

Additive Package for Marine Engine Lubrication

FIELD OF THE INVENTION

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This invention relates to the lubrication of two-stroke and four-stroke marine diesel internal combustion engines, the former usually being referred to as cross-head engines and the latter as trunk piston engines. Respective lubricants for these applications are usually known as marine diesel cylinder lubricants ("MDCL's") and
10 trunk piston engine oils ("TPEO's").

BACKGROUND OF THE INVENTION

Cross-head engines are slow engines with a high to very high power range.
15 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.

Trunk piston engines may be used in marine, power-generation and rail
20 traction applications, and have a higher speed than cross-head engines. A single lubricant (TPEO) is used for crankcase and cylinder lubrication. All major moving parts of the engine, i.e. the main and big end bearings, camshaft and valve gear, are lubricated by means of a pumped circulation system. The cylinder liners are lubricated partially by splash lubrication and partially by oil from the circulation
25 systems that finds its way to the cylinder wall through holes in the piston skirt via the connecting rod and gudgeon pin.

Marine lubricants are routinely formulated with metal detergent additives. A practical problem in use of detergents for this purpose is that certain combinations of
30 salicylate and sulfonate detergents exhibit stability problems evidenced by gel or phase separation.

The aim of this invention is to reduce or overcome such problems.

SUMMARY OF THE INVENTION

It is now found that the use of additives exemplified by methylene-bridged alkylphenols enables the above problem to be overcome.

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Thus, the present invention provides in one aspect an additive package for a two-stroke or four-stroke marine engine lubricating oil composition, comprising: an oil of lubricating viscosity in a minor amount; a major amount of (A) an overbased metal hydroxybenzoate detergent additive and (B) an overbased metal sulfonate detergent additive; and (C) an oil-soluble hydrocarbylphenol-aldehyde condensate additive in an amount in the range of 1 to 10, preferably 3 to 5, mass; wherein the ratio of (A) to (B), expressed as mmol of soap, is in the range of 90:10 to 10:90, preferably 80:20 to 25:75; and wherein the additive package preferably has a TBN of 100 to 450, more preferably 150 to 400, using ASTM D2896.

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In a second aspect, there is provided a two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity, in a major amount, blended with a minor amount of the additive package defined above; wherein the composition, when a two-stroke engine composition, has a TBN of 10 to 120, preferably 40 to 100, using ASTM D2896, and, when a four-stroke engine composition, has a TBN of 25 to 60, using ASTM D2896.

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The additive package is preferably used at a treat rate of 15 to 30 mass % to produce the two-stroke composition, and at a treat rate of 10 to 20 mass % for the four-stroke engine composition.

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The lubricating oil composition preferably includes from 0.15 to 1.5 mass % of the oil-soluble hydrocarbylphenol-aldehyde condensate additive for the two-stroke composition, and from 0.1 to 1 mass % of the oil-soluble hydrocarbylphenol-aldehyde condensate additive for the four-stroke engine.

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In further aspects the present invention comprises:-

the use of 1 to 10 mass% of additive (C) in a marine diesel cylinder lubricant that contains additives (A) and (B), as defined above and in the above ratio, to improve the stability of additives (A) and (B) in the lubricant; and

- 5 a method of lubricating a cross-head marine diesel engine comprising supplying a composition of the above aspect of the invention to the piston/cylinder of the engine during its operation.

10 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;

15 “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;

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“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.

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“major amount” means 40 or even 50 mass % or more of a composition, preferably 60 mass % or more, even more preferably 70 mass % or more, and most preferably 80 mass % or more;

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“minor amount” means less than 50 mass % of a composition, preferably less than 40 mass %, even more preferably less than 30 mass %, most preferably less than 20 mass %, and most preferably less than 10 mass %;

“TBN” means total base number as measured by ASTM D2896.

Furthermore in this specification, if and when used:

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“calcium content” is as measured by ASTM 4951;

“phosphorus content” is as measured by ASTM D5185;

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“sulphated ash content” is as measured by ASTM D874;

“sulphur content” is as measured by ASTM D2622;

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

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.

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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

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

OIL OF LUBRICATING VISCOSITY

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The lubricant composition contains a major proportion 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 greater than 60, typically greater than 70, mass % of the composition.

Natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil);
5 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.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted
10 hydrocarbon oils such as polymerized and interpolymers of 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
15 diphenyl ethers and alkylated diphenyl sulphides and derivatives, analogues and homologues thereof.

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc.,
20 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-polyiso-propylene glycol ether having a molecular weight of 1000 or diphenyl ether of poly-ethylene glycol having a molecular weight of 1000 to 1500); and mono- and
25 polycarboxylic esters thereof, for example, the acetic acid esters, mixed C₃-C₈ fatty acid esters and C₁₃ oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl
30 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
5 two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

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.

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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)
15 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.

20 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
25 unrefined oils.

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:

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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.

Analytical Methods for Base Stock are tabulated below:

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

Table E-1

The present invention preferably embraces those of the above oils containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur as the oil of lubricating viscosity, e.g. Group II, III, IV or V. 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. The invention is not however limited to use of the above-mentioned base stocks; thus it may, for example, include use of Group I basestocks and of bright stock.

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.

ADDITIVES (A) and (B)

Each of these is a detergent, being an additive that reduces formation of 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.

A 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 preferably an alkali metal or alkaline earth metal additive such as an overbased oil-soluble or oil-dispersible calcium, magnesium, sodium or barium salt of a surfactant selected from an acid, wherein the 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. The metal of the oil-soluble surfactant salt may be the same or different from that of the metal of the oil-insoluble salt. Preferably the metal, whether
5 the metal of the oil-soluble or oil-insoluble salt, is calcium.

The TBN of the detergent may be low, i.e. less than 50 mg KOH/g, medium, i.e. 50-150 mg KOH/g, or high, i.e. over 150 mg KOH/g, as determined by ASTM D2896. Preferably the TBN is medium or high, i.e. more than 50 TBN. More
10 preferably, the TBN is at least 60, more preferably at least 100, more preferably at least 150, and up to 500, such as up to 350 mg KOH/g, as determined by ASTM D2896.

In detergent (A), the surfactant is selected from a hydroxybenzoic acid, a
15 particular example being a salicylic acid and wherein the salt is a salicylate. Salicylate detergents are well known in the art.

In detergent (B), the surfactant is selected from a sulfonic acid wherein the salt is a sulfonate. Sulfonate detergents are also well known in the art.

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Detergents that may be used are those that are hydrocarbyl (such as alkyl) substituted, such as those known in the art.

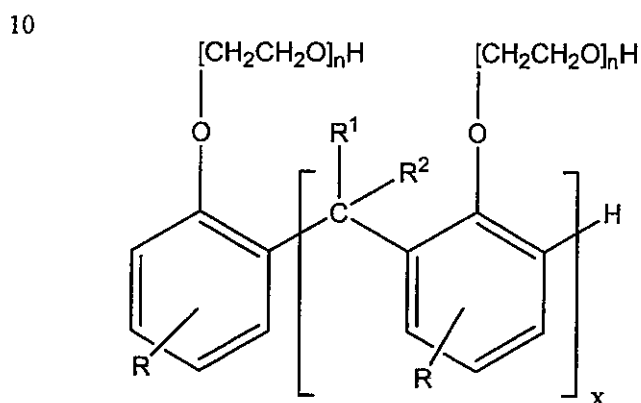
As stated above, the ratio of (A) to (B), expressed as mmol of soap, is in the
25 range of 90:10 to 10:90. As examples of the upper limit of the range there may be mentioned 80:20 and 75:25. As an example of the lower limit of the range these may be mentioned 25:75. Said upper and lower limits may be independently combined to provide sub-ranges.

30 **ADDITIVE (C): e.g. Methylene – Bridged Alkyl Phenols (“MBAP’s”)**

These are known in the art and may comprise an oil-soluble mixture of oxyalkylated hydrocarbylphenol condensates wherein oxyalkyl groups prepared from

phenolic functional groups have the formula $-(R'O)_n$ —where R' is an ethylene, propylene or butylene group; and n is independently from 0 to 10; less than 45, preferably less than 30, mole % of the phenolic functional groups of the condensates are non-oxyalkylated; and more than 55 mole % of the phenolic functional groups of
5 the condensates are mono-oxyalkylated.

Such condensates may be represented by the following general structural formula:



wherein:

x is 1 to 50, preferably 1 to 40, more preferably 1 to 30;

15 R^1 and R^2 are H, hydrocarbyl groups having 1 to 12 carbon atoms, or hydrocarbyl groups having 1 to 12 carbon atoms and at least one heteroatom; and

R is a hydrocarbyl group having 9 to 100, preferably 9 to 70, most preferably, 9 to 50, carbon atoms.

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EP-A-2 374 866 describes such condensates in more detail. MBAP's constitute one embodiment thereof.

As stated above (C) is present in an amount in the range of 1 to 10, preferably
25 3 to 5, mass%. As examples of sub-ranges, there may also be mentioned 1 to 7 and 1 to 5 mass%.

For the avoidance of doubt, it is stated that an MBAP used in this invention may be capped or uncapped.

MARINE LUBRICANTS

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Marine Diesel Cylinder Lubricant ("MDCL")

An MDCL may employ 10-35, preferably 13-30, most preferably 16-24, mass % of a concentrate or additive package, the remainder being base stock. It preferably includes at least 50, more preferably at least 60, even more preferably at least 70, mass % of oil of lubricating viscosity based on the total mass of MDCL. Preferably, the MDCL has a compositional TBN (using ASTM D2896) of 10-100, such as 70-100 or 40-100, preferably 60-90, more preferably 70-80.

15 The following may be mentioned as examples of typical proportions of additives in an MDCL.

Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
20 detergent(s)	1-20	3-15
dispersant(s)	0.5-5	1-3
anti-wear agent(s)	0.1-1.5	0.5-1.3
pour point dispersant	0.03-1.15	0.05-0.1
25 base stock	balance	balance

Trunk Piston Engine Oil ("TPEO")

A TPEO may employ 7-35, preferably 10-28, more preferably 12-24, mass % of a concentrate or additives package, the remainder being base stock. Preferably, the TPEO has a compositional TBN (using D2896) of 25-60, such as 25-55.

The following may be mentioned as typical proportions of additives in a TPEO.

	Additive	Mass% a.i. (Broad)	Mass % a.i. (Preferred)
5	detergent(s)	0.5-12	2-8
	dispersant(s)	0.5-5	1-3
	anti-wear agent(s)	0.1-1.5	0.5-1.3
	oxidation inhibitor	0.2-2	0.5-1.5
	rust inhibitor	0.03-0.15	0.05-0.1
10	pour point dispersant	0.03-1.15	0.05-0.1
	base stock	balance	balance

The terms 'oil-soluble' or 'oil-dispersible' 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.

It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby the additives can be added simultaneously to the oil of lubricating viscosity to form the lubricating oil composition. Dissolution of the additive package(s) into the lubricating oil may be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive package(s) will typically be formulated to contain the additive(s) in proper amounts to provide the desired concentration, and/or to carry out the intended function in the final formulation when the additive package(s) is/are combined with a predetermined amount of base lubricant.

Thus, the additives may be admixed with small amounts of base oil or other compatible solvents together with other desirable additives to form additive packages containing active ingredients in an amount, based on the additive package, of, for example, from 2.5 to 90, preferably from 5 to 75, most preferably from 8 to 60,
5 mass % of additives in the appropriate proportions, the remainder being base oil.

The final formulations may typically contain about 5 to 40 mass % of the additive packages(s), the remainder being base oil.

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EXAMPLES

The present invention is illustrated by, but not limited to, the following
15 examples.

STABILITY TEST METHOD

A calcium salicylate detergent (basicity index 1.35) and a calcium sulfonate
20 detergent (basicity index 22.0) in various proportions were mixed in a single stage, assisted by stirrers and hotplates, at 75°C for 30 minutes with 1% diluent oil. This provided a set of mixes.

Each resulting mix was poured into graduated glass stability tubes and tested
25 over a period of 12 weeks at room temperature and at 60°C.

The stability tubes were visually inspected each week for, as evidence of additive instability, gel formation, phase separation, amount of sediment dropping to the bottom of the tube, and haziness.

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Testing was carried out on mixes that contained methylene-bridged dodecyl phenoxy ethanol (an uncapped "MBAP") and on mixes that did not.

RESULTS

RATIO (mmol/mmol): SALICYLATE/SULFONATE								
MBAP (mass %)	90/10		75/25		50/50		25/75	
0	OK	12	gel/phase sep ⁿ	3	gel	1	gel	>3
	OK	12	gel/phase sep ⁿ	2	gel	1	gel	3
1	OK	12	OK	12	gel	1	gel	>3
	OK	12	gel/phase sep ⁿ	5	gel	1	gel	2
3	OK	12	OK	12	gel/phase sep ⁿ	3	gel	>3
	OK	12	gel/phase sep ⁿ	7	gel/phase sep ⁿ	6	gel	>3
5	OK	12	OK	12	OK	12	OK	12
	OK	12	OK	12	OK	12	OK	12

Key:

OK : no additive stability problems observed

gel/phase sepⁿ : additive instability (gel formation more severe than phase separation)

numbers : number of weeks at which stability performance was observed and reported (first number at room temperature testing; second number at 60°C testing)

10 The above data show that:

1. at a 90/10 ratio, no stability problems were observed, even in the absence of MBAP.
- 15 2. at a 75/25 ratio, problems were observed in the absence of MBAP; the room temperature tests indicated no stability problems at 1, 3 and 5 mass % MBAP; 60°C tests indicated an improvement at 1 and 3 mass % MBAP and no problem at 5 mass % MBAP.
- 20 3. at a 50/50 ratio, problems were observed in the absence of MBAP and at 1 mass % MBAP; 3 mass % MBAP tests gave rise to some

improvement; 5 mass% MBAP tests indicated no stability problems both at room temperature and at 60°C.

- 5
4. at a 25/75 ratio, problems were observed with no MBAP; at 1 and 3 mass % MBAP, the room temperature results being worse than the 60°C results; 5 mass% MBAP tests indicated no stability problems both at room temperature and at 60°C.

CLAIMS

1. An additive package for a two-stroke or four-stroke marine engine lubricating oil composition, comprising less than 50 mass % of an oil of lubricating viscosity; more than 50 mass % of (A) an overbased metal hydroxybenzoate detergent additive and (B) an overbased metal sulfonate detergent additive; and (C) an oil-soluble hydrocarbylphenolaldehyde condensate additive in an amount in the range of 1 to 10, preferably 3 to 6, mass %; wherein the ratio of (A) to (B), expressed as mmol of soap, is in the range of 90:10 to 10:90, preferably 80:20 to 20:80.
2. A two-stroke or four-stroke marine engine lubricating oil composition comprising an oil of lubricating viscosity in a major amount, and blended with a minor amount of the additive package claimed in claim 1; wherein the composition, when a two-stroke engine composition, has a TBN of 10 to 120, preferably 40 to 100, using ASTM D2896; and, when a four-stroke engine composition, has a TBN of 25 to 60, using ASTM D2896.
3. The additive package or composition of claims 1 or 2, where (A) is an overbased calcium salicylate detergent.
4. The additive package or composition of any one of the preceding claims, where (B) is an overbased calcium sulfonate detergent.
5. The additive package or composition of any one of the preceding claims, where (C) is a methylene-bridged alkylphenol, the hydroxyl groups of which are either capped or uncapped.
6. The composition of any one of claims 2 to 5 in the form of a marine diesel cylinder lubricant.
7. The use of 1 to 10 mass% of the additive (C), as defined in claim 1 or claim 5, in an additive package for a marine diesel lubricant that contains

additives (A) and (B), as defined in claim 1 and in the ratio of claim 1, to improve the stability of additives (A) and (B) in the lubricant.

8. A method of lubricating a cross-head marine diesel engine comprising supplying a composition of any of claims 2 to 6 to the piston/cylinder of the engine during its operation.