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(54) **Marine diesel engine lubricating compositions**

(57) A lubricating oil composition for a marine diesel engine comprises a major amount of an oil of lubricating viscosity and minor amounts of

- (a) an oil-soluble ashless dispersant
- (b) an oil-soluble overbased metal detergent whose surfactant system is derived from one or more surfactants, said one surfactant being a salicylate, such as at least two different surfactants; and
- (c1) a first oil-soluble anti-oxidant being sulfur-containing or phenolic or both, and/or
- (c2) an oil-soluble aromatic amine anti-oxidant.

**EP 1 046 698 A1**

**Description**

**[0001]** This invention relates to a lubricating oil composition for marine applications, particularly for use as a marine diesel lubricant for both cross-head engines and trunk piston engines for improving resistance to viscosity increase in use.

**[0002]** The term "marine" does not restrict the engines to those used in water-borne vessels; as is understood in the art, it includes land-based engines of the above types, such as used for power-generation.

**[0003]** Lubricating oils for cross-head engines and trunk piston engines are known and are known to include, as additives to improve their performance, ashless dispersants and overbased detergents. International Patent Application PCT/EP97/0269 describe detergents, the surfactant of which includes a salicylate, for such applications.

**[0004]** However, a problem when using a lubricant that contain such detergents is the tendency of its viscosity to rise with time for reasons that include oxidative degradation. In fact, the viscosity can rise to levels such as to render the lubricant unacceptable to engine manufacturers and therefore unsuitable for its intended purpose. This invention solves the problem by using defined anti-oxidants in the lubricants; it has surprisingly been found that their use can ensure stable lubricant viscosities over a period of time that are acceptable for the intended application-lifetime of the lubricant, during which, steady viscosity growth would normally be expected to occur.

**[0005]** Accordingly, a first aspect of the present invention is a lubricating oil composition for a marine diesel engine comprising a major amount of an oil of lubricating viscosity and, comprising or provided by admixing therewith or added thereto, minor amounts of the following additives:

- (a) an oil-soluble ashless dispersant;
- (b) an oil-soluble overbased metal detergent, the surfactant system of which is derived from one or more surfactants, said one surfactant being a salicylate, such as at least two different surfactants; and;
- (c1) a first oil-soluble anti-oxidant being sulfur-containing or phenolic or both, or
- (c2) an oil-soluble aromatic amine anti-oxidant, or both of (c1) and (c2), the TBN of the composition being at least 10, such as at least 20, and the viscosity index of the composition being at least 90, preferably at least 100, more preferably at least 105.

**[0006]** A second aspect of the present invention is the use of additives (a), (b) and one or both of (c1) and (c2), as defined in the first aspect of the invention, to enhance the resistance to viscosity increase of a lubricating oil composition for a marine diesel engine comprising the additives.

**[0007]** A third aspect of the present invention is a method of lubricating a marine diesel engine, such as a trunk piston engine, which comprises supplying to the engine a lubricating oil composition according to the first aspect of the invention.

**[0008]** "Major amount" means in excess of 50 mass % of the composition.

**[0009]** "Minor amount" means less than 50 mass % of the composition, both in respect of stated additive and in respect of the total mass % of all of the additives present in composition, reckoned as active ingredient of the additive or additives.

**[0010]** "Comprises or comprising" or cognate words is taken to specify the presence of stated features, steps, integers or components, but does not preclude the presence or addition of one or more other features, steps, integers, components or groups thereof.

**[0011]** "TBN" (Total Base Number) is as measured by ASTM D2896, and the viscosity index is as defined by ASTM D2270.

**[0012]** The features of the invention will now be discussed in more detail below.

Marine Diesel Engines

**[0013]** The lubricating oil composition of the present invention may be suitable for use in a 4-stroke trunk piston engine having an engine speed of 100-1,500 rpm, e.g. 300-1,000 rpm, and a brake horse-power (BHP) per cylinder of 50-3,000 preferably 100-2,000. The engine can also be a 2-stroke cross-head engine having a speed of 40-200 rpm, preferably 60-120 rpm and a BHP per cylinder of 500-10,000. Preferably, the engine is a trunk piston engine.

Lubricant Composition

**[0014]** Preferably, the TBN of the lubricant composition is at least 20, for example in the range of from 20 to 100, such as from 30 to 70. Preferably, the viscosity index of the lubricant composition is at least 90, such as at least 95, especially at least 110.

**[0015]** The lubricant composition may, for example, have a kinematic viscosity at 100°C (as measured by ASTM

D445) of at least 10, preferably at least 12, more preferably in the range of from 13 to 30, for example from 13 to 25,  $\text{mm}^2\text{s}^{-1}$ .

#### Lubricating Oil

**[0016]** The oil of lubricating viscosity (sometimes referred to as lubricating oil) may be any oil suitable for the lubrication of a cross-head engine or a trunk piston engine. The lubricating oil may suitably be an animal, a vegetable or a mineral oil. Suitably the lubricating oil is a petroleum-derived lubricating oil, such as a naphthenic base, paraffinic base or mixed base oil. Alternatively, the lubricating oil may be a synthetic lubricating oil. Suitable synthetic lubricating oils include synthetic ester lubricating oils, which oils include diesters such as di-octyl adipate, di-octyl sebacate and tri-decyl adipate, or polymeric hydrocarbon lubricating oils, for example liquid polyisobutene and poly-alpha olefins. Commonly, a mineral oil is employed. The lubricating oil may generally comprise greater than 60, typically greater than 70, mass % of the composition, and typically have a kinematic viscosity at  $100^\circ\text{C}$  of from 2 to 40, for example from 3 to 15,  $\text{mm}^2\text{s}^{-1}$  and a viscosity index of from 80 to 100, for example from 90 to 95.

**[0017]** Another class of lubricating oils is hydrocracked oils, where the refining process further breaks down the middle and heavy distillate fractions in the presence of hydrogen at high temperatures and moderate pressures. Hydrocracked oils typically have kinematic viscosity at  $100^\circ\text{C}$  of from 2 to 40, for example from 3 to 15,  $\text{mm}^2\text{s}^{-1}$  and a viscosity index typically in the range of from 100 to 110, for example from 105 to 108.

**[0018]** The term 'brightstock' as used herein refers to base oils which are solvent-extracted, de-asphalted products from vacuum residuum generally having a kinematic viscosity at  $100^\circ\text{C}$  of from 28 to 36  $\text{mm}^2\text{s}^{-1}$  and are typically used in a proportion of less than 30, preferably less than 20, more preferably less than 15, most preferably less than 10, such as less than 5, mass %, based on the mass of the composition.

#### (a) Ashless Dispersant

**[0019]** A dispersant is an additive for a lubricating composition whose primary function is to hold solid and liquid contaminants in suspension, thereby passivating them and reducing engine deposits at the same time as reducing sludge depositions. Thus, 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.

**[0020]** "Ashless" means that the dispersant is a non-metallic organic material that forms substantially no ash on combustion, in contrast to metal-containing, hence ash-forming, materials. Ashless dispersants comprise a long chain hydrocarbon with a polar head, the polarity being derived from inclusion of, e.g. an O, P or N atom. The hydrocarbon is an oleophilic group that confers oil-solubility, having, for example 40 to 500 carbon atoms. Thus, ashless dispersants may comprise an oil-soluble polymeric hydrocarbon backbone having functional groups that are capable of associating with particles to be dispersed. Typically, the dispersants comprise amine, alcohol, amide, or ester polar moieties attached to the polymer backbone often via a bridging group. The ashless dispersant may be, for example, selected from oil-soluble salts, esters, amino-esters, amides, imides, and oxazolines of long chain hydrocarbon-substituted mono- and dicarboxylic acids or their anhydrides; thiocarboxylate derivatives of long chain hydrocarbons; long chain aliphatic hydrocarbons having a polyamine attached directly thereto, and Mannich condensation products formed by condensing a long chain substituted phenol with formaldehyde and polyalkylene polyamine, such as described in US-A-3,442,808.

**[0021]** The oil-soluble polymeric hydrocarbon backbone is typically an olefin polymer or polyene, especially polymers comprising a major molar amount (i.e., greater than 50 mole %) of a  $\text{C}_2$  to  $\text{C}_{18}$  olefin (e.g., ethylene, propylene, butylene, isobutylene, pentene, octene-1, styrene), and typically a  $\text{C}_2$  to  $\text{C}_5$  olefin. The oil-soluble polymeric hydrocarbon backbone may be a homopolymer (e.g., polypropylene or polyisobutylene) or a copolymer of two or more of such olefins (e.g., copolymers of ethylene and an alpha-olefin such as propylene or butylene, or copolymers of two different alpha-olefins). Other copolymers include those in which a minor molar amount of the copolymer monomers, e.g., 1 to 10 mole %, is an  $\alpha,\omega$ -diene, such as a  $\text{C}_3$  to  $\text{C}_{22}$  non-conjugated diolefin (e.g., a copolymer of isobutylene and butadiene, or a copolymer of ethylene, propylene and 1,4-hexadiene or 5-ethylidene-2-norbornene). Atactic propylene oligomers typically having an  $\bar{M}_n$  of from 700 to 5000 may also be used, as described in EP-A-490454, as well as heteropolymers such as polyepoxides.

**[0022]** A preferred class of olefin polymers is polybutenes, specifically polyisobutenes (PIB) or poly-n-butenes, such as may be prepared by polymerization of a  $\text{C}_4$  refinery stream. Other preferred classes of olefin polymers are ethylene alpha-olefin (EAO) copolymers and alpha-olefin homo- and copolymers having in each case a high degree (e.g., >30%) of terminal vinylidene unsaturation, such as described in WO-94/13709, which may be functionalised and aminated to give dispersants.

**[0023]** Dispersants include, for example, derivatives of long chain hydrocarbon-substituted carboxylic acids, exam-

ples being derivatives of high molecular weight hydrocarbyl-substituted succinic acid. A noteworthy group of dispersants are 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; and BE-A-66,875 that may be post-treated to improve their properties, such as borated (as described in US-A-3,087,936 and -3,254,025), fluorinated and oxydated. 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.

#### (b) Overbased Metal Detergents

**[0024]** A detergent is an additive that reduces formation of piston deposits, for example high-temperature varnish and lacquer deposits, in engines; it normally has acid-neutralising properties and is capable of keeping finely divided solids in suspension. Most detergents are based on metal "soaps", that is metal salts of acidic organic compounds, sometimes referred to as surfactants.

**[0025]** Detergents generally comprise a polar head with a long hydrophobic tail, the polar head comprising a metal salt of an acidic organic compound. 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 overbased detergents of this invention may have a TBN of at least 200, preferably at least 250, especially at least 300, such as up to 600.

**[0026]** Surfactants that may be used, in addition to salicylate, include sulfonates, phenates, sulfurized phenates, thiophosphonates, and naphthenates and other oil-soluble carboxylates. Sulfurized phenates are preferred. The metal may be an alkali or alkaline earth metal, e.g., sodium, potassium, lithium, calcium, and magnesium. Calcium is preferred.

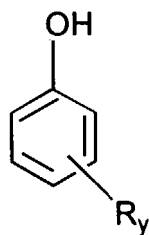
**[0027]** Surfactants for the surfactant system of the overbased metal compounds preferably contain at least one hydrocarbyl group, for example, as a substituent on an aromatic ring. The term "hydrocarbyl" as used herein means that the group concerned is primarily composed of hydrogen and carbon atoms and is bonded to the remainder of the molecule via a carbon atom, but does not exclude the presence of other atoms or groups in a proportion insufficient to detract from the substantially hydrocarbon characteristics of the group. Advantageously, hydrocarbyl groups in surfactants for use in accordance with the invention are aliphatic groups, preferably alkyl or alkylene groups, especially alkyl groups, which may be linear or branched. The total number of carbon atoms in the surfactants should be at least sufficient to impart the desired oil-solubility.

**[0028]** Salicylate surfactants used in accordance with the invention may be non-sulfurized or sulfurized, and may be chemically modified and/or contain additional substituents, for example, as discussed below for phenates. Processes similar to those described below may also be used for sulfurizing a hydrocarbyl-substituted salicylic acid, and are well known to those skilled in the art. 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.

**[0029]** Preferred substituents in oil-soluble salicylic acids from which salicylates in accordance with the invention may be derived are the substituents represented by R in the discussion below of phenols. In alkyl-substituted salicylic acids, the alkyl groups advantageously contain 5 to 100, preferably 9 to 30, especially 14 to 20, carbon atoms.

**[0030]** Phenate surfactants for use in this invention, may be non-sulfurized or, preferably, sulfurized. Further, phenate includes those containing more than one hydroxyl group (for example, from alkyl catechols) or fused aromatic rings (for example, alkyl naphthols) and those which have been modified by chemical reaction, for example, alkylene-bridged and Mannich base-condensed and saligenin-type (produced by the reaction of a phenol and an aldehyde under basic conditions).

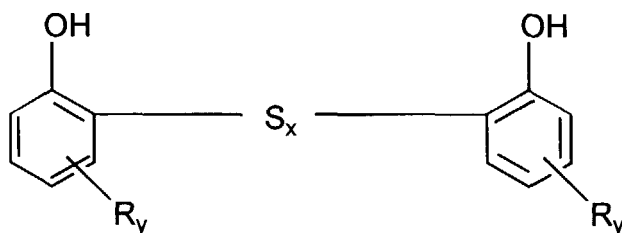
**[0031]** Preferred phenols on which the phenate surfactants are based may be derived from the formula I below:



I

where R represents a hydrocarbyl group and y represents 1 to 4. Where y is greater than 1, the hydrocarbyl groups may be the same or different.

**[0032]** The phenols are frequently used in sulfurized form. Sulfurized hydrocarbyl phenols may typically be represented by the formula II below:



II

where x is generally from 1 to 4. In some cases, more than two phenol molecules may be linked by  $S_x$  bridges.

**[0033]** In the above formulae, hydrocarbyl groups represented by R are advantageously alkyl groups, which advantageously contain 5 to 100, preferably 5 to 40, especially 9 to 12, carbon atoms, the average number of carbon atoms in all of the R groups being at least about 9 in order to ensure adequate solubility in oil. Preferred alkyl groups are nonyl (tripropylene) groups.

**[0034]** In the following discussion, hydrocarbyl-substituted phenols will for convenience be referred to as alkyl phenols.

**[0035]** A sulfurizing agent for use in preparing a sulfurized phenol or phenate may be any compound or element which introduces  $-(S)_x-$  bridging groups between the alkyl phenol monomer groups, wherein x is generally from 1 to about 4. Thus, the reaction may be conducted with elemental sulfur or a halide thereof, for example, sulfur dichloride or, more preferably, sulfur monochloride. If elemental sulfur is used, the sulfurization reaction may be effected by heating the alkyl phenol compound at from 50 to 250, preferably at least 100, °C. The use of elemental sulfur will typically yield a mixture of bridging groups  $-(S)_x-$  as described above. If a sulfur halide is used, the sulfurization reaction may be effected by treating the alkyl phenol at from -10 to 120, preferably at least 60, °C. The reaction may be conducted in the presence of a suitable diluent. The diluent advantageously comprises a substantially inert organic diluent, for example mineral oil or an alkane. In any event, the reaction is conducted for a period of time sufficient to effect substantial reaction. It is generally preferred to employ from 0.1 to 5 moles of the alkyl phenol material per equivalent of sulphurizing agent.

**[0036]** Where elemental sulfur is used as the sulfurizing agent, it may be desirable to use a basic catalyst, for example, sodium hydroxide or an organic amine, preferably a heterocyclic amine (e.g., morpholine).

**[0037]** Details of sulfurization processes are well known to those skilled in the art.

**[0038]** Regardless of the manner in which they are prepared, sulfurized alkyl phenols useful in preparing overbased metal compounds generally comprise diluent and unreacted alkyl phenols and generally contain from 2 to 20, preferably 4 to 14, most preferably 6 to 12, mass % of sulfur, based on the mass of the sulfurized alkyl phenol.

**[0039]** As indicated above, the term "phenol" as used herein includes phenols which have been modified by chemical reaction with, for example, an aldehyde, and Mannich base-condensed phenols.

**[0040]** Aldehydes with which phenols may be modified include, for example, formaldehyde, propionaldehyde and butyraldehyde. The preferred aldehyde is formaldehyde. Aldehyde-modified phenols suitable for use are described in, for example, US-A-5 259 967.

**[0041]** Mannich base-condensed phenols are prepared by the reaction of a phenol, an aldehyde and an amine. Examples of suitable Mannich base-condensed phenols are described in GB-A-2 121 432.

**[0042]** In general, the phenols may include substituents other than those mentioned above provided that such substituents do not detract significantly from the surfactant properties of the phenols. Examples of such substituents are methoxy groups and halogen atoms.

**[0043]** The detergent may, for example, be a complex comprising an overbased mixture of a sulfurised calcium alkyl phenate and a calcium alkyl salicylate, e.g. a hybrid material in which the phenate and salicylate surfactant groups are incorporated during the overbasing process.

**[0044]** Particular examples of hybrid materials include:

i) an overbased calcium detergent comprising a surfactant system derivable, and preferably derived, from at least two surfactants, at least one of which is a phenol or a derivative thereof and the other, or at least one other, of which is a surfactant other than a phenol surfactant, the proportion, measured as described herein, of said phenol in the surfactant system being at least 10 mass % and the overbased detergent having a TBN:% surfactant ratio (as hereinafter defined) of at least 10.

Independently of the TBN:% surfactant ratio, the proportion of phenol in the surfactant system is at least 20 mass %, preferably at least 40 mass %, more preferably at least 45 mass %, such as in the range of from 50 to 90 mass %. Independently of the phenol proportion, the TBN:% surfactant ratio is at least 11, preferably at least 14, more preferably at least 16, advantageously at least 16, especially at least 19, more especially at least 21, for example at least 25, such as up to 30 or more, or up to 40 or more.

ii) an overbased calcium detergent comprising a surfactant system derivable, and preferably derived, from at least two surfactants, at least one of which is a salicylic acid or a derivative thereof, and the other, or at least one other, of which is a surfactant other than a salicylic acid surfactant, the proportion, measured as described herein, of the said salicylic acid in the surfactant system being at least 10 mass %, and the overbased detergent having a TBN:% surfactant ratio (as hereinafter defined) of at least 10.

Independently of the TBN:% surfactant ratio, the proportion of salicylic acid in the surfactant system is at least 20 mass %, preferably at least 30 mass %, more preferably at least 45 mass %, such as in the range of from 50 to 90 mass %. Independently of the salicylic acid proportion, the TBN:% surfactant ratio is at least 11, preferably at least 14, more preferably at least 16, advantageously at least 18, especially at least 19, more especially at least 21, for example at least 25, such as up to 30 or more, or up to 40 or more.

iii) an overbased calcium detergent comprising a surfactant system derivable, and preferably derived, from phenol and sulfonic acid, the proportions, measured as described herein, of phenol to sulfonic acid in the surfactant system being in the range of from 15:85 to 95:15 mass %, preferably 30:70 to 70:30 mass %, especially 40:60 to 60:40 mass %; and the TBN:% surfactant ratio (as hereinafter defined) of at least 15, preferably at least 17, especially 19 or more.

iv) an overbased calcium detergent comprising a surfactant system derivable, and preferably derived, from phenol, salicylic acid and sulfonic acid, the proportions, measured as described herein, of phenol to salicylic acid to sulfonic acid in the surfactant system being in the range of from 5 to 90 mass %: 5 to 90 mass %: 20 to 80 mass %; preferably 20 to 80 mass %: 20 to 80 mass %: 10 to 50 mass %; more preferably 30 to 50 mass %: 25 to 50 mass %: 15 to 35 mass %; and the TBN:% surfactant ratio (as hereinafter defined) of at least 10, preferably at least 12, especially 14 or more.

**[0045]** Preferably, the TBN of the hybrid material is at least 330, such as at least 350, more preferably at least 400, most preferably in the range of from 400 to 600, such as up to 500.

**[0046]** Typically, the amount of overbased metal compound in a lubricant composition is at least 0.5 mass %, based on the active ingredient, particularly in the range of from 0.5 to 20 mass %, based on the mass of the composition, such as from 2 to 12, e.g. 2 to 7, mass %.

**[0047]** The percentage of surfactant in the overbased calcium detergent, and the percentages of the individual surfactants, for example, phenol, in the surfactant system, are the percentages measured by the method set out below.

1. Dialysis of the overbased detergent

**[0048]** A known amount (A g, approximately 20 g) of the liquid overbased calcium detergent compound (substantially free from other lubricating oil additives) is dialysed through a membrane in a Soxhlet extractor (150 mm height x 75 mm internal diameter) using n-hexane siphoning at a rate of 3 to 4 times per hour for 20 hours. The membrane should be one which retains substantially all the metal-containing material, and passes substantially all the remainder of the sample. An example of a suitable membrane is a gum rubber membrane supplied by Carters Products, Division of Carter Wallace Inc., New York, NY 10105 under the trade name Trojans. The dialysate and residue obtained on completion of the dialysis step are evaporated to dryness, any remaining volatile material then being removed in a vacuum oven (100°C at less than 1 torr or less than about 130 Pa). The mass of the dried residue, in grams, is designated B. The percentage (C) of overbased detergent material in the liquid sample is given by the equation:

$$C = \frac{B}{A} \times 100\%$$

**[0049]** Background information for the dialysis technique is given by Amos, R. and Albaugh, E.W. in "Chromatography in Petroleum Analysis", Altgelt, K.H. and Gouw, T.H., Eds, pages 417 to 422, Marcel Dekker, Inc., New York and Basel, 1979.

2. Determination of TBN : % total surfactant ratio

**[0050]** A known amount (D g, approximately 10 g) of the dried residue is hydrolyzed as specified in sections 8.1 to 8.1.2 of ASTM D3712, except that at least 200 ml of 25 % by volume hydrochloric acid (sp. gr. 1.18) is used in section 8.1.1. The amount of hydrochloric acid used should be sufficient to effect acidification/hydrolysis of the overbased detergent residue into organic materials (surfactants) and inorganic materials (calcium-containing materials, for example, calcium chloride). The combined ether extracts are dried by passing them through anhydrous sodium sulphate. The sodium sulphate is rinsed with clean ether, and the combined ether solutions are evaporated to dryness (at approximately 110°C) to yield a hydrolyzed residue. The mass of the dried hydrolyzed residue, in grams, is designated E.

**[0051]** The percentage, Y, of total surfactants in the original liquid overbased detergent is given by the equation

$$Y = \frac{E}{D} \times C$$

and the TBN : % total surfactant ratio, X, is given by the equation

$$X = \frac{\text{TBN of the liquid overbased detergent}}{Y}$$

**[0052]** It will be noted that, in determining X, the mass of the surfactants in their free form (that is, not in the form of a salt or other derivative) is used.

3. Determination of individual surfactants (in their free form) in the surfactant system

**[0053]** The techniques described below isolate the individual surfactants, in hydrolyzed form, from the hydrolyzed surfactant mixture derived from the overbased detergent. As indicated below, the proportion of each individual surfactant is the proportion by mass of the individual surfactant, in hydrolyzed form, in the hydrolyzed surfactant mixture. Thus, where, for example, the overbased detergent contains a calcium phenate/sulphonate/salicylate surfactant system, the proportions of the individual surfactants in the surfactant system are expressed as the proportions of phenol, sulphonic acid and salicylic acid respectively

**[0054]** The proportions of individual surfactants may be determined by the following method.

**[0055]** A known amount (F g, approximately 1 g) of the dried hydrolyzed residue obtained as described above is placed at the top of a 450 x 25 mm (internal diameter) fritted glass column filled with 60-100 US mesh Florisil. Florisil is magnesium silicate with a CAS number of 8014-97-9. The column is eluted with a 250 ml portion of each of seven solvents of increasing polarity, namely, heptane, cyclohexane, toluene, ethyl ether, acetone, methanol, and, lastly, a mixture of 50 volume % chloroform, 44 volume % isopropanol, and 6 volume % ammonia solution (sp. gr. 0.88). Each

fraction is collected, evaporated to dryness, and the resulting residue is weighed and then analyzed to determine the amount ( $G^1$ ,  $G^2$ ,  $G^3$  ... g) and nature of the surfactant(s) contained in the fraction.

**[0056]** Analysis of the fractions (or of the hydrolyzed residue) can be carried out by, for example, chromatographic, spectroscopic, and/or titration (colour indicator or potentiometric) techniques known to those skilled in the art. Where the overbased detergent contains a sulphonate surfactant and a salicylate surfactant, the sulphonic acid and salicylic acid obtained by hydrolysis of these surfactants will usually be eluted from the column together. In this case, and in any other case where it is necessary to determine the proportion of sulphonic acid in a mixture containing it, the proportion of sulphonic acid in the mixture can be determined by the method described by Epton in Trans.Far.Soc. April 1948, 226.

**[0057]** In the above method, the mass (in grams, designated  $H^1$ ) of a given surfactant, in hydrolyzed form, is determined from the fraction(s) containing it, and thus the proportion of that surfactant in the surfactant system of the original overbased detergent is

$$\frac{H^1}{F} \times 100\%$$

**[0058]** The percentages (by mass) of the individual surfactants (in their free form, that is, not in the form of a salt or other derivative) based on the surfactant system can be predicted from the proportions of the surfactants used as starting materials, provided that the percentage of 'reactive ingredient' (r.i.) is known for each of the surfactant starting materials. The percentage of the total surfactants (in their free form) in the liquid overbased product can then be predicted, and the TBN : % surfactant ratio can be determined. As used herein, the term 'reactive ingredient' is the percentage by mass of surfactant that will be associated with the metal calcium.

**[0059]** In another embodiment, the detergent may, for example, comprise a sulphurized and then overbased mixture of a calcium alkyl phenate and a calcium alkyl salicylate: an example is described in EP-A-750,659, namely a detergent-dispersant additive for lubricating oil of the sulfurised and superalkalinised, alkaline earth alkylsalicylate-alkylphenate type, characterised in that:

a) the alkyl substituents of the said alkylsalicylate-alkylphenate are in a proportion of at least 35 wt.% and at most 85 wt.% of linear alkyl in which the number of carbon atoms is between 12 and 40, preferably between 18 and 30 carbon atoms, with a maximum of 65 wt.% of branched alkyl in which the number of carbon atoms is between 9 and 24 and preferably 12 carbon atoms;

b) the proportion of alkylsalicylate in the alkylsalicylate-alkylphenate mixture is at least 22 mole % and preferably at least 25 mole %, and

c) the molar proportion of alkaline earth base with respect to alkylsalicylate-alkylphenate as a whole is between 1.0 and 3.5.

#### (c1) First Anti-oxidant

**[0060]** Examples of sulfur-containing antioxidants (compounds) are alkaline earth metal salts of alkylphenolthioesters having preferably  $C_5$  to  $C_{12}$  alkyl side chains, calcium nonylphenol sulfide, ashless oil-soluble phenates and sulfurized phenates, phosphosulfurized or sulfurized hydrocarbons, phosphorus esters and other sulfur-containing molybdenum-containing compounds. Other examples of sulfur-containing antioxidants are metal salts of dihydrocarbyl dithiophosphate or dihydrocarbyl dithiocarbamate compounds, wherein the metal is selected from Zn, Mn, Ni, Al, Group 1 metals and Group 2 metals. Other sulfur-containing compounds include those described in EP-A-699 759, for example, sulfides of oils, fats or polyolefins, in which a sulfur group having two or more sulfur atoms is joined and bonded together in a molecular structure. Examples include sulfurized sperm oil, sulfurized pinene oil, sulfurized soybean oil, sulfurized polyolefin, sulfurized esters, dialkyl disulfide, dialkyl polysulfide, dibenzyl disulfide, ditertiary butyl disulfide, polyolefine polysulfide, thiadiazole type compound such as bis-alkyl polysulfide thiadiazole, and sulfurized phenol.

**[0061]** Particularly preferred are the sulfurized alkyl phenols described above in connection with the preparation of phenate surfactants, such as represented by formula II.

**[0062]** Phenolic anti-oxidants include those known in the art.

#### (c2) Aromatic Amine Anti-Oxidants

**[0063]** Examples of suitable aromatic amine-containing antioxidants are aromatic amines which have at least one aromatic group directly attached to at least one amine nitrogen atom. Secondary aromatic amines, especially those



having two aromatic groups attached to the same amine nitrogen atom, are preferred, but the use of other aromatic amines is not excluded. The amines may contain one or more aromatic groups, for example at least two aromatic groups. Where two aromatic groups are present, both are preferably bonded directly to the same amine nitrogen. Compounds in which two aromatic groups are linked by a covalent bond or by an atom or group (e.g., an oxygen or sulfur atom, or a -CO-, -SO<sub>2</sub>- or alkylene group) may be used. Aromatic rings, which are preferably hydrocarbon, may be unsubstituted or substituted by one or more substituents selected from alkyl, cycloalkyl, alkoxy, aryloxy, acyl, acylamino, hydroxy, and nitro groups. Amines containing alkyl-substituted aromatic hydrocarbon rings are preferred, especially those containing two alkyl-substituted phenyl groups. Preferred N-aryl amines are naphthylamines and, especially, diphenylamines, including alkyl substituted diphenylamines, wherein the alkyl group may be the same or different and have 1 to 28 carbon atoms. Other nitrogen-containing antioxidants, for example, phenothiazine type compounds, may also be used.

**[0064]** Other known additives may be incorporated into the lubricating oil compositions of the invention provided they are different from the additives defined in the invention. They may, for example, include dispersants; detergents, e.g. single or mixed detergent systems; rust inhibitors; anti-wear agents; anti-oxidants; corrosion inhibitors; friction modifiers or friction reducing agents; pour point depressants; anti-foaming agents; viscosity modifiers; and surfactants.

**[0065]** They can be combined in proportions known in the art.

**[0066]** Typical proportions for additives for a TPEO (a trunk piston engine oil) are as follows:

| Additive                      | Mass % a.i.* (Broad) | Mass % a.i.* (Preferred) |
|-------------------------------|----------------------|--------------------------|
| Detergent(s)                  | 0.5-15               | 2-7                      |
| Dispersant(s)                 | 0.5-5                | 1-3                      |
| Anti-wear agent(s)            | 0.1-1.5              | 0.5-1.3                  |
| Anti-oxidant                  | 0.1-3                | 0.5-1.5                  |
| Rust inhibitor                | 0.03-0.15            | 0.05-0.1                 |
| Pour point depressant         | 0.03-0.15            | 0.05-0.1                 |
| Mineral or synthetic base oil | Balance              | Balance                  |

\* Mass % active ingredient based on the final oil.

**[0067]** Typical proportions for additives for a MDCL (a marine diesel cylinder lubricant) are as follows:

| Additive                      | Mass % a.i.* (Broad) | Mass % a.i.* (Preferred) |
|-------------------------------|----------------------|--------------------------|
| Detergent(s)                  | 1-25                 | 3-12                     |
| Dispersant(s)                 | 0.5-5                | 1-3                      |
| Anti-wear agent(s)            | 0.1-1.5              | 0.5-1.3                  |
| Anti-oxidant                  | 0.1-5                | 0.5-3                    |
| Pour point depressant         | 0.03-0.15            | 0.05-0.1                 |
| Mineral or synthetic base oil | Balance              | Balance                  |

\* Mass % active ingredient based on the final oil.

**[0068]** When a plurality of additives are employed it may be desirable, although not essential, to prepare one or more additive packages or concentrates comprising the additives, whereby several additives 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, components a) and b) 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 % by weight, additives in the appropriate proportions, the remainder being base oil.

**[0069]** The final formulations may typically contain about 5 to 40 mass % of the additive package(s) with the remainder being base oil.

**[0070]** The term 'active ingredient' (a.i.) as used herein refers to the additive material that is not diluent.

**[0071]** 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.

**[0072]** 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.

#### Examples

**[0073]** The present invention is illustrated by but in no way limited to the following examples.

#### Components

**[0074]** The components used in the examples were as follows.

#### Overbased Metal Detergents:

##### **[0075]**

X - an overbased calcium salt of surfactants phenol, sulfonic acid and salicylic acid (phenate/sulfonate/salicylate) prepared as follows.

**[0076]** Toluene (490 g), methanol (330 g), water (30 g) and 150N diluent oil (22 g) were introduced into a reactor and mixed while maintaining the temperature at approximately 20°C. Calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) (150 g) was added, and the mixture was heated to 40°C, with stirring. To the slurry obtained in this way was added a mixture, maintained at 40°C, of phenol surfactant (127 g), sulphonic acid surfactants (98 g), as specified below, and toluene (100 g) followed by a further quantity (50 g) of toluene. A salicylic acid surfactant (172g), also as specified below, was introduced into the mixture.

**[0077]** After neutralization of the surfactants by the calcium hydroxide, the temperature of the mixture was reduced to approximately 28°C and was maintained at approximately 28°C while carbon dioxide (62 g) was injected into the mixture at a rate such that substantially all the carbon dioxide was absorbed in the reaction mixture to form the basic material. The temperature was then raised to 60°C over 60 minutes, following which the mixture was cooled to a temperature of approximately 28°C over 30 minutes. At 28°C, a further quantity of calcium hydroxide (122 g) was added and carbon dioxide (62 g) was charged. After this second carbonation step, the temperature was raised to 60°C over 90 minutes.

**[0078]** Subsequently, the polar solvents were distilled off and the product was filtered to remove sediment. The remaining volatile material was then distilled off and diluent oil (122 g) was added.

**[0079]** The phenol used in the preparation above was a sulphurized alkyl phenol, synthesized from sulphur monochloride and a 65/35 (by mass) blend of tertiary nonyl (tripropylene) phenols (predominantly para-substituted) and tertiary dinonyl phenols (predominantly 2,4-substituted) (a.i. = 84; r.i. = 40); the sulfonic acid used in the preparation above was an alkyl benzene sulfonic acid derived from  $\text{SO}_3$  (in liquid  $\text{SO}_2$ ) with a molecular mass of 683 (a.i. = 96; r.i. = 84); and the salicylic acid used in the preparation was an alkyl salicylic acid (a.i. = 98; r.i. = 70).

#### Dispersant:

##### **[0080]**

P - a polyisobutenyl succinic anhydride - polyamine reaction product.

Anti-oxidants**[0081]**

- 5 Q - a nonyl phenyl sulphide  
R - a nonyl substituted diphenylamine

Other Components10 **[0082]**

S - a zinc dialkyldithiophosphate (ZDDP) made from primary C8 and secondary C4 alcohols

15 T - a zinc dialkyldithiophosphate (ZDDP) made from a primary C8 alcohol.

U - a demulsifier

Lubricant Compositions and Tests

- 20 **[0083]** Lubricant compositions as marine diesel lubricating oils were prepared by admixing with a basestock the component X and components P to U, as identified above. The admixing was carried out by blending at elevated temperature. The composition contained the following proportions by mass %: X 11.4; Q 7.5; R 7.5; P 2.22.

- [0084]** The lubricating composition was tested by periodically sampling and measuring its kinematic viscosity at 100°C according to the method ASTM D445 during use of the composition to lubricate marine diesel engine. Tests were  
25 carried out on two different medium speed trunk piston marine diesel engines.

Results

- [0085]** The results obtained in the tests are shown in Tables 1 and 2 below, where viscosities are expressed in  
30  $\text{mm}^2\text{s}^{-1}$  at 100°C.

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| ENGINE          | Initial Viscosity | Maximum Viscosity | Test Duration (h) | Viscosity Increase (%) |
|-----------------|-------------------|-------------------|-------------------|------------------------|
| Wartsila 8L46   | 13.5              | 14.22             | 4,500             | 5.33                   |
| MAN B+W 7L48/60 | 14.0              | 14.61             | 3,000             | 4.36                   |

- 40 **[0086]** The results show a very low increase in viscosity compared with what might be expected in the above types of engine: the limit set by the engine builders allows for an increase of about 30%.

- [0087]** It should also be noted that, in the practice of this invention, as the detergent, there may be used one where the surfactant system is derived from a 2-hydroxybenzene sulfonic acid or from an alkaryl ethanoic acid, e.g. in the form of their calcium salts, and/or as an anti-oxidant, there may be used a zinc dihydrocarbyl dithiophosphate (ZDDP).

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**Claims**

1. A lubricating oil composition for a marine diesel engine comprising a major amount of an oil of lubricating viscosity and, comprising or provided by admixing therewith or added thereto, minor amounts of the following additives:

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- (a) an oil-soluble ashless dispersant;  
(b) an oil-soluble overbased metal detergent, the surfactant system of which is derived from one or more surfactants, said one surfactant being a salicylate, such as at least two different surfactants; and  
(c1) a first oil-soluble anti-oxidant being sulfur-containing or phenolic or both, or  
55 (c2) an oil-soluble aromatic amine anti-oxidant,

or both of (c1) and (c2),

the TBN of the composition being at least 10, such as at least 20, and the viscosity index of the composition being

at least 90, preferably at least 100, more preferably at least 105.

- 5
2. The composition as claimed in claim 1 wherein the detergent has a TBN of at least 200, preferably at least 250, especially at least 300, such as up to 600.
3. The composition as claimed in claim 1 or claim 2 wherein the detergent is a calcium compound.
4. The composition as claimed in any of the preceding claims wherein at least one of the surfactants is a phenate.
- 10 5. The composition as claimed in claim 4 wherein the detergent is a complex comprising an overbased mixture of a sulfurised calcium alkyl phenate and a calcium alkyl salicylate.
6. The composition as claimed in claim 4 wherein the detergent is a sulphurised and then overbased mixture of a calcium alkyl phenate and a calcium alkyl salicylate.
- 15 7. The composition of any of the preceding claims wherein the sulfur-containing anti-oxidant is an ashless sulfurised alkylphenol.
8. The composition of any of the preceding claims wherein the aromatic amine anti-oxidant is an alkylated secondary amine.
- 20 9. A method of lubricating a marine diesel engine, such as a trunk piston engine, which comprises supplying to the engine a lubricating oil composition as claimed in any of the preceding claims.
- 25 10. The use of additives (a), (b) and one or both of (c1) and (c2), as defined in claim 1, to enhance the resistance to viscosity increase of a lubricating oil composition for a marine diesel engine comprising the additives.
11. The method of claim 9 or the use of claim 10 where the marine diesel engine is a trunk piston engine.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 1236

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                              |                                                                                                                                                     |                                         |      |
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| The present search report has been drawn up for all claims                                                                                                                                                                                                    |                                                                                                                                                                                                                                                                                           |                                                                                                                                                                                                                                                                              |                                                                                                                                                     |                                         |      |
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EPO FORM 1503 03 82 (P04C01)



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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 20 1236

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                                                                                      |                                                        |                                              |
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EPO FORM 1503 03 82 (P04C01)

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EP 00 20 1236

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