[0043] Sulfonate detergents that may be used include oil-soluble neutral and overbased sulfonates of a metal, particularly the alkali or alkaline earth metals, e.g. sodium, potassium, lithium, calcium and magnesium. The most commonly-used metals are calcium and magnesium, which may both be present in detergents used in a lubricant.

Sulfonate Detergent A

[0044] Sulfonate Detergent A is an overbased calcium sulfonate detergent. It is characterised by a TBN of 500 - 600 on an active ingredients basis.

Sulfonate Detergent B

[0045] Sulfonate Detergent B is an overbased calcium sulfonate detergent. It is characterised by a TBN of 650 to 750 on an active ingredients basis.

Phenate Detergent A

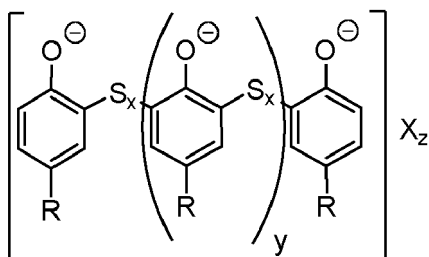
[0046] Phenate Detergent A is an overbased sulfurized calcium phenate detergent derived from tetrapropenylphenol.

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The detergent is synthesised according to well established single stage methods (i.e. sulfuration and overbasing stages are conducted simultaneously as described in EP 2682451 B1). It is characterised by a TBN of 400 to 450 on an active ingredients basis.

Generalised Structure:

[0047]



$x = 1 - 7$, $y = 1 - 10$, $R = C_{12}$ rich branched alkyl, $X = H$ or M , where M is an alkali or alkaline earth metal. $z = y+2$ if $X = H$ or an alkali metal. $z = (y+2)/2$ if $X =$ alkaline earth metal.

Phenate Detergent B

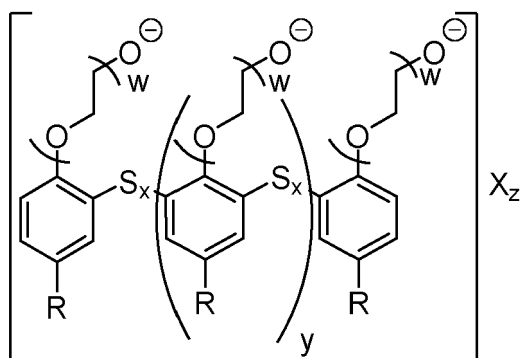
[0048] Phenate Detergent B is an overbased sulfonated calcium phenate detergent derived from tetrapropenylphenol. The detergent is synthesised according to well established two stage methods (i.e. sulfuration and overbasing stages are conducted independently as described in EP 2682451 B1 and US 3,801,507). It has the same generalised structure as Phenate Detergent A. It is characterised by a TBN of 375 to 425 on an active ingredients basis.

Capped Phenate Detergent B

[0049] Capped Phenate Detergent B is derived from Phenate Detergent B described above, which has been subsequently oxyalkylated by reaction with 10 to 50, such as 15 to 40 or 20 to 30, % by mass of an alkylene carbonate relative to the detergent additive on an active ingredients basis. It is characterised by a TBN of 325 to 375 on an active ingredients basis.

Generalised Formula:

[0050]



$w = 0 - 10$, $x = 1 - 7$, $y = 1 - 10$, $R = C_{12}$ rich branched alkyl, $X = H$ or M , where M is an alkali or alkaline earth metal. $z = y+2$ if $X = H$ or an alkali metal. $z = (y+2)/2$ if $X =$ alkaline earth metal.

Wear Inhibitor

[0051] Wear inhibitors reduce friction and excessive wear and are usually based on compounds containing sulfur or

phosphorus or both, for example that are capable of depositing polysulfide films on the surfaces involved. Noteworthy are the dihydrocarbyl dithiophosphates, such as the zinc dialkyl dithiophosphates (ZDDPs). ZDDPs may be prepared in accordance with known techniques by first forming a dihydrocarbyl dithiophosphoric acid (DDPA), usually by reaction of one or more alcohols or a phenol with P_2S_5 , and then neutralising the formed DDPA with a zinc compound. For example, a dithiophosphoric acid may be made by reaction with mixtures of primary and secondary alcohols. Alternatively, multiple dithiophosphoric acids can be prepared where the hydrocarbyl groups on one acid are entirely secondary in character and the hydrocarbyl groups on the other acids are entirely primary in character. To make the zinc salt, any basic or neutral zinc compound could 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.

Formulations

[0052] Two sets of lubricating formulations (sets 1 and 2) were prepared using the above phenate detergent components noting that they did not contain sulfonate detergents.

Formulation Set	1			2		
Formulation	Ref. 1'	Ref. 1''	Ex. 1	Ref. 2'	Ref. 2''	Ex. 2
Phenate Detergent A	2.38	-	-	9.127	-	-
Phenate Detergent B	-	2.29	-	-	8.79	-
Capped Phenate Detergent B	-	-	2.38	-	-	9.127
Oil of Lubricating Viscosity	97.62	97.71	97.62	90.873	91.21	90.873
Lubricant Total	100.00	100.00	100.00	100.00	100.00	100.00

[0053] Two sets of MDCL formulations were prepared by blending various selections of the above components.

Formulation Set	3			4		
Formulation	Ref. 3'	Ref. 3''	Ex. 3	Ref. 4'	Ref. 4''	Ex. 4
Non-Borated Dispersant				1.013	1.013	1.013
Borated Dispersant	3.920	3.920	3.920			
Sulfonate Detergent A	21.000	21.000	21.000			
Sulfonate Detergent B				11.152	11.152	11.152
Phenate Detergent A	2.380			9.127		
Phenate Detergent B		2.290			8.790	
Capped Phenate Detergent B			2.540			9.730
Wear Inhibitor	0.280	0.280	0.280			
Oil of Lubricating Viscosity	0.420	0.420	0.420	0.508	0.508	0.508
Additive Package Total	28.00	27.91	28.16	21.80	21.46	22.40
Oil of Lubricating Viscosity	52.00	52.09	51.84	58.20	58.54	57.60
Oil of Lubricating Viscosity	20.00	20.00	20.00	20.00	20.00	20.00
Lubricant Total	100.00	100.00	100.00	100.00	100.00	100.00

[0054] Each formulation in set 3 contained 3.920g of borated dispersant, 21.000g of Sulfonate Detergent A, and 0.280g of a wear inhibitor. Reference formulation 3' contained 2.380g of Phenate Detergent A and had a package total of 28.00g; reference formulation 3'' contained 2.290g of Phenate Detergent B and had a package total of 27.91g; invention (Inventive example) formulation 3 contained 2.540g of Capped Phenate Detergent B and had a package total of 28.16g.

[0055] Each formulation in set 4 contained 1.013g of non-borated dispersant and 11.152g of Sulfonate Detergent B.

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Reference formulation 4' contained 9.127g of Phenate Detergent A and had a package total of 21.80g; reference formulation 4" contained 8.790g of Phenate Detergent B and had a package total of 21.46g; invention (Inventive example) formulation 4 contained 9.730g of Capped Phenate Detergent B and a package total of 22.40g.

Tests

[0056] Each formulation was tested using the HT-HFRR test. A laboratory rig based on a HT-HFRR (EP2719751 A2) has been developed to evaluate cylinder oils in terms of their ability to prevent breakdown of the lubricating film at elevated temperatures.

[0057] The HT-HFRR rig is run at elevated temperatures and the friction coefficient (Fc) is recorded. The friction coefficient decreases with increasing temperature due to the viscosity decrease of the MDCL, until a temperature at which oil film break-down begins and the friction coefficient (Fc) starts to increase with increasing temperature. By evaluating oils of known field performance in the HT-HFRR rig, it was demonstrated that one of the most critical points to predict oil performance is the temperature at which the lowest friction coefficient (Fc) is recorded.

[0058] The test was performed under the following conditions:

- An electromagnetic vibrator oscillated a steel ball over a small amplitude while pressing it with a load of 4N against a stationary steel disc.
- The lower fixed disc was heated electrically and fixed below the MDCL. The temperature was ramped from 80°C to 380°C over the course of 15 minutes.

Results

[0059] Results are shown in Tables 1 and 2 below, giving respective results for formulation sets 1, 2, 3 and 4. HT-HFRR values are displayed as temperature (°C) at minimum friction, where a higher value indicates superior wear protection performance.

Table 1

Formulation Set	1			2		
Formulation	Ref. 1'	Ref. 1"	Ex. 1	Ref. 2'	Ref. 2"	Ex. 2
Phenate Detergent A	2.380			9.127		
Phenate Detergent B		2.290			8.790	
Capped Phenate Detergent B			2.380			9.127
HT-HFRR	310.0	300.0	340.8	349.4	343.9	368.8

[0060] The results show that in each of sets 1 and 2, in the absence of a sulfonate, wear inhibitor or dispersant, the formulations of the invention gave better results than the respective reference formulations.

Table 2

Formulation Set	3			4		
Formulation	Ref. 3'	Ref. 3"	Ex. 3	Ref. 4'	Ref. 4"	Ex. 4
Phenate Detergent A	2.380			9.127		
Phenate Detergent B		2.290			8.790	
Capped Phenate Detergent B			2.540			9.730
HT-HFRR	324.5	306.4	359.5	265.0	255.1	359.3

[0061] The results show that, in each of sets 3 and 4, the formulations of the invention gave better results than the respective reference formulations.

Claims

1. The use of an oxyalkylated sulfurized alkylphenol detergent additive in an internal combustion engine lubricant to provide control of and/or improvement of the wear performance of the lubricant.
2. The use of claim 1 where the detergent additive has been oxyalkylated by reaction with 10 to 50, such as 15 to 40 or 20 to 30, % by mass of an alkylene carbonate relative to the detergent additive on an active ingredient basis.
3. The use of claim 2 where the alkylene carbonate is ethylene carbonate, propylene carbonate or butylene carbonate.
4. The use of any of claims 1 to 3 where, if neutralised, partially neutralised or overbased, the detergent comprises an alkali or alkaline earth metal, preferably calcium.
5. The use of any of claims 1 to 4 wherein the oxyalkyl groups have the formula



where R' is ethylene, propylene or butylene, and n is independently from 1 to 10.

6. The use of any of claims 1 to 5 where the phenyl groups of the alkylphenol are substituted with one or more hydrocarbyl groups having 9 to 100, preferably 9 to 70 or 9 to 50, carbon atoms.
7. The use of any of claims 1 to 6 where the lubricant is a marine diesel cylinder lubricant.
8. The use of claim 7 where the lubricant lubricates the inner walls and the piston ring pack of the engine cylinder.
9. The use of any of claims 7 and 8 where the TBN of the lubricant is in the range of 5 to 160.
10. The use of any of claims 7 to 9 where the total detergent concentration in the lubricant is from greater than 50 up to 99, such as 60 to 98 or 70 to 95, % as a percentage by mass of the total active ingredient.
11. The use of any of claims 1 to 6 where the lubricant further comprises an overbased sulfonate, preferably calcium, detergent.
12. The use of claim 11 where the sulfonate detergent has a TBN in the range of 250 to 800 on an active ingredient basis.
13. The use of any of claims 7 to 10 where the lubricant further comprises an overbased sulfonate, preferably calcium, detergent having a TBN in the range of 250 to 800 on an active ingredient basis and in a concentration of 20 to 95, such as 30 to 90 or 40 to 85, % as a percentage by mass of the total active ingredient.
14. The use of any of claims 1 to 13 where the lubricant further comprises a non-sulfurised oxyalkylated alkylphenol, such as in a concentration of 0.01 to 10% as a percentage by mass of the total active ingredient.
15. The use of any of claims 1 to 14 where the lubricant further comprises a borated or non-borated dispersant additive, such as a polyalkenyl succinimide.
16. A method of operating an internal combustion engine comprising supplying to the engine, in operation of the engine, an internal combustion engine lubricant comprising an oxyalkylated sulfurized alkylphenol detergent additive wherein the detergent additive provides control of and/or improvement in the engine's wear performance.
17. The method of claim 16 where the engine is a marine diesel two-stroke cross-head engine, lubricant is a marine diesel cylinder lubricant and supply of the lubricant is to the engine cylinder, such as its inner walls and its piston ring pack.



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Application Number
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