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(72) Inventors:  
• **Glass, Robert**  
**Abingdon, Oxfordshire OX13 6BB (GB)**  
• **Bishop, Helen**  
**Abingdon, Oxfordshire OX13 6BB (GB)**  
• **Checinska, Agata**  
**Abingdon, Oxfordshire OX13 6BB (GB)**

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(71) Applicant: **Infineum International Limited**  
**Abingdon,**  
**Oxfordshire OX13 6BB (GB)**

(74) Representative: **Lewis, Pauline Therese et al**  
**PO Box 1**  
**Milton Hill**  
**Abingdon**  
**Oxfordshire OX13 6BB (GB)**

(54) **Marine engine lubrication**

(57) Two-stroke cross-head marine compression-ignited engine system lubrication is effected by a composition comprising a major amount of an oil of lubricating viscosity containing at least 50 mass % of a basestock containing greater than or equal to 90 % saturates and less than or equal to 0.03 % sulphur or a mixture thereof, and respective minor amounts of an oil-soluble over-

based metal alkyl salicylate detergent and an oil-soluble polyalkenyl-substituted carboxylic acid anhydride or an oil-soluble alkylated phenol. The presence of the anhydride or the phenol improves asphaltene dispersency in the lubricant.

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**Description****FIELD OF THE INVENTION**

5 **[0001]** This invention relates to system oil lubrication of a two-stroke cross-head marine compression-ignited engine. This invention relates to a system oil for a two-stroke cross-head marine compression-ignited engine.

**BACKGROUND OF THE INVENTION**

10 **[0002]** Two-stroke marine diesel engines are compression-ignition engines in which each piston rod is connected to the crankshaft by a cross-head bearing. They are lubricated by two separate lubricants: cylinder oil and system oil. The cylinder oil is a 'once-through' lubricant that is burnt in the combustion chamber, excess cylinder oil being drained via the cylinder oil duct. The crankcase of the engine is lubricated by the system oil which lubricates the bearings and journals as well as cooling the piston undercrown.

15 **[0003]** Due to the low stress placed upon it, the system oil is not changed. It needs to be able to cope with contamination arising from cylinder drain oil passing through the stuffing box; system oils blended with Group I base oils are able to cope with this contamination. However, higher saturate base oils (such as Group II) have been shown to be detrimental in respect of asphaltene dispersancy, which may deposit on the undercrown of the pistons and on the crankcase. This constitutes a problem in devising system lubricants that are blended with higher saturate base oils.

20 **[0004]** WO 2008/119936 A1 ('936) describes system lubrication and mentions Group I and Group II basestocks for system oils. It also describes use of calcium alkyl salicylate detergents soap in a system oil. It does not, however, exemplify use of Group II basestocks nor does it mention the above problem regarding Group II basestocks.

**SUMMARY OF THE INVENTION**

25 **[0005]** The invention is concerned with ameliorating the above problem by incorporating a polyalkenyl-substituted carboxylic acid anhydride or an alkylated phenol in a salicylate-containing system oil blended with a higher saturates basestock. Use of such anhydrides or phenols is not described in '936. WO 2008/021737 A2 ('737) describes use of such anhydrides in marine lubricants, but does not mention system lubrication. It mentions salicylate detergents but exemplifies only sulphonate/phenate detergents.

30 **[0006]** A first aspect of the invention is a system lubricating oil composition (i.e. a system oil) for a two-stroke cross-head marine compression-ignited engine, the composition having a TBN of less than 18, preferably less than 15, preferably 5 to 9, and comprising, or being made by admixing:

35 (A) an oil of lubricating viscosity, in a major amount, containing 50 mass% or more of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur or a mixture thereof;

(B) an oil-soluble overbased metal alkyl salicylate detergent, in a minor amount; and

40 (C) in a minor amount, an oil-soluble polyalkenyl-substituted carboxylic acid anhydride, the, or at least one, polyalkenyl group being derived from a polyalkene having a number average molecular weight of from 200 to 3,000, or an oil-soluble alkylated phenol, preferably an oil-soluble alkylated phenol derived from cashew nut shell liquid (CNSL).

45 **[0007]** A second aspect of the invention is a method of providing system lubrication to a two-stroke cross-head marine compression-ignited engine, which comprises lubricating the crankcase of the engine with a system lubricating oil composition of the first aspect of the invention.

**[0008]** A third aspect of the invention is a combination of the crankcase of a two-stroke cross-head marine compression-ignited engine and a system lubricating oil composition of the first aspect of the invention.

50 **[0009]** A fourth aspect of the invention is the use of detergent (B) as defined in the first aspect of the invention in combination with a polyalkenyl-substituted carboxylic acid anhydride or alkylated phenol (C) as defined in the first aspect of the invention in respective minor amounts in a system lubricating oil composition for a two-stroke cross-head marine compression-ignited engine, which composition comprises an oil of lubricating viscosity in a major amount and contains 50 mass % or more of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur or a mixture thereof, to improve asphaltene dispersancy during operation of the engine, fueled by a heavy fuel oil, and its system lubrication by the composition, in comparison with analogous operation when the same amount of

55 (B) is used in the absence of (C).

**[0010]** In this specification, the following words and expressions, if and when used, have the meanings ascribed below:

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"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;

"major amount" means 50 mass % or more of a composition;

"minor amount" means less than 50 mass % of a composition;

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

**[0011]** 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;

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

**[0012]** 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.

**[0013]** 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**

**[0014]** The features of the invention will now be discussed in more detail below.

#### **OIL OF LUBRICATING VISCOSITY (A)**

**[0015]** The 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 mm<sup>2</sup>/sec, as measured at 100°C.

**[0016]** 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.

**[0017]** 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 derivative, analogues and homologues thereof.

**[0018]** 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-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 polycarboxylic esters thereof, for example, the acetic acid esters, mixed C<sub>3</sub>-C<sub>8</sub> fatty acid esters and C<sub>13</sub> oxo acid diester of tetraethylene glycol.

**[0019]** 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, alkylnalonic 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.

**[0020]** Esters useful as synthetic oils also include those made from C<sub>5</sub> to C<sub>12</sub> monocarboxylic acids and polyols and polyol esters such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

**[0021]** 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.

**[0022]** 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. Refined oils are similar to unrefined oils except that the oil is further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation, are known to those skilled in the art. Re-refined oils are obtained by processes similar to those used to provide refined oils but begin with oil that has already been used in service. Such re-refined oils are also known as reclaimed or reprocessed oils and are often subjected to additional processing using techniques for removing spent additives and oil breakdown products.

**[0023]** 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.

**[0024]** 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

**[0025]** By way of example, the present invention embraces Group II, Group III and Group IV basestocks and also 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 hydro-

carbons 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.

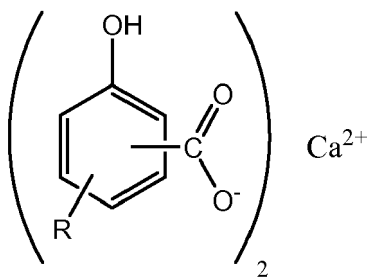
**[0026]** As stated, the oil of lubricating viscosity in this invention contains 50 mass % or more of the defined basestock or a mixture thereof. Preferably, it contains 60, such as 70, 80 or 90, mass % or more of the defined basestock or a mixture thereof. The oil of lubricating viscosity may be substantially all the defined basestock or a mixture thereof. The basestock may for example be a Group II, Group III or Group IV basestock.

#### METAL ALKYL SALICYLATE DETERGENT (B)

**[0027]** A metal detergent is an additive based on so-called metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants. They generally comprise a polar head with a long hydrophobic tail. Overbased metal detergents, which comprise neutralized metal detergents as the outer layer of a metal base (e.g. carbonate) micelle, may be provided by including large amounts of metal base by reacting an excess of a metal base, such as an oxide or hydroxide, with an acidic gas such as carbon dioxide.

**[0028]** In the present invention, (B) is an overbased metal, such as calcium, alkyl-substituted salicylate.

**[0029]** Such a detergent, where the metal is calcium, typically has the structure shown:



wherein R is a linear alkyl group. There may be more than one R group attached to the benzene ring. The COO<sup>-</sup> group can be in the ortho, meta or para position with respect to the hydroxyl group; the ortho position is preferred. The R group can be in the ortho, meta or para position with respect to the hydroxyl group.

**[0030]** Salicylic acids are typically prepared by the carboxylation, by the Kolbe-Schmitt process, of phenoxides, and in that case, will generally be obtained (normally in a diluent) in admixture with uncarboxylated phenol. Salicylic acids may be non-sulphurized or sulphurized, and may be chemically modified and/or contain additional substituents. Processes for sulphurizing an alkyl salicylic acid are well known to those skilled in the art, and are described, for example, in US 2007/0027057.

**[0031]** The alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 24, carbon atoms.

**[0032]** The term "overbased" is generally used to describe metal detergents in which the ratio of the number of equivalents of the metal moiety to the number of equivalents of the acid moiety is greater than one. The term 'low-based' is used to describe metal detergents in which the equivalent ratio of metal moiety to acid moiety is greater than 1, and up to about 2.

**[0033]** By an "overbased calcium salt of surfactants" is meant an overbased detergent in which the metal cations of the oil-insoluble metal salt are essentially calcium cations. Small amounts of other cations may be present in the oil-insoluble metal salt, but typically at least 80, more typically at least 90, for example at least 95, mole %, of the cations in the oil-insoluble metal salt, are calcium ions. Cations other than calcium may be derived, for example, from the use in the manufacture of the overbased detergent of a surfactant salt in which the cation is a metal other than calcium. Preferably, the metal salt of the surfactant is also calcium.

**[0034]** Carbonated overbased metal detergents typically comprise amorphous nanoparticles. Additionally, there are disclosures of nanoparticulate materials comprising carbonate in the crystalline calcite and vaterite forms.

**[0035]** The basicity of the detergents may be expressed as a total base number (TBN). A total base number is the amount of acid needed to neutralize all of the basicity of the overbased material. The TBN may be measured using ASTM standard D2896 or an equivalent procedure. The detergent may have a low TBN (i.e. a TBN of less than 50), a medium TBN (i.e. a TBN of 50 to 150) or a high TBN (i.e. a TBN of greater than 150, such as 150-500). The basicity may also be expressed as basicity index (BI) which is the molar ratio of total base to total soap in the overbased detergent.

**[0036]** The treat rate of additive (B) in the lubricating oil composition may for example be in the range of 0.1 to 10,

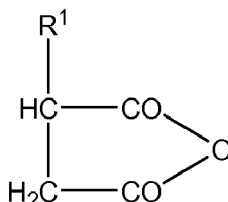
preferably 0.5 to 9, more preferably 1 to 8, even more preferably 1-6, mass %.

### POLYALKENYL-SUBSTITUTED CARBOXYLIC ACID ANHYDRIDE OR ALKYLATED PHENOL (C)

5 **[0037]** The anhydride may be mono or polycarboxylic, preferably dicarboxylic. The polyalkenyl group preferably has from 8 to 400, such as 8 to 100, carbon atoms.

**[0038]** General formulae of exemplary anhydrides may be depicted as

10



15

where R<sup>1</sup> represents a C<sub>8</sub> to C<sub>100</sub> branched or linear polyalkenyl group:

**[0039]** The polyalkenyl moiety may have a number average molecular weight of from 200 to 3000, preferably from 350 to 950.

20 **[0040]** Suitable hydrocarbons or polymers employed in the formation of the anhydrides of the present invention to generate the polyalkenyl moieties include homopolymers, interpolymers or lower molecular weight hydrocarbons. One family of such polymers comprise polymers of ethylene and/or at least one C<sub>3</sub> to C<sub>28</sub> alpha-olefin having the formula H<sub>2</sub>C=CHR<sup>1</sup> wherein R<sup>1</sup> is straight or branched chain alkyl radical comprising 1 to 26 carbon atoms and wherein the polymer contains carbon-to-carbon unsaturation, preferably a high degree of terminal ethenylidene unsaturation. Preferably, such polymers comprise interpolymers of ethylene and at least one alpha-olefin of the above formula, wherein R<sup>1</sup> is alkyl of from 1 to 18 carbon atoms, and more preferably is alkyl of from 1 to 8 carbon atoms, and more preferably still of from 1 to 2 carbon atoms. Therefore, useful alpha-olefin monomers and comonomers include, for example, propylene, butene-1, hexene-1, octene-1, 4-methylpentene-1, decene-1, dodecene-1, tridecene-1, tetradecene-1, pentadecene-1, hexadecene-1, heptadecene-1, octadecene-1, nonadecene-1, and mixtures thereof (e.g., mixtures of propylene and butene-1, and the like). Exemplary of such polymers are propylene homopolymers, butene-1 homopolymers, ethylene-propylene copolymers, ethylene-butene-1 copolymers, propylene-butene copolymers and the like, wherein the polymer contains at least some terminal and/or internal unsaturation. Preferred polymers are unsaturated copolymers of ethylene and propylene and ethylene and butene-1. The interpolymers may contain a minor amount, e.g. 0.5 to 5 mole % of a C<sub>4</sub> to C<sub>18</sub> non-conjugated diolefin comonomer. However, it is preferred that the polymers comprise only alpha-olefin homopolymers, interpolymers of alpha-olefin comonomers and interpolymers of ethylene and alpha-olefin comonomers. The molar ethylene content of the polymers employed is preferably in the range of 0 to 80 %, and more preferably 0 to 60 %. When propylene and/or butene-1 are employed as comonomer(s) with ethylene, the ethylene content of such copolymers is most preferably between 15 and 50 %, although higher or lower ethylene contents may be present.

35 **[0041]** These polymers may be prepared by polymerizing alpha-olefin monomer, or mixtures of alpha-olefin monomers, or mixtures comprising ethylene and at least one C<sub>3</sub> to C<sub>28</sub> alpha-olefin monomer, in the presence of a catalyst system comprising at least one metallocene (e.g., a cyclopentadienyl-transition metal compound) and an alumoxane compound. Using this process, a polymer in which 95 % or more of the polymer chains possess terminal ethenylidene-type unsaturation can be provided. The percentage of polymer chains exhibiting terminal ethenylidene unsaturation may be determined by FTIR spectroscopic analysis, titration, or C<sup>13</sup> NMR. Interpolymers of this latter type may be characterized by the formula POLY-C(R<sup>1</sup>)=CH<sub>2</sub> wherein R<sup>1</sup> is C<sub>1</sub> to C<sub>26</sub> alkyl, preferably C<sub>1</sub> to C<sub>18</sub> alkyl, more preferably C<sub>1</sub> to C<sub>8</sub> alkyl, and most preferably C<sub>1</sub> to C<sub>2</sub> alkyl, (e.g., methyl or ethyl) and wherein POLY represents the polymer chain. The chain length of the R<sup>1</sup> alkyl group will vary depending on the comonomer(s) selected for use in the polymerization. A minor amount of the polymer chains can contain terminal ethenyl, i.e., vinyl, unsaturation, i.e. POLY-CH=CH<sub>2</sub>, and a portion of the polymers can contain internal monounsaturations, e.g. POLY-CH=CH(R<sup>1</sup>), wherein R<sup>1</sup> is as defined above. These terminally unsaturated interpolymers may be prepared by known metallocene chemistry and may also be prepared as described in U.S. Patent Nos. 5,498,809; 5,663,130; 5,705,577; 5,814,715; 6,022,929 and 6,030,930.

45 **[0042]** Another useful class of polymers is polymers prepared by cationic polymerization of isobutene, styrene, and the like. Common polymers from this class include polyisobutenes obtained by polymerization of a C<sub>4</sub> refinery stream having a butene content of about 35 to about 75 mass %, and an isobutene content of about 30 to about 60 mass %, in the presence of a Lewis acid catalyst, such as aluminum trichloride or boron trifluoride. A preferred source of monomer for making poly-n-butenes is petroleum feedstreams such as Raffinate II. These feedstocks are disclosed in the art such as in U.S. Patent No. 4,952,739. Polyisobutylene is a most preferred backbone of the present invention because it is

readily available by cationic polymerization from butene streams (e.g., using  $\text{AlCl}_3$  or  $\text{BF}_3$  catalysts). Such polyisobutylenes generally contain residual unsaturation in amounts of about one ethylenic double bond per polymer chain, positioned along the chain. A preferred embodiment utilizes polyisobutylene prepared from a pure isobutylene stream or a Raffinate I stream to prepare reactive isobutylene polymers with terminal vinylidene olefins. Preferably, these polymers, referred to as highly reactive polyisobutylene (HR-PIB), have a terminal vinylidene content of at least 65%, e.g., 70%, more preferably at least 80%, most preferably, at least 85%. The preparation of such polymers is described, for example, in U.S. Patent No. 4,152,499. HR-PIB is known and HR-PIB is commercially available under the tradenames Glissopal™ (from BASF) and Ultravis™ (from BP-Amoco).

**[0043]** Polyisobutylene polymers that may be employed are generally based on a hydrocarbon chain of from 400 to 3000. Methods for making polyisobutylene are known. Polyisobutylene can be functionalized by halogenation (e.g. chlorination), the thermal "ene" reaction, or by free radical grafting using a catalyst (e.g. peroxide), as described below.

**[0044]** To produce (C) the hydrocarbon or polymer backbone may be functionalized, with carboxylic anhydride-producing moieties selectively at sites of carbon-to-carbon unsaturation on the polymer or hydrocarbon chains, or randomly along chains using any of the three processes mentioned above or combinations thereof, in any sequence.

**[0045]** Processes for reacting polymeric hydrocarbons with unsaturated carboxylic, anhydrides and the preparation of derivatives from such compounds are disclosed in U.S. Patent Nos. 3,087,936; 3,172,892; 3,215,707; 3,231,587; 3,272,746; 3,275,554; 3,381,022; 3,442,808; 3,565,804; 3,912,764; 4,110,349; 4,234,435; 5,777,025; 5,891,953; as well as EP 0 382 450 B1; CA-1,335,895 and GB-A-1,440,219. The polymer or hydrocarbon may be functionalized, with carboxylic acid anhydride moieties by reacting the polymer or hydrocarbon under conditions that result in the addition of functional moieties or agents, i.e., acid, anhydride, onto the polymer or hydrocarbon chains primarily at sites of carbon-to-carbon unsaturation (also referred to as ethylenic or olefinic unsaturation) using the halogen assisted functionalization (e.g. chlorination) process or the thermal "ene" reaction.

**[0046]** Selective functionalization can be accomplished by halogenating, e.g., chlorinating or brominating the unsaturated  $\alpha$ -olefin polymer to about 1 to 8 mass %, preferably 3 to 7 mass % chlorine, or bromine, based on the weight of polymer or hydrocarbon, by passing the chlorine or bromine through the polymer at a temperature of 60 to 250°C, preferably 110 to 160°C, e.g., 120 to 140°C, for about 0.5 to 10, preferably 1 to 7 hours. The halogenated polymer or hydrocarbon (hereinafter backbone) is then reacted with sufficient monounsaturated reactant capable of adding the required number of functional moieties to the backbone, e.g., monounsaturated carboxylic reactant, at 100 to 250°C, usually about 180°C to 235°C, for about 0.5 to 10, e.g., 3 to 8 hours, such that the product obtained will contain the desired number of moles of the monounsaturated carboxylic reactant per mole of the halogenated backbones. Alternatively, the backbone and the monounsaturated carboxylic reactant are mixed and heated while adding chlorine to the hot material.

**[0047]** While chlorination normally helps increase the reactivity of starting olefin polymers with monounsaturated functionalizing reactant, it is not necessary with some of the polymers or hydrocarbons contemplated for use in the present invention, particularly those preferred polymers or hydrocarbons which possess a high terminal bond content and reactivity. Preferably, therefore, the backbone and the monounsaturated functionality reactant, (carboxylic reactant), are contacted at elevated temperature to cause an initial thermal "ene" reaction to take place. Ene reactions are known.

**[0048]** The hydrocarbon or polymer backbone can be functionalized by random attachment of functional moieties along the polymer chains by a variety of methods. For example, the polymer, in solution or in solid form, may be grafted with the monounsaturated carboxylic reactant, as described above, in the presence of a free-radical initiator. When performed in solution, the grafting takes place at an elevated temperature in the range of about 100 to 260°C, preferably 120 to 240°C. Preferably, free-radical initiated grafting would be accomplished in a mineral lubricating oil solution containing, e.g., 1 to 50 mass %, preferably 5 to 30 mass % polymer based on the initial total oil solution.

**[0049]** The free-radical initiators that may be used are peroxides, hydroperoxides, and azo compounds, preferably those that have a boiling point greater than about 100°C and decompose thermally within the grafting temperature range to provide free-radicals. Representative of these free-radical initiators are azobutyronitrile, 2,5-dimethylhex-3-ene-2, 5-bis-tertiary-butyl peroxide and dicumene peroxide. The initiator, when used, typically is used in an amount of between 0.005% and 1% by weight based on the weight of the reaction mixture solution. Typically, the aforesaid monounsaturated carboxylic reactant material and free-radical initiator are used in a weight ratio range of from about 1.0:1 to 30:1, preferably 3:1 to 6:1. The grafting is preferably carried out in an inert atmosphere, such as under nitrogen blanketing. The resulting grafted polymer is characterized by having carboxylic acid (or derivative) moieties randomly attached along the polymer chains: it being understood, of course, that some of the polymer chains remain ungrafted. The free radical grafting described above can be used for the other polymers and hydrocarbons of the present invention.

**[0050]** The preferred monounsaturated reactants that are used to functionalize the backbone comprise mono- and dicarboxylic acid material, i.e., acid, or acid derivative material, including (i) monounsaturated  $\text{C}_4$  to  $\text{C}_{10}$  dicarboxylic acid wherein (a) the carboxyl groups are vicinyl, (i.e., located on adjacent carbon atoms) and (b) at least one, preferably both, of said adjacent carbon atoms are part of said mono unsaturation; (ii) derivatives of (i) such as anhydrides or  $\text{C}_1$  to  $\text{C}_5$  alcohol derived mono- or diesters of (i); (iii) monounsaturated  $\text{C}_3$  to  $\text{C}_{10}$  monocarboxylic acid wherein the carbon-

carbon double bond is conjugated with the carboxy group, i.e., of the structure  $-C=C-CO-$ ; and (iv) derivatives of (iii) such as  $C_1$  to  $C_5$  alcohol derived mono- or diesters of (iii). Mixtures of monounsaturated carboxylic materials (i) - (iv) also may be used. Upon reaction with the backbone, the monounsaturations of the monounsaturated carboxylic reactant becomes saturated. Thus, for example, maleic anhydride becomes backbone-substituted succinic anhydride, and acrylic acid becomes backbone-substituted propionic acid. Exemplary of such monounsaturated carboxylic reactants are fumaric acid, itaconic acid, maleic acid, maleic anhydride, chloromaleic acid, chloromaleic anhydride, acrylic acid, methacrylic acid, crotonic acid, cinnamic acid, and lower alkyl (e.g.,  $C_1$  to  $C_4$  alkyl) acid esters of the foregoing, e.g., methyl maleate, ethyl fumarate, and methyl fumarate.

**[0051]** To provide the required functionality, the monounsaturated carboxylic reactant, preferably maleic anhydride, typically will be used in an amount ranging from about equimolar amount to about 100 mass % excess, preferably 5 to 50 mass % excess, based on the moles of polymer or hydrocarbon. Unreacted excess monounsaturated carboxylic reactant can be removed from the final dispersant product by, for example, stripping, usually under vacuum, if required.

**[0052]** The alkylated phenol may be derived from cashew nut shell liquid (CNSL), such as hydrogenated cardanol which predominantly contains 3-pentadecylphenol.

**[0053]** A characteristic structural feature of the alkyl phenol derived from CNSL is meta hydrocarbyl-substitution of the aromatic ring where the substituent is attached to the ring at its first ( $C_1$ ) carbon atom. This structural feature is not available by chemical alkyl phenol synthesis such as the Friedel-Crafts reaction of phenol with olefins. The latter typically gives mixtures of ortho and para alkyl phenols (but only around 1 % of meta alkyl phenols), and where attachment of the alkyl group to the aromatic ring is at the second ( $C_2$ ) or higher carbon atom.

**[0054]** Cardanol, the product obtained by distilling technical CNSL, typically contains 3-pentadecylphenol (3 %); 3-(8-pentadecenyl) phenol (34-36 %); 3-(8, 11-pentadecadienyl) phenol (21-22 %); and 3-(8, 11, 14-pentadecatrienyl) phenol (40-41 %), plus a small amount of 5-(pentadecyl) resorcinol (c. 10 %), also referred to as cardol. Technical CNSL contains mainly cardanol plus some polymerized material. Cardanol may therefore be expressed as containing significant amounts of meta-linear hydrocarbyl substituted phenol, where the hydrocarbyl group has the formula  $C_{15}H_{25-31}$  and is attached to the aromatic ring at its first carbon atom ( $C_1$ ).

**[0055]** Thus, both cardanol and technical CNSL contain significant quantities of material having long linear unsaturated side chains and only small quantities of material with long linear saturated side chains. The present invention may employ material where a major proportion, preferably all of the phenol, contains material with long linear saturated side chains. Such latter material is obtainable by hydrogenating cardanol; a preferred example is 3-(pentadecyl) phenol, where the pentadecyl group is linear and is attached to the aromatic ring at its first carbon atom. It may constitute 50 or more, 60 or more, 70 or more, 80 or more, or 90 or more, mass % of the additive of the invention. It may contain small quantities of 3-(pentadecyl) resorcinol.

**[0056]** The alkylated phenol may be the product of the Friedel-Crafts alkylation of phenol with a  $C_{14}/C_{16}/C_{18}$  mixture of linear alpha olefins (small levels of other olefins also present, e.g.  $C_{12}$  and  $C_{20}$ ). This produces a product that is highly  $C_2$  attached (alkyl chain attached at 2nd carbon to the aromatic ring), with some  $C_3$  and higher attachment also seen. A mixture of ortho- and para- alkylated species (approximately 70% to 30%) are observed, along with around 10% dialkylated material.

**[0057]** The treat rate of additive (C) in the lubricating oil composition may for example, be 0.1 to 10, preferably 0.5 to 9, more preferably 1 to 8, mass %.

## CO-ADDITIVES

**[0058]** The lubricating oil composition of the invention may comprise further additives, different from and additional to (B) and (C). Such additional additives may, for example include ashless dispersants, other metal detergents, anti-wear agents such as zinc dihydrocarbyl dithiophosphates, anti-oxidants and demulsifiers. In some cases, an ashless dispersant need not be provided.

**[0059]** It may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby additives (B) and (C) can be added simultaneously to the base oil 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, additives (B) and (C), in accordance with the present invention, 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, mass % of additives in the appropriate proportions, the remainder being base oil.



**EXAMPLES**

[0060] The present invention is illustrated by but in no way limited to the following examples.

5 **COMPONENTS**

[0061] The following components were used:

10 Component (A):

(A1): an API Group II 600R basestock from Chevron

(A2): an API Group I basestock

15 Component (B):

(B1): a calcium salicylate detergent having a basicity index of 5.5.

20 Component (C):

(C1) A polyisobutene succinic anhydride ("PIBSA") derived from a polyisobutene of number average molecular weight 950 (72% ai).

25 (C2) Hydrogenated cardenol ("CNSL" phenol)

(C3) Friedel-Crafts alkylated phenol ("SHOP" phenol)

HFO: a heavy fuel oil, ISO-F-RMK380

30 **SYSTEM LUBRICANTS**

[0062] Selections of the above components were blended to give a range of system lubricating oil compositions. Some of the lubricants are examples of the invention and others are reference examples for comparison purposes. The compositions of the lubricants tested are shown in the tables below under the "RESULTS" heading.

35 **TESTING**

**Light Scattering**

40 [0063] Test lubricants were evaluated for asphaltene dispersancy using light scattering according to the Focused Beam Reflectance Method ("FBRM"), which predicts asphaltene agglomeration.

[0064] The FBRM test method was disclosed at the 7th International Symposium on Marine Engineering, Tokyo, 24th - 28th October 2005, and was published in 'The Benefits of Salicylate Detergents in TPEO Applications with a Variety of Base Stocks', in the Conference Proceedings. Further details were disclosed at the CIMAC Congress, Vienna, 21st - 24th May 2007 and published in "Meeting the Challenge of New Base Fluids for the Lubrication of Medium Speed Marine Engines - An Additive Approach" in the Congress Proceedings. In the latter paper it is disclosed that by using the FBRM method it is possible to obtain quantitative results for asphaltene dispersancy that predict performance for lubricant systems based on base stocks containing greater than or less than 90% saturates, and greater than or less than 0.03% sulphur. The predictions of relative performance obtained from FBRM were confirmed by engine tests in marine diesel engines.

[0065] The FBRM probe contains fibre optic cables through which laser light travels to reach the probe tip. At the tip, an optic focuses the laser light to a small spot. The optic is rotated so that the focussed beam scans a circular path between the window of the probe and the sample. As particles flow past the window they intersect the scanning path, giving backscattered light from the individual particles.

55 [0066] The scanning laser beam travels much faster than the particles; this means that the particles are effectively stationary. As the focussed beam reaches one edge of the particle there is an increase in the amount of backscattered light; the amount will decrease when the focussed beam reaches the other edge of the particle.

[0067] The instrument measures the time of the increased backscatter. The time period of backscatter from one particle

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is multiplied by the scan speed and the result is a distance or chord length. A chord length is a straight line between any two points on the edge of a particle. This is represented as a chord length distribution, a graph of numbers of chord lengths (particles) measured as a function of the chord length dimensions in microns. As the measurements are performed in real time the statistics of a distribution can be calculated and tracked. FBRM typically measures tens of thousands of chords per second, resulting in a robust number-by-chord length distribution. The method gives an absolute measure of the particle size distribution of the asphaltene particles.

[0068] The Focused beam Reflectance Probe (FBRM), model Lasentec D600L, was supplied by Mettler Toledo, Leicester, UK. The instrument was used in a configuration to give a particle size resolution of 1  $\mu\text{m}$  to 1mm. Data from FBRM can be presented in several ways. Studies have suggested that the average counts per second can be used as a quantitative determination of asphaltene dispersancy. This value is a function of both the average size and level of agglomerate. In this application, the average count rate (over the entire size range) was monitored using a measurement time of one minute per reading over 30 minutes.

[0069] The test lubricant formulations were heated to 60°C and stirred at 400rpm; when the temperature reached 60°C the FBRM probe was inserted into the sample and measurements made for 30 minutes. An aliquot of heavy fuel oil (10% w/w) was introduced into the lubricant formulation under stirring using a four blade stirrer (at 400 rpm). A value for the average counts per second was taken when the count rate had reached an equilibrium value.

### RESULTS

[0070] The results of the FBRM tests are summarised in the tables below, where lower particle count values indicate better performance.

**TABLE 1**

Three system lubricants contained a zinc-containing dispersant booster with 0.5 % nitrogen and 0.95 % zinc, and 10 % HFO. The lubricants also contained the salicylate detergent (B1) at a treat rate of 3.8%. One lubricant comprised a Group I basestock and no PIBSA; the second lubricant comprised a Group II basestock and no PIBSA; the third lubricant comprised a Group II basestock and PIBSA (C) at a treat rate of 7 %.

<b>GROUP I (A1)</b>	<b>GROUP II (A2)</b>	<b>GROUP II + PIBSA</b>
26, 431	39,032	14,812

[0071] The numbers are particulate counts.

[0072] The results show that, in Group II oil, salicylate gives an inferior performance than its use in Group I oil. However, the right-hand column shows that addition of PIBSA significantly improves the performance of salicylate to the extent that it is better than the Group I salicylate-containing lubricant.

**TABLE 2**

A set of system lubricants, of 5 BN, comprised a Group II basestock (A1) and a salicylate package (B1) at a treat rate of 2%. PIBSA, CNSL phenol and SHOP phenol were either absent or present in different amounts as indicated.

<b>Mass %</b>	<b>PIBSA Particle Count(s)</b>	<b>"CNSL" Particle Counts</b>	<b>"SHOP" Particle Counts</b>
-	7,160	7,160	7,160
2	1,621	5,944	6,241
4	831	1,329	4,757
6	454	28	1,770
8	366	77	317

[0073] The results show that improvement occurs at the lowest treat rate of 2 % and that further improvement is possible at higher treat rates. It should be noted that, at higher treat rates, viscosity may be increased.

### Claims

1. A system lubricating oil composition for a two-stroke cross-head marine compression-ignited engine, the composition having a TBN of less than 18, preferably less than 15, and comprising, or being made by admixing:

(A) an oil of lubricating viscosity, in a major amount, containing 50 mass% or more of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur or a mixture thereof;

(B) an oil-soluble overbased metal, such as calcium, alkyl salicylate detergent, in a minor amount; and  
(C) in a minor amount, an oil-soluble polyalkenyl-substituted carboxylic acid anhydride, the, or at least one,  
polyalkenyl group being derived from a polyalkene having a number average molecular weight of from 200 to  
3,000, or an oil-soluble alkylated phenol, preferably an oil-soluble alkylated phenol derived from cashew nut  
shell liquid (CNSL).

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2. The system lubricating oil composition of claim 1 where the oil of lubricating viscosity contains more than 60 mass  
% of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03% sulphur or a  
mixture thereof.

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3. The system lubricating oil composition of claim 1 or 2 where the basestock is a Group II, Group III or Group IV  
basestock.

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4. The system lubricating oil composition of any of claims 1-3 where (B) is C<sub>9</sub> to C<sub>30</sub> alkyl-substituted.

5. The system lubricating oil composition of any of claims 1-4 where the polyalkenyl substituent in (C) has from 8 to  
400, such as 12 to 100, especially 16 to 64, carbon atoms.

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6. The system lubricating oil composition of any of claims 1-5 where the polyalkenyl substituent in (C) has a number  
average molecular weight of from 350 to 1000, such as from 500 to 1000.

7. The system lubricating oil compositions of any of claims 1-6 where the polyalkenyl-substituted carboxylic acid  
anhydride in (C) is a succinic anhydride.

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8. The system lubricating oil composition of claim 7 where (C) is a polybutene succinic anhydride.

9. The system lubricating oil composition of any of claims 1-4 where (C) is a hydrogenated cardenol.

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10. The system lubricating oil composition of any of claims 1-4 where (C) is a predominantly C2 Friedel-Crafts alkylated  
phenol.

11. The system lubricating oil composition of any one of the preceding claims, wherein the TBN is more than 1, preferably  
more than 3, even more preferably more than 5.

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12. The system lubricating oil composition of any one of the preceding claims, wherein the TBN is less than 10.

13. A method of providing system lubrication to a two-stroke cross-head marine compression-ignited engine, which  
comprises lubricating the crankcase of the engine with a system lubricating oil composition of any of claims 1-12.

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14. A combination of the crankcase of a two-stroke cross-head marine compression-ignited engine and a system lubri-  
cating oil composition of any of claims 1-12.

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15. The use of detergent (B) as defined in claim 1 in combination with a polyalkenyl-substituted carboxylic acid anhydride  
or alkylated phenol (C) as defined in claim 1 in respective minor amounts in a system lubricating oil composition for  
a two-stroke cross-head marine compression-ignited engine, which composition has a TBN of less than 18, preferably  
less than 15, and which composition comprises an oil of lubricating viscosity in a major amount and contains 50  
mass % or more of a basestock containing greater than or equal to 90% saturates and less than or equal to 0.03%  
sulphur or a mixture thereof, to improve asphaltene dispersancy during operation of the engine, fueled by a heavy  
fuel oil, and its system lubrication by the composition, in comparison with analogous operation when the same  
amount of (B) is used in the absence of (C).

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